ARC PHOTOVOLTAICS CENTRE OF EXCELLENCE ANNUAL REPORT 2014
# CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. DIRECTOR'S REPORT</td>
<td>1</td>
</tr>
<tr>
<td>2. STAFF LIST</td>
<td>4</td>
</tr>
<tr>
<td>3. RESEARCH</td>
<td></td>
</tr>
<tr>
<td>3.1. INTRODUCTION TO RESEARCH</td>
<td>9</td>
</tr>
<tr>
<td>3.2. FACILITIES AND INFRASTRUCTURE</td>
<td>15</td>
</tr>
<tr>
<td>3.3. FIRST GENERATION: WAFER-BASED PROJECTS</td>
<td>39</td>
</tr>
<tr>
<td>3.4. SECOND GENERATION: SILICON, ORGANIC AND OTHER “EARTH ABUNDANT” THIN-FILMS</td>
<td>145</td>
</tr>
<tr>
<td>3.5. THIRD GENERATION: ADVANCED CONCEPTS</td>
<td>231</td>
</tr>
<tr>
<td>3.6. SILICON PHOTONICS AND DEVICE CHARACTERISATION</td>
<td>263</td>
</tr>
<tr>
<td>4. PUBLICATIONS</td>
<td>281</td>
</tr>
</tbody>
</table>
1. DIRECTORS’ REPORT

Photovoltaics involves the direct conversion of light, normally sunlight, into electricity when falling upon devices known as solar cells. Silicon is the most common material used to make these photovoltaic cells, similarly to its key role in microelectronics.

The Australian Research Council (ARC) Photovoltaics Centre of Excellence commenced at the University of New South Wales (UNSW) on 13th June, 2003 with funding initially until 31st December 2007. Upon review in 2005 and 2006, this funding was extended until 31st December 2010. Criteria for such extension included “progress of the Centre towards becoming independent of the ARC Centres of Excellence Scheme for funding”. With the rapid growth of the photovoltaics industry since the Centre’s commencement and the Centre’s strong and seminal links to this industry, the Centre was clearly in a much stronger position for independent operation beyond 2010 than many others in its funding cohort. Accordingly, while remaining under the ARC Centres of Excellence umbrella beyond 2010 in recognition of the quality of its research, the Centre is now dependent upon industry-related funding for research with near-term outcomes and upon more academically-orientated ARC, ARENA and international schemes for its long-term research. Total research funding for the Centre from industry and other funding sources reached record levels in 2014 with the expectation of further increases during 2015.

The Centre’s mission remains to advance silicon photovoltaic research on three separate fronts, as well as to apply these advances to the related field of silicon photonics. A significant development in 2014 towards the fulfillment of the Centre’s mission has been the successful establishment of a new Solar Industrial Research Facility (SIRF) in response to unprecedented support and funding from many of the world’s largest solar cell manufacturers throughout the world wishing to collaborate and exploit the Centre’s newest developments and latest generation of wafer-based technology. The educational activities of the former Key Centre for Photovoltaic Engineering are also integrated into the Centre.

Over the period of funding and in subsequent years, photovoltaics has become the world’s most rapidly growing energy source, with markets increasing at a compounded rate of above 40%/year over this period. The electricity generating capacity of new photovoltaic product installed in 2006 exceeded new nuclear power capacity for the first time, with the gap widening significantly every year since. In Germany, photovoltaics has been the largest source of new electricity generating capacity for each of the last five years and became the largest such source across Europe in 2011, ahead of wind generators and gas turbines. Reducing prices, at least partly traceable to past Centre initiatives, means that technology has reached “retail grid parity” in most parts of the world, where the cost of electricity generated using photovoltaics can compete at the point of use with normal retail electricity prices in many parts of the world. This is expected to lead to a period of self-sustaining growth with photovoltaics positioned to become one of the world’s major industries of the 21st century. Even in Sydney where “cheap” electricity is supplied by power stations built on coal fields, photovoltaics is now competitive with retail electricity prices without subsidies.

Most present photovoltaic sales are of “first-generation” solar cells made from silicon wafers, similar to the wafers used in microelectronics. The Centre maintains its world-leadership with these “first-generation” devices, with several international records for the highest-performing silicon cells in several categories, although the record for the outright highest-performing cells was recently captured by Panasonic with their “HIT” cell technology. First-generation Centre research addresses the dual challenges of reducing cost and further improving efficiency. The rapid growth of the industry is generating widespread interest in ongoing innovations of the Centre’s first generation technology with several distinct technologies now in large-scale production with product valued at several $billions having been deployed in the field.

Silicon is quite brittle so silicon wafers have to be reasonably thick, presently more than a tenth of a millimetre, to be sufficiently rugged for processing into solar cells with reasonable yield. Without this mechanical constraint, silicon would perform well even if very thin, even 100 times thinner than present wafers. Centre researchers have pioneered an approach where very thin silicon layers are deposited directly onto a sheet of glass with the glass providing the required mechanical strength. This “second-generation” approach gives enormous potential cost savings. Not only are the costly processes involved in making wafers
no longer required, but also there is an enormous savings in silicon material. Cells also can be made more quickly over the entire area of large glass sheets. The Centre is at the forefront of international research with such “second-generation”, silicon based approaches, with the first commercial product from “spin-off”, CSG Solar, several megawatt fields now operating in Europe. The Centre is now investigating electron-beam evaporation of silicon onto the glass substrate, a much quicker process than the plasma-enhanced, chemical deposition processes used to date, and also diode laser processing of the deposited films. A parallel approach introduced by new internationally leading member of the academic staff, Professor Allen Barnett, involves growing thin layers of single crystal silicon epitaxially by CVD and then transferring such layers onto a supporting substrate such as steel. Since arrival at UNSW, Professor Barnett’s new team has already achieved world record performance levels for such devices.

Steps to broaden “second generation” activities from silicon to both silicon and carbon were boosted by the appointment of a new academic staff member, Dr Ashraf Uddin, commencing on-duty early in 2009, with this organic solar cell work supported by an ARC Discovery Grant. The activities were further broadened in subsequent years through the awarding of several research grants to Dr Xiaojing Hao to develop “earth abundant” CZTS (copper-zinc-tin-sulphide) solar cell technology. By combining these four relatively benign and abundant elements in appropriate proportions, a tetrahedrally co-ordinated “synthetic silicon” compound can be produced with some advantages over silicon, such as stronger light absorption and more potential for bandgap control by alloying with similar compounds.

The “second generation” thin-films have a clear potential cost advantage over the silicon wafer-based approach, due mainly to reduced material costs. In large enough production volumes, even these reduced material costs will dominate thin-film costs. This has led to the Centre’s interest in advanced “third-generation” thin-film solar cells using advanced photovoltaic concepts to target significant increases in energy-conversion efficiency. Higher conversion efficiency means more power from a given investment in materials, reducing overall power costs. The Centre’s experimental program in this area is focusing on a number of exciting areas such as “all-silicon” tandem solar cells, where high energy-bandgap cells are stacked on top of lower-bandgap devices. The silicon bandgap is controlled by quantum-confinement of carriers in small silicon quantum-dots dispersed in an amorphous matrix of silicon oxide, nitride or carbide. One application of these devices is to boost the efficiency of reasonably standard silicon cell technologies as upper cells in a tandem configuration. Several other materials combinations for these boosting tandems are also being investigated: these include new approaches to highly efficient III-V cells on active silicon substrates, the earth abundant and non-toxic CuZnSnS$_4$ as an ideally matched upper cell and leveraging the recent meteoric rise in perovskite efficiencies in tandem architectures on silicon cell tandems. Conversion of the solar spectrum to be more directly suitable for single junction cells forms another set of projects being researched in Advanced Concepts. Up or down-conversion of incident light or multiple exciton generation or singlet fission, or combinations of these, are all being investigated. They can all be used, individually or in combination, to narrow the spectral range falling on a cell thus boosting its efficiency by more effectively using the energy of each photon. “Hot Carrier” cells based on extraction of the excess energy of the carriers immediately after generation (energy that is normally lost as heat) are also of great interest since they offer the potential for very high efficiencies close to the thermodynamic limit, but can conceptually use relatively simple device structures. Although their implementation poses daunting challenges, considerable progress on addressing these has been made. Again such hot carrier approaches can be used in disruptive completely new design devices or in evolutionary approaches to boost the efficiency of fairly standard solar cells, perhaps even in retrofit configurations. In addition other brand new concepts are continuously being evaluated for their potential and applicability and if found suitable being developed into new project areas. Currently these include Quantum Antennae, advanced photonic light trapping, near field plasmonics coupling, phononic engineering in nanostructures and optical cooling of device structures. The growing importance of “third-generation” solar cells using advanced photovoltaic concepts combined with the academic excellence of the world-leading research conducted at UNSW by Professor Gavin Conibeer and his team has been reflected in the appointment of Professor Conibeer as the new Executive Research Director of the ARC Photovoltaics Centre of Excellence. This appointment took place in April 2014 and has contributed significantly to the subsequent ground breaking achievements in “third-generation” photovoltaics which are a highlight of this report.

In recent years, rapid advances in a range of these important “third-generation” or “advanced concept” areas, and a series of strong collaborations with all of the other major groups in each of these areas worldwide,
would appear to justify the establishment of a separate ARC funded Centre of Excellence in Third Generation Photovoltaics to operate in parallel with the “self-funded” existing ARC Photovoltaics Centre of Excellence that focuses on the more applied and commercially significant research that generates its own sustainable funding through industry related funding sources. The highly complementary interaction this arrangement would offer will be a highly effective way to develop concepts from first inception, through proof of principle research, to research of high efficiency devices in the Advanced Concepts CoE, and then to development of commercially robust devices and architecture in the Photovoltaics CoE and finally to commercial product with appropriate industrial partners.

The final Centre research strand involves silicon photonics where the emphasis is upon using our experience with solar cells, using light to produce electricity, to the reverse problem of engineering silicon devices that use electricity to produce light. The Centre holds the international record for the light emission performance from bulk silicon, in both electroluminescent and photoluminescent devices. Emphasis is now upon exploiting our expertise in silicon light emission to develop new techniques for silicon wafer and cell characterisation. A Centre “spin-off” company, BT Imaging, consolidated its position as the premium equipment supplier internationally using this approach since 2011.

In addition to these four research strands, the activities of the former Key Centre for Photovoltaic Engineering have been integrated into the ARC Centre of Excellence. The tenth year of students from the Bachelor of Engineering (Photovoltaics and Solar Energy) program graduated during 2014. This program has been enormously successful, attracting some of the best and brightest students entering the University and providing the human resources to fuel the recent growth of the industry. The ninth year of students has now graduated from the Centre’s second undergraduate program, leading to a Bachelor of Engineering (Renewable Energy). The excellence of these undergraduate students is such that many have gone on to do research degrees in all areas of the Centre activities contributing to the rapid rise of higher degree research student numbers to the current record of 125. Several of these HDR students have carried on further to first become postdocs and then full academics within the school with their own research programs. This strong educational mentoring activity critically underpins the highly effective research environment in the school. Its highly complementary synergy boosts both school research and educational effectiveness and is the envy of many groups worldwide.

Another significant development during 2014 was the first full year of operation of the new ARENA Australia/US collaborative Centre, the Australian Centre for Advanced Photovoltaics (ACAP). The primary Australian node for ACAP is UNSW under the Directorship of Professor Martin Green, while the lead US institution with funding from the US DOE, is Arizona State University (ASU) under the Directorship of Professor Christiana Honsberg, formerly from UNSW. The outstanding achievements of the latter have been rewarded with the IEEE’s William Cherry Award, arguably the industry’s most prestigious and important prize. Another significant development during 2014 was the appointment of a new Head of School (HOS), in the person of Professor Darren Bagnall, formerly of the University of Southampton in the United Kingdom where he had held a senior appointment for 15 years. Outgoing HOS, Richard Corkish, after 10 years of excellent service as HOS, has taken on the position of Chief Operating Officer for the new Centre ACAP.

We thank all those who contributed to the Centre’s success during 2014. The present continues to be a very exciting time for photovoltaics. More are recognising the possibility of a future where solar cells provide a significant part of the world’s energy needs, without the environmental problems and escalating costs associated with present approaches. The reality of the transition to “grid parity” is expected to make the coming decade a time of rapid change for the industry, with an accelerated pace of adoption of newer, lower cost technologies pioneered by the Centre.

Professor Stuart R. Wenham,
Director
2. **STAFF AND STUDENT LIST**

**Director**
Stuart Ross Wenham, BE BSc PhD UNSW, FTSE, FIEEE, FIEAust
(Scientia Professor)

**Executive Research Director**
Gavin Conibeer, BSc MSc London, PhD Southampton
(Professor)

**Business, Technology & Operations Manager**
Mark D. Silver, BE UNSW, GM QAGSM

**Postgraduate Co-ordinator**
Alistair B. Sproul, BSc (Hons) Sydney, PhD UNSW (until March 2014)
Gavin Conibeer, BSc MSc London, PhD Southampton (since April 2014)

**Undergraduate Co-ordinator**
Ivan Perez-Wurfl, PhD Uni. of Colorado, Boulder

**Undergraduate Industrial Training Co-ordinator**
Ashraf Uddin, BSc (Hons) MSc Dhaka U, Bangladesh; PhD Osaka U, SMIEEE

**Scientia Professor**
Martin Andrew Green, AM, BE MEngSc Qld., PhD DSc(Hon) MCM, DEng UNSW, FAA, FTSE, FIEEE

**Professors**
Darren Bagnall, BEng PhD Salford
Allen Barnett, BSEE, MS U Illinois, PhD Carnegie-Mellon U

**Associate Professors**
Chee Mun Chong, BSc BEng (Hons) PhD UNSW
Evatt Hawkes, BSc (Hons) BEng (Hons) W. A ust., PhD Cantab.
Alistair B. Sproul, BSc (Hons) Sydney, PhD UNSW
Thorsten Trupke, PhD Karlsruhe
Ashraf Uddin, BSc (Hons) MSc Dhaka U, Bangladesh; PhD Osaka U, SMIEEE

**Senior Lecturers**
Stephen Bremner, BSc (Hons), PhD UNSW
Richard Corkish, BEng (Com) RMIT, PhD UNSW
Shujuan Huang, BE MENG Tsinghua Uni., PhD Hiroshima Uni.
Alison Lennon, BSc (Hons) Sydney, PhD Sydney, PhD UNSW
Santosh Shrestha, PhD UNSW
Geoffrey J. Stapleton, BE UNSW
Ashraf Uddin, BSc (Hons) MSc Dhaka U, Bangladesh; PhD Osaka U, SMIEEE
Muriel Watt, BSc N.E., PhD Murdoch

**Lecturers**
Anna Bruce, BE (Hons) PhD UNSW
Merlinde Kay BSc (Hons), PhD UNSW
Ivan Perez-Wurfl, PhD Uni. of Colorado, Boulder

**Associate Lecturers**
Emily Mitchell, BE PhD UNSW
Long Seng To, BE (Hons) BA UNSW (until May 2014)

**Senior Research Fellows**
Malcolm Abbott, BE (Elec. Eng. Hons 1st class), PhD UNSW
Anita W.Y. Ho-Baillie, BE PhD UNSW (returned Apr 2012)
Mark Keevers, BSc (Hons) PhD UNSW (since Jan 2012)
Dirk König, Dipl. Ing. (EE) Dr. rer. nat. (Ph) Chemnitz
Sergey Varlamov, PhD Moscow

Research Fellows
Ian Brazil, BA BAI, Dubl., M Eng DCU, PhD UNSW, MIEI (since Oct 2012)
Patrick Campbell, BSc BE PhD UNSW
Matthew Edwards, BE (Hons 1) PhD UNSW
Xiaojing Hao, BE, MSEE Northeastern Uni., China
Shujuan Huang, BE, ME Tsinghua Uni., PhD Hiroshima Uni.
Henner Kampwerth, MSc Freiburg, PhD UNSW
Emily Mitchell, BE PhD UNSW
David Payne, M Eng (Electronic Engineering) University of Southampton UK
Ivan Perez-Wurfl, PhD Uni. of Colorado, Boulder
Supriya Pillai, B. Tech (India), PhD UNSW
Mark Snow, BSc Swansea (Wales) and PhD Cardiff (Wales)

Post-Doctoral Fellows
Jose Ignacio Bilbao, BEng (EE) MEngSc UC Chile, PhD UNSW
Catherine Chan, BE PV (Hons), BSc Phys, PhD UNSW (since September 2014)
Jessica Kai Copper, BEng (Hons), PhD UNSW
Hongtao Cui, BEng(Hons) Dalian U of Technol., PhD UNSW
Armin Dehghan, PhD, U Western Ontario, Canada
Matthew Edwards, BE (Class 1 Hons) PhD UNSW
Yu Feng, BE, ZJU China, BE PhD UNSW
Brett Hallam, BE (1st class Hons & Uni Medal) BSc PhD UNSW (since September 2014)
Jialiang Huang, BSc, PhD UNSW
Craig Johnson, BSc EE (Hons) Georgia Inst. Tech., PhD UNSW (since Aug 2012)
Siva Karaturi (since Feb 2013)
Sammy Lee, BSc (Hons), PhD UNSW (since Oct 2012)
Ly Mai, BE UNSW, PhD UNSW
Bernhard Mitchell, MSc Uni Konstanz, PhD UNSW
Zi Ouyang, BSc Nju China, PhD UNSW.
Robert Patterson, BSc. (Hons) Queens U CAN, M.Sc. U Alberta CAN; PhD UNSW
Abhnil Prasad, BSc USP Fiji, MSc JNU India, PhD UOA NZ
Binesh Puthen-Veettil, BTech India, PhD UNSW
Jing Rao (VC’s Post-Doctoral Research Fellow) (until March 2015)
Murad Tayebjee, BSc(Adv) Hons I Phys Usyd, PhD Chem Usyd
Ishwara Thilini Wijesingha Seneviratna, BSc. (Hons) Colombo U, Sri Lanka; PhD IC London, UK
Budi Tjahjono PhD UNSW, M Com UNSW, BEng UNSW
Xi Wang, BEng Qingdao University, China; PhD Georgia Institute of Tech, USA (since Mar 2013)
Xiaoqing Wen, BSc M Sc Zhejiang Uni. China, PhD Swinburne
Yang Yang, PhD UNSW

Visiting Professors/Fellows
Robert Bardos, BSc (Hons), PhD Melbourne
Lanying Yang (until Sept 2014)
Lyu Hui (until Feb 2015)

Professional Officers
Patrick Campbell, BSc BE PhD UNSW
Kian Fong Chin, BE QUT, MEngSc QUT, MEngSc UNSW
Mark Griffin, BE UNSW
Yidan Huang, BSc Anhui
Robert Largent, AS USA
Hamid R. Mehrvarz, PhD UNSW
Tom Puzzer, BSc PhD UNSW
Nancy Sharopeam, BE U Sudan for Sci. & Tech., Sudan, ME UNSW (since Jun 2012)
Nicholas Shaw, BE UNSW, PhD UNSW
Lawrence Soria, AssocDipCompAppl W’gong
Bernhard Vogl
Alan Yee, BE UTS

Research Assistants

Vincent Allen
Christopher Antonini
Avantika Basu
Nino Borojevic
Catherine Chan
Mitchell Eadie
Hua Fan
Shahla Flynn
Brett Hallam
Jianshu Han
Florian Hess
Martin Hidas
Pei Hsuan
Jiali Wang
Xiao Jin
Edwards Law
Sammy Lee
Raymond Leung
Yang Li
Dong Lin
Xiaolei Liu
Zhang Liu
Zhong Lu
Nitin Nampalli
Ben Noone
Yuanjiang Pei
James Rudd
Ming See
Nicholas Shaw
Lei (Arian) Shi
Adeleine Sugianto
Mohsen Talei
Anthony Teal
Valantis Vais
Zhenyu Wan
Xi Wang
Gangqi Xu
Xiao Han
Yu Yao
Sharon Young

TETB Admin Unit

Kimberly Edmunds, M Ed Lead UNSW (until August 2014)
Maria Schwensen (since September 2014)
Theresa Wisniewski (since September 2014)
Mei Lee (since September 2014)

Financial Officer

Elena Estrina (until August 2014)

Administrative Staff

Mathew Cheung
Sue Edwards
Jill Lewis
Mable Fong
Joyce Ho
Caroline Latimer

PhD Students

Taufiq Mohammad Abdullah
Chaho Ahn
Xin Rui An
Vincent Allen
Wenkai Cao
Catherine Chan
Kah Howe Chan
Yuan-Chih Chang
Jian Chen
Ran Chen
Sheng Chen
Weijian Chen
Simon Chung
Jack Killian Colwell
Bruno Gustavo Concha Ramon
Brianna Conrad
Jie Cui
Xiaolei Liu
Zhang Liu
Zhong Lu
Nitin Nampalli
Ben Noone
Yuanjiang Pei
James Rudd
Ming See
Nicholas Shaw
Lei (Arian) Shi
Adeleine Sugianto
Mohsen Talei
Anthony Teal
Valantis Vais
Zhenyu Wan
Xi Wang
Gangqi Xu
Xiao Han
Yu Yao
Sharon Young
Xi Dai
Martin Diaz
Claire Disney
Rhett Evans
Hua Fan
Neeti Gupta
Brett Hallam (until August 2014)
Phillip Hamer
Jianshu Han
Pei-Chieh Hsiao
Andy Hsieh
Zoe Yoko Hungerford
Jia, Xuguang
Jessica Yajie Jiang
Yu Jiang
Mattias Juhl
Miga Jung
K yung K im
Nicole K otulak
Dongchen L an
Chang-Y eh L ee
Dun L i
Hongzhao L i
Y ang L i
Zhongtian L i
Yu anxun (Steven) L iao
Steven L impert
Dong L in
Shu L in
Z iyun L in
X iaolei L iu
X u L iu
Z iheng L iu
Doris L u
Zhong L u
Qingshan M a
A rman M abboubi S oufiani
Ibraheem A l M ansouri
Nitin N ampalli
Shin y oun g N oh
K ei ta N omodo
M ohd Z amir P akhuruddin
J ongsung P ark
A obo P u
F ang Q i
J ohn R odriguez
Chao Shen
R ui Sheng
Lei (A drian) S hi
Su ntrana S myth
A nastasia S oeriyadi
L ihui S ong
N ingle S ong
M athew So on
K aiwen Sun

M asters Students
M ark F ogarty
Naoya K obamoto
Ye Lin

T aste of R esearch Summer Scholars
Khairul A zmeer A zmi
Raymond C arlaw
D aniel C hen
Tsun Hang (J ohn) F ung
S ihong G ong
N icholas Gorman

U ngraduate T hesis Students
Masirullah M asir A hmadzai
Isabel M argaret B audish
Zyrah J ane B ernardino
J oanne M arion Borkowski
Le Ngoc Sang B ui

Peinan T eng
A rastoo T eymouri
A lexander T o
J inning T ong
Bo W ang
K ai W ang
Li W ang
Lu W ang
Pei W ang
Q ian W ang
S isi W ang
Xi W ang
A lison W enham
N ed W estern
S anghun W oo
Q iyu an W u
L ingfeng W u
M atthew W right
H ongze X ia
Chang Y an
Chien-J en (T erry) Y ang
J ianfeng Y ang
Y ao Y ao
Yu Yao
H su-L iang Y en
Lin Yuan
J ae S ung Y un
H ai xiang Z h ang
P engfei Z h ang
Qiuyang Z h ang
T ian Z h ang
Y i Z hang
Z ewen Z hang
Z hi long Z hang
J ing Z hao
X in Z hao
Z ibo Z hou

Li W ang
Z hi long Z hang
F angzhou Z hou

Moon Yong K im
Benjamin H oey K w un Lau
Brian Liang
W enguang Lin
V ictor T an
X iao B o X u

Xi Chen
Y uling Chen
John Anthony C hilton
Frances C hristodoulou
C an Chu
3. **RESEARCH**

3.1 **Introduction to Research**

Photovoltaics, the direct conversion of sunlight to electricity using solar cells, is recognised as one of the most promising options for a sustainable energy future, with the photovoltaics industry poised to become one of the world’s largest of the 21st century. The ARC Photovoltaics Centre of Excellence commenced in mid-2003, combining previous disparate strands of work supported under a variety of programs, into a coherent whole addressing the key challenges facing photovoltaics, as well as “spin-off” applications in microelectronics and optoelectronics. The Centre was funded by the ARC until December 2010 and has since been funded under a variety of other schemes, with record levels of research funding being received in 2014. In particular, increasing interest from industry in the Centre’s commercially significant technologies has led to a substantial increase in the number of the world’s leading cell manufacturers choosing to directly fund, support and engage in collaborative research with the Centre. A new model for interfacing with industry was adopted in 2014 where a consortium approach was preferred over the establishment of independent collaborative research agreements with individual companies. It appears that for a number of reasons, many of the largest companies are now willing to work together in developing and commercialising the Centre’s technologies rather than as previously in isolation. The changed attitude has in part been contributed to by tougher times following the world financial crisis, although several companies have indicated that their determination to have access to the latest generation of Centre technology has become more important to them than who they have to team up with. The net result is a very positive one for the Centre with industry funding now being able to be pooled in support of a larger core research program rather than being split into many smaller parcels with corresponding isolated but overlapping projects.

Whereas the near-term commercially relevant research is receiving strong funding support from industry, cell manufacturers are in general reluctant to fund longer-term technology development such as the breakthroughs being achieved through the Centre’s team working in the area of Third Generation or Advanced Concept Photovoltaics. Never-the-less, the high calibre of the Centre’s work being done in Advanced Concept Photovoltaics continues to attract significant funding through National Competitive Grants from ARC and ARENA and internationally competitive grants such as GCEP and USASEC. The academic excellence and breadth of such internationally leading work would appear to justify the establishment of an independent ARC funded Centre of Excellence. The latter would be independent of the existing Photovoltaics Centre of Excellence that is self funded through its focus on industrially relevant research and corresponding support from industry and associated funding schemes such as ARC Linkage and ARENA grants. Two such Centre’s of Excellence would complement each other particularly well in an area widely recognised by experts as being of particular importance to Australia and the world’s future energy requirements. The technology breakthroughs funded from the ARC Advanced Concept PV Centre of Excellence would continuously transfer to the existing ARC Photovoltaics Centre of Excellence to develop and demonstrate its commercial importance and to secure separate industry funding for the ongoing self-funded development and adaptation towards industry adoption and large-scale manufacturing. This would thus establish an efficient conduit for new advanced concepts to first be researched to proof of principle and then be developed through to commercial products.

From a broader perspective, the Centre’s photovoltaics research is divided into three interlinked strands addressing near-term, medium-term and long-term needs, respectively. The present photovoltaic market is dominated by “first-generation” product based on silicon wafers, either single-crystalline as in microelectronics (Fig. 3.1.1) or a lower-grade multicrystalline wafer. This market dominance is likely to continue for at least the next decade. First-generation production volume is growing rapidly, with a huge effort directed to streamlining manufacturing to reduce costs while, at the same time, improving the energy conversion efficiency of the product. Also important is the reduction of the thickness of the starting silicon wafer without losing performance or decreasing yield, to save on material use.
Figure 3.1.1: “First-generation” wafer-based technology (BP Solar Saturn Module, the photovoltaic product manufactured in the highest volume by BP in Europe, using UNSW buried-contact technology).

The Centre’s first-generation research is focussed on these key issues. Building upon the success of “buried-contact” solar cell, the first of the modern high-efficiency cell technologies to be successfully commercialised (Fig. 3.1.1), the Centre has developed several other high-efficiency processes in commercial production or close to this, based on Centre innovations in laser and ink-jet processing. Sales under licence are now well over $1 billion.

Although costs are reducing rapidly, wafers have been expensive and need quite careful encapsulation, since brittle and also thermally mismatched to the glass coversheet, making first-generation technology reasonably material-intensive. Several companies worldwide are attempting to commercialise “second-generation” thin-film cell technology based on depositing thin layers of the photoactive material onto supporting substrates or superstrates, usually sheets of glass (Fig. 3.1.2). Although materials other than silicon are of interest for these films, silicon avoids problems that can arise with these more complex compounds due to stability, manufacturability, moisture sensitivity, toxicity and resource availability issues.
The Centre is developing a thin-film approach based on the use of the same high quality silicon used for first-generation production, but deposited as a thin layer onto glass. The main emphasis is on the development of lower-cost deposition and processing approaches (such as deposition by evaporation rather than PECVD). The Centre also commenced activities on carbon-based, organic solar cells during 2009 and a program on other “earth abundant” materials, particularly CZTS (Cu$_2$ZnSnS$_4$) in 2010. More recently, a research program on the promising Perovskite materials has been initiated with a particular interest in evaluating their compatibility with silicon wafer-based technology for the fabrication of high performance low cost tandem devices. Funding for such research has increased sharply during 2014 with a combination of new ARENA grants and also funding from industry.

At the present time, such second-generation thin-films are entering the market in increasing quantities. Large-scale commercialisation of thin-film product leads to a different manufacturing cost structure composed to the wafer-based product. However, costs again increasingly become dominated by material cost as production increases, for example, by the cost of the glass sheet on which the cells are deposited.

More power from a given investment in material can be obtained by increasing energy-conversion efficiency. This leads to the possibility of a longer-term third-generation of solar cell referred to earlier. This type of solar cell is distinguished by the fact that it is both high-efficiency and thin-film. To illustrate the cost leverage provided by efficiency, Fig. 3.1.3 shows the relative cost structures of the three generations being studied by the Centre. This figure plots efficiency against manufacturing cost, expressed in US$/square metre. First-generation technology has relatively high production cost per unit area and moderate likely efficiencies at the module level (14-20%). The dotted lines in Fig. 3.1.3 show the corresponding cost/watt, the market metric. Values below US$0.50/watt are now common for large Asian manufacturers of First Generation products, particularly those from China. As seen from Fig 3.1.3, this has been an unexpected outcome with First Generation PV modules having not been previously expected to achieve cost prices significantly below $1/W. This surprisingly good performance and progress of First Generation technology appears to have added to the reluctance of companies at this stage to fund potentially revolutionary Third Generation PV...
research from UNSW, even though it is well recognised by experts internationally that one of the Third Generation concepts must eventually dominate over First Generation devices for photovoltaics in general to reach their full potential.

Second-generation thin-film technology has a different cost structure as evident from this figure. Production costs per unit area are a lot lower, since glass or plastic sheets are a lot less expensive than silicon wafers. However, likely energy-conversion efficiencies are lower (6-15%). Overall, this trade-off produces costs/watt estimated as about 1.5-2.0 times lower than those of the wafer product, in large production volumes.

The third-generation was initially specified as a thin-film technology, which therefore would give manufacturing costs per unit area similar to second-generation, but is based on operating principles that do not constrain efficiency to the same limits as conventional cells (31% for non-concentrated sunlight for the latter). Unconstrained thermodynamic limits for solar conversion are much higher (74% for non-concentrated light, giving an idea of the scope for improvement). If a reasonable fraction of this potential can be realised, Fig. 3.1.3 suggests that third-generation costs per Watt could be lower than second-generation by another factor of 2 to 3.

Of the third-generation options surveyed by Centre researchers, “all-silicon” tandem cells based on bandgap-engineering using nanostructures was selected as the most promising for relatively near-term implementation (Fig. 3.1.4). This involves the engineering of a new class of mixed-phase semiconductor material based on partly-ordered silicon quantum-dots in an insulating amorphous matrix. The general CZTS material system may also have some potential here due to the range of bandgaps accessible. Rapid recent progress in reducing silicon wafer costs means that even tandem cells built on silicon wafers could fall into the targeted cost zone in Fig. 3.1.3. This realisation has resulted in the Centre initiating several programs investigating such silicon wafer-based tandem cells during 2011. Photon up-conversion and/or down-conversion as a way of “supercharging” the performance of relatively standard cells forms a second line of research. A third longer term program is the investigation of schemes for implementing hot-carrier cells. These have the potential to access some of the very high efficiencies up to 50% and beyond. They could be applied long term in a revolutionary new cell design or more likely in the medium term as another ultimate means of
Figure 3.1.4: Conceptual design of an all-silicon tandem cell based on Si-SiO₂ (or Si-Si₃N₄ or Si-SiC) quantum dot superlattices. Two solar cells of different bandgap controlled by quantum dot size are stacked on top of a third cell made from bulk silicon.

The fourth Centre strand of silicon photonics draws upon elements of all three of the photovoltaic strands. A by-product of this work has been the development of techniques based on silicon light-emission for characterising both completed devices, particularly solar cells, as well as silicon wafers at different stages of processing (Fig. 3.1.5). Developing this approach to its full potential has formed an increasingly large part of the Centre’s photonics program.
Figure 3.1.5: Schematic representation of a PL imaging system. An external light source is used to illuminate the silicon wafer or solar cell homogeneously. The luminescent emission (red arrows) from the sample is captured with a sensitive CCD camera. This technology was commercialised by Centre “spin-off” BT Imaging during 2008.
3.2 Facilities and Infrastructure

The ARC Photovoltaics Centre of Excellence is located at the Kensington campus of the University of New South Wales (UNSW), about 6 km from the heart of Sydney and close to its world famous beaches including Bondi, Coogee and Maroubra (Fig. 3.2.1).

Figure 3.2.1: Centre of Excellence location in Sydney.

Organisationally, the Centre of Excellence is located within the School of Photovoltaic and Renewable Energy Engineering (SPREE) within the Faculty of Engineering. The Centre of Excellence has a large range of laboratory facilities. Major changes have taken place during 2014 with the establishment of a Solar Industrial Research Facility (SIRF) in building G23 at the Kensington campus which is a separate building from the new Tyree Energy Technologies Building (TETB). The development and establishment of the latter was described in the 2013 Annual Report. During 2014 operations ceased at Bay St Botany facilities and also the facilities located in building G17 as shown in Figure 3.2.2, to permit their relocation to building H6 - the new Tyree Energy Technologies Building (TETB). F10 the Chemical Sciences Building houses the OPV laboratory.

The facilities include the Bulk Silicon Research Laboratories, the Device Characterisation Laboratory, the Optoelectronic Research Laboratories, the Thin-Film Vacuum Fabrication Clean Room Laboratories, the Metallisation + Inkjet/Aerosol Processing Laboratories and the Organic Photovoltaic (OPV) Laboratory. Other important resources are the Semiconductor Nanofabrication Facility (SNF) and Australian National Fabrication Facility (ANFF) jointly operated by the Faculty of Science and the Faculty of Engineering.

Additional equipment commonly used for solar cell work is found at the Mark Wainwright Analytical
Research Centre (MWAC) and elsewhere on the University campus. Included in this category are TEM/SEM electron microscopes, focused ion beam (FIB) specimen preparation equipment, X-ray diffraction, Raman spectroscopy, AFM and surface analysis equipment. TEM, ellipsometry and a femtosecond time resolved photoluminescence measurement system are also regularly accessed at Sydney University.

In 2012 the integration of laboratories commenced in UNSW’s new flagship energy efficient Tyree Energy Technologies Building (TETB), a building with a 6-Star rated Green Star design. Specific details about significant additions in 2014 are found under the laboratory headings that follow.

**Figure 3.2.2**: Layout of laboratories and other facilities within G17, the Electrical Engineering Building, Kensington Campus. The TETB, Building G23 and the OPV laboratory in the Chemical Sciences Building are not shown.

The Centre of Excellence has two computer networks. In 2014 the Kensington Research and Administrative network consists of 1 intranet server (hosted on Central IT infrastructure), 2 Internet web-servers (hosted on Central IT infrastructure), 1 centrally hosted licence server and over 200 client workstations. An additional 71 computers are dedicated to the computer control of laboratory and other equipment. In addition a web-based lab-equipment booking system is in place for the equipment in Rm 140 TETB.

The computer resources are used for measurement, modelling/simulations, equipment control, document control, laboratory design support, Internet access, general administrative purposes and maintaining the Centre’s presence on the Internet.

Each postgraduate research student is allocated a dedicated personal computer and has access to shared computer resources.

The Centre upgraded Linux (Beowulf) 64bit cluster has an estimated computational power of 6.6 Teraflops to support the demanding Density-Functional-Hartree-Fock and molecular dynamical computations. A second 544 core, 4.6 Teraflop, cluster has been installed for complementary investigations of energy efficiency and renewable energy via computational fluid dynamics techniques.
A powerful Linux workstation runs TCAD simulations for the Plasmonics group and servers manage data from the grid connect PV system above the UNSW swimming pool and from the grid connected solar arrays on the TETB roof. These data are used in PV grid connect power systems research.

To support undergraduate work there is a second network for students and an Internet capable web-server that gathers and displays data collected from solar arrays on the roof of the Electrical Engineering building. These data can be viewed using a web browser and can be made available for Internet access.

The Laboratory Development and Operations Team develops and maintains core Centre and laboratory facilities. During 2014, the team, under the leadership of Mark Silver, comprised of an additional 5 equivalent full-time and 9 casual + part-time employees, including: electrical engineers, a computer/network manager, electronic/computer/laboratory technicians and administrative staff.

**Bulk Silicon Research Laboratories**

The Centre houses the largest and most sophisticated bulk silicon solar cell research facility in Australia, incorporating both the High Efficiency and Buried Contact/Bulk Cell Laboratories. Total TETB laboratory processing space of over 1300 m² (including the Metallisation and Inkjet Aerosol Processing Laboratories, Device Characterisation and Optoelectronic Research Labs) at the west of the Kensington Campus and is serviced with filtered and conditioned air, process cooling water, processing gases, ultra pure water supply, chemical fume cupboards, local exhausts and abatement. Another 480 m² of combined roof space accommodates fixed PV arrays and over 360m² of accessible outdoor experimental space. Off site, approximately 500 m² are used for the storage of chemicals and equipment spare parts.

The laboratories are furnished with a range of processing and characterisation equipment including tube diffusion furnaces, 6 vacuum evaporation deposition systems, a laser-scribing machine, 3 laser doping machines, 3 rapid thermal annealers, four-point sheet-resistivity probe, silver/nickel and copper plating facility, visible wavelength microscopes, 2 wafer mask aligners, spin-on diffusion system/photoresist spinners, electron beam deposition system, metallisation belt furnace, manual and automatic screen printers.

In 2013 two state of the art tube furnace systems were installed in TETB Rm 162 laboratory. Both systems support up to 156mm square wafer processing. The furnaces were complemented by a new vacuum thermal evaporator for aluminium depositions and reconditioned mask aligner, wet chemical benches and spin rinse dryer units. Together they form the beachhead for bulk silicon processing in the TETB.
Figure 3.2.3: Atmospheric pressure tube furnace.

Figure 3.2.4: CNC Laser Scribe Tool.

The laser scribe tool, shown in Figure 3.2.4, has a 20 watt Nd:YAG laser for infrared operation (1064 nm) and an optional frequency doubler for green operation (532 nm). The work stage is CNC controlled allowing 1 micron positional accuracy and table speeds approaching 25 cm/second across an area of 15 cm by 15 cm. The tool is used primarily for Buried Contact and bulk silicon solar cell fabrication, cutting 35-micron wide laser grooves as deep as 100 microns into silicon wafers and scribing wafers in preparation for cleaving. It can also be used to cut other suitable materials, such as stainless steel.

Multi-Purpose Laboratory TETB Rm 139

This laboratory supports Perovskite, Colloidal Quantum Dot, CZTS and bulk silicon cell work.
Equipment includes a 4 port glove box with internal quad source organic and metal evaporator and spin coater, a rapid thermal annealer, rapid thermal sulphurisation furnace, Hall Effect measurement system, a line beam diode laser system, Langmuir-Blodgett trough, spin coater, rotary evaporator and centrifuge.

**Figure 3.2.5:** Rm 139 Glove Box for Perovskite cells.

**Device Characterisation Laboratory**

The Device Characterisation laboratory was the first laboratory to be relocated to the TETB in March 2012.

It houses characterisation equipment including “Dark Star”, the Centre's station for temperature controlled illuminated and dark current-voltage measurements, the Centre’s Fourier-transform infrared spectroscopy system (FTIR), frequency dependent impedance analyser, ellipsometer, Sinton photoconductance lifetime equipment, wafer probing station, open circuit voltage versus illumination measurement system (Suns-Voc), 4 point resistivity probe, spectral response system and spectrophotometer with integrating sphere.

In 2008 a multi function wafer mapping tool, shown in Figure 3.2.6, was installed. This unit provides state of the art capability for the measurement of carrier lifetime, bulk resistivity, emitter sheet resistance and Light Beam Induced Current (LBIC) on wafer samples.

Additions in 2009 included a high speed commercial flash cell tester with 156 mm square wafer capability as shown in Fig 3.2.7, a replacement UV/VIS/NIR spectrophotometer and a commercial Luminescence Inspection System (LIS) from spin off company BT Imaging.
In 2011 a spectroscopic ellipsometer was acquired that allows non-destructive thin film characterisation of samples at multiple wavelengths to determine thin film thicknesses and optical constants. Other new additions, located in other Centre laboratories, include a surface profiler, automatic 4 point probe and a front side grid contact resistance mapping tool.

In 2012 a new cryogenic micromanipulated probing station was commissioned for non-destructive testing of devices on full and partial wafers up to 51 mm in diameter. The instrument can be used to measure electrical, electro-optical, parametric, high impedance, DC and RF properties of materials and test devices.

The system operates over a temperature range of 77 K to 475 K. The probe station provides efficient temperature operation and control with a continuous refrigeration system using liquid nitrogen. A control heater allows precise sample stage temperature control, and along with the radiation shield heater, provides the probe station with fast thermal response.

The system has been configured with four micro-manipulated stages, each providing precise 3-axis control of the probe position. Two probe arms are equipped with probes rated to 1GHz. Probe tips are thermally linked to the sample stage to minimize heat transfer to the DUT. One probe arm is equipped with an optical fiber that can be placed a few microns away from the device to be tested.

In 2014 an X Ray Fluorescence (XRF) system was installed for the determination of the chemical composition of thin films.

An ECV junction profiling system in Rm 139 and optically assist IV and DLTS systems in Rm 144 add to the Centre’s portfolio of characterisation equipment.

Figure 3.2.6: Wafer Mapping Tool.
**Figure 3.2.6a:** oa-IV setup

**Figure 3.2.7:** Flash Cell Tester.
Optoelectronic Research Laboratories

Three Class 4 laser research laboratories support the Centre’s measurement capabilities. A broad range of equipment that can be used for experiments further supports the researcher. Various light sources are available, including intensity-stabilised lamps, various diode lasers, an ultra-tunable optical parametric oscillator and a super continuum laser. Detection equipment includes various cooled cameras, liquid-nitrogen-cooled analogue detectors together with lock-in amplifiers, and two state-of-the-art fibre spectrometers and two gated avalanche photodiodes coupled to time-correlated single-photon-counting electronics.

Recent additions include an experimental photoluminescence imaging setup to generate new parameter maps of cells, a continuous-wave PL spectrometer to with IR extension to measure response spectra, a complex time-resolved double PL spectroscopy to measure wavelength-resolved decay curves, two different setups to measure angular-resolved optical scattering characteristics of various surfaces at different wavelengths, a photothermal deflection spectroscopy setup to measure optical absorption properties and a wavelength modulated spectral response system to measure exciton binding energies.

Figure 3.2.8: Optical characterisation bench.

Thin-Film Vacuum Fabrication Clean Room Laboratories

These laboratories are equipped with a range of equipment for thin-film deposition and patterning, including a plasma-enhanced chemical vapour deposition (PECVD) system, 5 sputtering systems (including multi-target), a large area plasma etcher, a reactive ion etcher (RIE), a resistively heated vacuum evaporator, a thermal vacuum evaporator, UHV electron beam evaporator system for high “industrial” rate silicon and other thin film deposition, a glass washing machine, a rapid thermal processing (RTP) machine and an optical microscope with digital image acquisition system. Other on campus equipment of use in thin-film projects is located within the Semiconductor Nanofabrication Facility.

A sulphurisation furnace system was installed to support CZTS research. The furnace is a dual chamber split tube type. Sulphur vapour is carried in N2 along the quartz tube from one chamber
where S is heated to the next where precursors absorb the vapour. All unabsorbed S vapour leaving the chamber in the exhaust stream is condensed before reaching air, to avoid SO₂ formation.

The PECVD system, shown in Fig. 3.2.9, has a 40 x 20 cm² process platen and can handle large-area silicon wafers as well as smaller pieces. Two types of plasma excitation (remote microwave and direct RF) are available. The machine is used for the low-temperature deposition of thin dielectric films (silicon nitride, silicon dioxide, silicon oxy-nitrides) and of amorphous silicon. The dual-cylinder, remote microwave plasma source produces excellent-quality silicon nitride and silicon dioxide films, with precise control over the stoichiometry at temperatures up to 500°C. Amorphous and microcrystalline silicon films can also be deposited in the system.

The sputter tools have up to five separate targets. Each target can be operated independently of one and other, allowing users to co-sputter a thin film from more than one target and deposit multilayers without breaking vacuum. Three power supplies are available with substrate biasing. The custom made systems can handle substrates up to 150mm x 150mm. Excellent film purity is assured as the systems incorporate a load-lock. Computer control can be used for most operations, including substrate heating, allowing precise multilayers to be deposited repeatedly.

Figure 3.2.9: Remote plasma PECVD machine.

Figure 3.2.10: Thermal and e-beam Evaporator.
Metallisation and Inkjet/Aerosol Deposition Processing Laboratories

The Metallisation Laboratory equipment includes a fast metallization firing furnace capable of processing 156 mm square wafers; a high temperature semiconductor muffle furnace; module laminator; light soaking reliability tool; spin on dopers; FIP/LIP plating support; manual screen printer and a fully automatic production scale screen printer.

This Inkjet/Aerosol Deposition laboratory houses the Centre’s inkjet printing development systems. The laboratory is used to develop solar processing “inks” (chemical solutions) and for printing them onto a solar wafer under computer control. The aim is to develop low cost processing techniques for creating fine structures in solar cells. It is anticipated that the inkjet printing is capable of replacing processes such as laser scribing and photolithography for forming fine patterns for contacting but at a cost of at least 10 times cheaper. Equipment includes two ink jet material deposition printing systems, capable of depositing a wide range of materials onto different substrates, a surface tension meter and viscometer.
An aerosol deposition system has expanded our capability to print and deposit a larger range of materials at typically smaller resolution than the inkjet printers. The resultant reduction in material usage and loss is of great interest for production/manufacturing.

This light tight laboratory also accommodates three state of the art laser micromachining tools including mirror steered scanning lasers for laser doping.

**Figure 3.2.12:** Aerosol Deposition and Inkjet development systems.

**Figure 3.2.13:** Metallisation Belt Furnace
Figure 3.2.13a: Light Soaking Test System.

**Semiconductor Nanofabrication Facility**

The Centre also owns equipment within, and has access to, the Semiconductor Nanofabrication Facility (SNF) at the University. This is a joint facility shared by the Faculties of Science and Engineering and houses a microelectronics laboratory and a nanofabrication laboratory for e-beam lithography. The SNF provides an Australian capability for the fabrication of advanced nanoscale semiconductor devices and their integration with microelectronics. SNF research projects form an integrated effort to fabricate innovative semiconductor nanostructures using the latest techniques of electron beam patterning and scanning probe manipulation. A major applied objective of the facility is the development of a prototype silicon nuclear spin quantum computer. The capabilities of this facility were expanded to house the, NCRIS funded, Australian National Nanofabrication Facility (ANNF).

**Organic Photovoltaic Laboratory (OPV)**

The Organic Photovoltaic Devices group laboratory space in the Chemical Sciences Building has been in operation since 2011 for the processing and testing of organic photovoltaic devices and 3rd Generation photovoltaic devices.

The laboratory occupies a space of 42m² and consists of an acid-scrubbed fume cupboard, nitrogen-purged sample storage systems, nitrogen-atmosphere glovebox (comprising an internal liquid solution spinner and hotplate for device processing within an oxygen-free environment), a thermal evaporator system for formation of metallic contacts to organic devices, a liquid source spinner with exhausted work space hood, an aerosol deposition system for the application of TiO₂ films and a lighted I-V characterization system.

In 2013 a new thermal processing oven was commissioned for annealing processes of deposited organic layer, and TiO₂ films for OPV devices.
Figure 3.2.14a: Nitrogen-purged, glovebox for spin-on and thermal processing of organic photovoltaic devices in an oxygen-free atmosphere.

Figure 3.2.14b: Exhausted workspace for liquid source spinner
The installation of the first operational tool in the new Solar Industrial Research Facility (SIRF) was reported in the 2013 Annual Report. During 2014, numerous new tools were either installed and commissioned or delivered in preparation for installation. Most tools have been donated by companies such as Roth & Rau, Suntech, Meyer Berger, Sunshare, Kuttler, 3S and Schmid. In some cases, the tools have been donated primarily in support of collaborative research projects between UNSW and the respective companies, although in most other cases it has been clear that the intention of donating tools was so that they could be adapted to suit UNSW internationally leading technologies and for use by UNSW researchers, students and industry partners.

The SIRF forms a particularly important purpose for the Centre’s more commercially significant research and technologies to demonstrate their suitability for the industrial environment and large-scale manufacturing. This involves taking the laboratory technologies and developing and adapting them for use with the commercial tools in SIRF. This makes the SIRF particularly well suited for interfacing with industry such as for technology transfers. Collaborative research, pilot production of new technology or simply demonstration of the compatibility of state-of-the-art UNSW technology with fabrication with high throughput commercial tools.

UNSW has been particularly fortunate to attract Dr Bram Hoex into joining the team of academic staff in SPREE. Dr Hoex is particularly well known internationally for his industrially relevant research in silicon wafer-based photovoltaics that he has conducted in recent years at SERIS in Singapore where he was Deputy Director responsible for wafer-based technology development. Earlier technologies of Dr Hoex are now gaining traction commercially through licensing by industry. The SIRF will be particularly well suited for Dr Hoex’s industrially relevant research due to its
similarities to the laboratories at SERIS that comprised large-scale commercial tools similar to those being installed in SIRF.

The following photos show some of the key tools provided to UNSW by various companies for use in the SIRF.

(a)

(b)

**Figure 3.2.15:** Chemical baths for cleaning and texturing wafers prior to device processing at elevated temperatures.

**Figure 3.2.16:** Front-surface phosphorus emitter diffusion is one of the most important processes in terms of determining the final device performance and is shown below in Figure 3.2.16 taking place in SIRF at UNSW. In particular, the direct link between the emitter doping profile and the ability to hydrogen
passivate defects and recombination sites throughout the device via hydrogen charge-state control has not been previously recognised or understood prior to this work. This important relationship and the ability to optimise the corresponding processes for maximising device efficiencies have been captured within a patent portfolio developed as part of the “Advanced Hydrogen Passivation” work originating from UNSW projects.

Note in the photos below, the relatively large number of wafers as well as their size, able to be processed in a single operation when using the commercial tools in SIRF.
Dielectric deposition is carried out in SIRF at UNSW by PECVD to give the wafers the blue colour as shown in the photos below in Figure 3.2.17. To maximise the ability of the resulting dielectrics to act as good hydrogen sources for the subsequent hydrogen passivation processes, the dielectric layers are deposited at the relatively low temperature of 350degC to increase hydrogen content. Deposition parameters are also optimised so as to control the temperature at which the hydrogen is released. This is a particularly important aspect for the implementation of the hydrogen passivation technology to a range of different cell technologies that employ different thermal processes such as firing temperatures for the metallisation. The tool shown is the $3 million state-of-the-art MAiA tool donated to SIRF by Roth & Rau specifically for this hydrogen passivation work.
Figure 3.2.17: PECVD tool for the plasma enhanced deposition of a range of dielectric layers onto the silicon wafer surfaces such as for surface passivation, antireflection coating, hydrogen sources and chemical protection.

Advanced Hydrogen Passivation involves the use of hydrogen charge state manipulation to enhance both the mobility and reactivity of the hydrogen atoms. The tool below in Figure 3.2.18 donated by Meyer Berger, allows this hydrogen charge state manipulation through the use of varying illumination levels to control the carrier concentrations in the vicinity of the hydrogen atoms. Large improvements in material quality have been demonstrated and have contributed significantly to increased mono and multi cell efficiencies. This is particularly important for the multi material to reduce recombination in the vicinity of grain boundaries and other crystallographic defects that normally limit efficiencies to well below those normally achieved with the mono wafers.
Figure 3.2.18: One of only two Camini roller furnaces existing internationally shown in (a). This furnace has unique capabilities that suit it particularly well to UNSW’s innovative hydrogen passivation technology while simultaneously being well suited to conventional metallization firing such as required by screen-printed solar cells. Fig (b) shows a conventional Centrotherm belt furnace, also located in SIRF.

The Metallisation/Plating technology is perhaps the most advanced or at least important of all the newly developed technologies at UNSW. The International Technology Roadmap for Photovoltaics (ITRPV) produced by an international team of experts, predicts that plated cell metalisation will eventually displace the use of screen-printed contacts. This transition however is expected to take as long as 5-10 years (2014 ITRPV), due in part to this lack of suitable commercial plating tools for
large-scale manufacturing. To accelerate UNSW’s technology implementation into large-scale manufacturing at Suntech, the fabrication, installation and evaluation of the plating baths of Figure 3.2.19 have taken place in SIRF. These plating baths are based on the UNSW developed plating technology and are suitable for large-scale manufacturing. These baths were designed by Dr Ji, a world expert in plating technology and now an academic at UNSW, and have been constructed in China by the company Kuttler.
Figure 3.2.19: Plating baths suitable for large-scale manufacturing, designed by world expert Dr Ji for forming solar cell contacts based on the UNSW developed plating technology. Figure (d) are low throughput prototype plating baths.
Figure 3.2.20: Chemical baths for general chemical processing and cleaning with spin-dryers shown on the right.

UNSW is often credited with pioneering the use of lasers for photovoltaic device fabrication. Lasers are routinely used for a range of processes such as patterning dielectrics, selective emitter formation through laser doping, surface grooving for buried contacts, edge junction isolation, surface texturing, hydrogen charge-state control, localised heating, etc. The laser types and corresponding specifications required vary somewhat for the various laser functions. SIRF consequently has several lasers available with more to follow. Two donated lasers are shown in Figure 3.2.21, one being UV with ps pulse lengths (left) while the other is Q-switched at 1064nm wavelength (right).

Following completion of device fabrication, cells are tested such as in the automated testing station of Figure 3.2.22 manufactured by Bacini and donated for use in SIRF.
Figure 3.2.21: Two donated lasers are shown, one being UV with ps pulse lengths (left) while the other is Q-switched at 1064nm wavelength (right).

Figure 3.2.22: Following completion of device fabrication, cells are tested in the automated testing station manufactured by Bacini.
Encapsulation is necessary to protect solar cells in the field from the environment, particularly moisture. Figure 3.2.23(a) is an environmental test chamber planned for installation in SIRF in mid 2015 to simulate and accelerate environmental testing of solar modules. A solar module is the term given to a collection of cells that have been electrically interconnected and then encapsulated. Figure 3.2.23(b) shows a state-of-the-art 3S laminator donated to SIRF for module fabrication taking place at UNSW.

Figure 3.2.23: (a) is an environmental test chamber while (b) is a laminator by 3S for encapsulating cells into a module.
3.3 First Generation Wafer Based Projects

Research Team:

University Staff
S. R. Wenham
A. Lennon (Group Leader - Anodisation, Inkjet and Plating Technologies)
M. A. Green
Allen Barnett (Group Leader - Thin Silicon)
C. M. Chong (Group Leader - Rear contacting)
M. Abbott (High efficiency Screen-printing technology)
B. Hallam (Group Leader - Advanced bulk and surface passivation)
Stephen Bremner
Gavin Conibeer (Group Leader - Third Generation concepts applied to wafer-based technologies)
T. Trupke (Group Leader - Photoluminescence Imaging)
A. Ho-Baillie (Group Leader - High Efficiency Cells)
H. Kampwerth (Group Leader - Characterisation)
M. Keevers (Senior Research Fellows - Spectrum Splitting)
A. Sugianto (Group Leader - Laser-doping technologies)
J. Jia (Group Leader - Commercialisation and tool design)
M. Edwards (Group Leader - Advanced interconnection and encapsulation technology)

Postdoctoral Fellows
B. Mitchell
A. Sugianto
Ian Brazil
M. Edwards
Xiaojing Hao
L. Mai
H. Mehrvarz
Ivan Perez-Wurfl
S. Pillai
B. Tjahjono

Postgraduate Research Students and Research Assistants
Ibraheem Al Mansouri
Xinrui An
N. Borojevic
C. Chan
Jian Chen
Brianna Conrad
Hongtao Cui
Jie Cui
Martin Diaz
L. Gu
B. Hallam
P. Hamer
Alex Han
Yajie (Jessica) Jiang
Mattias Klaus Juhl
Sammy Lee
M. Lenio
Dun Li
Hongzhao Li
Hua Li
Dong Lin
Ziheng Liu
D. Lu
Fang Qi
J. Roderiguez
Kenneth Schmieder
Chao Shen
Anastasia Soeriyadi
Lihui Song
Peinan Teng
Alexander To
K. Valliappan
D. Wang
Li Wang
Lu Wang
S. Wang
Alison Wenham
N. Western
Bo Xiao
G. Xu
Yang Yang
Y. Yao
Y. Yeung
L. Zhang
Xi Zhu

Research Associate
Wayne Zhenyu Wan (Research Associate)

Technology Transfer Team

Managers
• D. Jordan (Team leader)
• C.M. Chong (Deputy Team Leader – Devices)
• M. Edwards (Deputy Team Leader – Program Manager)
• S. Wenham (Technical Director)

Team Members
• C. Chan
• C. M. Chong
• B. Hallam
• P. Hamer
• A. Lennon
• L. Mai
• A. Sugianto
• B. Tjahjono
• A. Wenham

NewSouth Innovations
• D. Gronowski
• T. Montaldo
3.3.1 High Performance Cell Research

3.3.1.1 High Efficiency Silicon Cells

Research Team:
M. A. Green
A. Ho-Baillie
H. Kampwerth
H. Mehrvarz
S. Pillai
Yang Yang

Plasmonic scatterers were applied to the rear of modified planar PERT cells to investigate efficiency improvements from such cells close to the band gap of Si. Even nominal efficiency increase from this regime would be promising to exceed our record efficiency of Si solar cell of 25%. The plasmonic structures were compared to different reflectors - both diffuse (such as white paint) and specular (such as silver (Ag) and aluminium (Al)), and also detached reflectors similar to our previous study [3.3.3.1.1].

Ag MNP were applied to the rear in two configurations.
1. In a single reflector configuration (Fig. 3.3.1.1.1b)
2. In a double reflector configuration (Fig. 3.3.1.1.2)

Figure 3.3.1.1.1: Solar cell schematic of the single reflecting layer structures used in the study: (a) Evaporated Al (E Al) or Evaporated Ag (E Ag); (b) Ag nanoparticles (Ag MNP); (c) White Paint (WP); (d) Detached Al mirror (D Al) or Detached Ag mirror (D Ag) or Detached White Paint (D WP).

Figure 3.3.1.1.2: Solar cell schematic of the double reflecting structures used in the study: (a) Ag MNP/Al/Ag mirror; (b) Ag MNP/Ag mirror/D Ag; (c) Ag MNP/MgF₂/E Al or Ag MNP/MgF₂/E Ag; (d) Ag MNP/MgF₂/WP.

The single reflectors as shown in Fig. 3.3.1.1 are categorised into three general types: (1) Planar reflectors are the conventional evaporated metal reflectors using an Al or Ag layer as a mirror
(specular reflection) whereby the light is reflected at the same angle as incident light. (2) Scattering or diffuse reflectors consist of Ag nanoparticles or commercial white paint. The Ag nanoparticles were fabricated by self-assembly technique of thermal evaporation of a thin Ag film followed by a N₂ atmosphere anneal at 200°C. A mass thickness of 28 nm was used as the precursor layer for the Ag nanoparticles. This mass thickness has been found to give the best results as reported in previous study [3.3.1.1.1]. (3) The third type of single reflector used a detached reflector layer that was deposited on another substrate and placed on the cell so that it is optically coupled to the cell with air as buffer layer. It can either be a metal film or a layer having scattering properties. In this study with single reflectors two different thicknesses for the passivating SiO₂ were used: 55 nm and 96 nm.

To further capitalize on the benefits brought about by the Ag MNP reflector, improved double layer reflectors were investigated as shown in Fig. 3.3.1.1.2. The additional reflector is introduced to eliminate the plasmon-induced out coupling losses and light transmitted, such that light can be redirected back into Si. The second reflector is either detached or separated by a 500 nm dielectric spacer layer. In this study we use MgF₂. The thickness of the dielectric layer is important and was optimized as well. The layer which acts as a caulking layer to eliminate shunting. a dielectric over-coating film can provide better adhesion and better protection of the metal nanoparticles that would otherwise be easily removed during handling and in between processes. Moreover, if a second reflector were applied, the dielectric could help to isolate the first layer Ag nanoparticles from the second scattering or reflecting layers that could potentially interfere with the scattering properties of the first layer. A very recent study has found that the second reflector separated by MgF₂ film also prevents Ag MNP from plasmonic degradation. The rear passivating SiO₂ thickness in this part of the study was 34 nm.

**Figure 3.3.1.1.3:** Current enhancement calculated from 900 nm to 1200 nm for solar cell with various single layer reflectors and two different passivating oxide thicknesses: 55 nm and 96 nm. Enhancements are compared to the bare case.

Figure 3.3.1.1.3 shows a comparison of the performance of each of the single reflectors compared to the bare case. The scattering silver MNP clearly show the best enhancement. The effect of the oxide layer thickness is also clearly evident, thinner layers provide better coupling of the scattered light into Si (55nm SiO₂ in this case).

In light of the benefits brought about by the Ag MNP, improved double layer reflectors were developed to reflect back any transmitted/scattered light back into the cell. The two reflecting-layers either have an air gap or 500 nm MgF₂ sandwiched in between. EQE enhancements by various double layer reflectors (shown in Fig. 3.3.1.1.4) over the single Ag nanoparticles reflector were calculated by Eqn. 3.3.1.1.1.
EQE enhancement double = EQE double layer reflector / EQE single nano Ag reflector

(3.3.1.1.1)

Figure 3.3.1.1.4: EQE enhancements for solar cells with various double reflectors compared to cells with single Ag MNP reflector. The inset of the figure shows the measured reflection at the rear Si interface as a function of incident angles for rear scheme “Si / SiO₂ / Al” and “Si / SiO₂ / Ag”. This measurement is enabled by using hemispherical silicon as substrate as reported previously [3.3.1.1.2].

The performance improvement of Ag over Al is clearly shown due to reduced parasitic absorption loss in Ag compared to Al (see inset of Fig. 3.3.1.1.4) which enhances rear side reflection in Si. Short circuit current enhancement by various double reflectors over single Ag MNP reflector was also calculated over the wavelength region of 900 nm - 1200 nm as shown in Fig. 3.3.1.1.5. We can conclude that suitable double reflector structures are those that utilize Ag as the second reflector. Even though the results suggest the use of an air-gap gives slightly higher current enhancement due to low parasitic losses in metal, this may not be practical.

Figure 3.3.1.1.5: Short circuit current enhancement over wavelength range of 900 nm to 1200 nm by the double layer reflectors compared to the single layer Ag MNP reflecting scheme.

Interference in our double reflector configuration for the evaporated metal case can occur not only due to the incident and back reflected light but due to the light scattered from the MNP introducing an
angular dependence. Hence the optimisation of the dielectric layer thickness is important for a plasmonic solar cell.

In this part of the work, five different thicknesses of MgF\(_2\) layer were investigated for the Ag MNP/MgF\(_2\)/E Ag double reflector, see Fig. 3.3.1.1.6. Ag was chosen as it yielded the best results. The precursor Ag film thickness was kept at 28 nm and the passivation oxide layer was 19 nm. We compared the enhancement in this case to the best single layer reflector which was the Ag MNP to understand the potential of improvement from the second reflector. It is very interesting to note that when the thickness of MgF\(_2\) is around 300 nm thick, there is a clear suppression of enhancement compared to the case with MNP only. This is due to interference effects and highlights the importance of proper choice of over-coating layer thickness.

Figure 3.3.1.1.6: EQE enhancements by the double layer reflector Ag MNP/MgF\(_2\)/E Ag when compared to the single Ag MNP reflector using different thicknesses of MgF\(_2\) and same SiO\(_2\) thickness of 19 nm.

To investigate the effect of light interference for a multilayer geometry, an optical model was built using W-VASE. This model does not account for Ag nanoparticles within the layers and accounts only for interference effect for a multilayer structure with Si as the ambient. In order to incorporate the scattering effect from the metal nanoparticles, we introduced angular data in the optical model. Figure 3.3.1.1.7 shows the rear reflection (into Si) for the structure Si / 20 nm SiO\(_2\) / MgF\(_2\) / Ag at 1100 nm wavelength for 0 nm - 600 nm thickness of MgF\(_2\).

Figure 3.3.1.1.7: Rear reflection at 1100 nm for various MgF\(_2\) thicknesses. Different curves indicate light with different angle \(\theta\) within MgF\(_2\) layer.

At normal incidence (\(\theta=0^\circ\)), the use of 100 nm - 200 nm MgF\(_2\) and also 500 nm MgF\(_2\) results in good reflection due to constructive interference. Minimum reflection due to destructive interference occurs when MgF\(_2\) thickness increases to 350 nm. However these results do not directly explain the higher
enhancements seen for MgF$_2$ thickness of 400 nm compared to the thickness of 200 nm and the minimum when the thickness is 300 nm from our experimental results. From Fig. 3.3.1.1.7 it can be concluded that the angular dependence cannot be ignored as phase shift in the layer (due to the dielectric layer and metal) becomes important and is the reason for the onset of interference effects.

The forward-scattered light by metal nanoparticles has an angular distribution with its peak intensity located within the angular range of $30^\circ$. From Fig. 3.3.1.1.7, if light travels within MgF$_2$ layer with an angle $\theta = 30^\circ$, the reflection would be at its minimum at 300 nm MgF$_2$ which explains the decrease in EQE from our experimental results. Reflection at 100 nm and 500 nm MgF$_2$ are all located near the wave crest of the sinusoidal curve so their values are clearly higher than the value at 300 nm MgF$_2$. As the angle of incidence further increases (from $30^\circ$ to $40^\circ$), reflection at 400 nm would be higher than that at 200 nm. As it may appear from our simulations and experimental results, scattered angle from the MNP is slightly larger than $30^\circ$ ($30^\circ$ - $40^\circ$). After optimising the over-coating MgF$_2$ thickness, the best-performing double layer reflector structure improves EQE by 4.5-fold at 1160 nm and enhances photocurrent by 25.6% (calculated from 900 nm to 1200 nm), compared to the configuration of state-of-art cells with metal back reflectors.

References


3.3.1.2 Fabrication of large area ultra-thin silicon solar cells

Research Team:
Allen Barnett
Malcolm Abbott
Stuart Wenham
Craig Johnson
Bram Hoex

Postgraduate research students:
Jack An
Alex Han
Alex Li
Peinan Teng
Alex To
Lu Wang
Alison Wenham

3.3.1.2.1 Overview
Thin crystalline silicon solar cells have potential to achieve high efficiency due to the potential for increased voltage. Thin silicon wafers are fragile so means of support must be provided. One attractive design that solves this problem is the ultra-thin silicon (UTSi) solar cell on steel. The silicon layer on this device is approximately 20\(\mu\)m thick, and a steel alloy substrate is bonded to the cell to provide mechanical support and back plane electrical connection. The thin crystalline silicon layer growth and electrical integration with a steel substrate ensures physical robustness while remaining flexible. Based on the PERL structure [3.3.1.2.3] and utilizing laser doping, light induced plating and shallow texturing technologies, this solar cell obtains the manufacturing potential of conventional wafer based solar cells. This design has achieved a conversion efficiency of 16.8% (NREL verified) on a 4cm\(^2\) device [3.3.1.2.1]. Scaling the design to 100cm\(^2\) demonstrates the manufacturing viability and potential of this technology. Scaling up to 100cm\(^2\) cells has also enabled interconnection and lamination studies.

3.3.1.2.2 Cell structure
Figure 3.3.1.2.1 illustrates the structure of the ultra-thin Si solar cell. The solar cell is approximately 20\(\mu\)m thick, bonded to a 125\(\mu\)m steel substrate. The 18\(\mu\)m n-type base is sandwiched between a 2\(\mu\)m n-type front surface field layer and a 1\(\mu\)m p-type rear emitter, both with relatively light doping. Optical enhancement is achieved by shallow texturing combined with a SiON\(_x\) anti-reflection coating, which also provides front surface passivation to the device. The front contact is formed by a stack of Ni and Cu with finger width of 30-60\(\mu\)m. The rear surface is contacted by Al through a layer of patterned thermal SiO\(_2\). The layer of Al also functions as the backside mirror in the UTSi device.
Figure 3.3.1.2.1: Structure of the UTSi solar cell

The immediate advantage of adapting an ultra-thin cell design, apart from eliminating the conventional kerf loss problem, is the potential to improve open circuit voltage by reducing bulk recombination. The modeled upper value for Voc is 767mV based on this structure [3.3.1.2.1], and can lead to 22% cell efficiency.

3.3.1.2.3 Device fabrication

The fabrication process of the UTSi solar cell begins at AmberWave Inc., with formation of a layer of porous Si on heavily doped p-type substrate wafers via anodic etching. The active layers of ultra-thin silicon are epitaxially grown over the porous Si by reduced pressure chemical vapor deposition at temperatures above 1000°C. During the growth, dopants are introduced into the layers resulting in formation of the n-type front surface and base regions, and the p-type emitter region. The n-type cell structure minimizes the potential of boron-oxygen defect problems, and the rear emitter prevents junction shunting during the laser doping process.

Once the semiconductor layers are formed, AmberWave then grows a layer of thermal SiO₂ on the rear side and creates point contact patterning followed by Al evaporation. The wafer is subsequently bonded to a 125µm steel alloy substrate and detached from the original silicon substrate, with the porous Si serving as a splitting layer[3.3.1.2.6]. These devices are then shipped to UNSW for solar cell fabrication.

At UNSW, the process starts by chemically removing the remaining porous silicon residues on the front surface from the detaching process. Shallow pyramidal textures are then formed using a KOH based solution, with isopropanol and polyethylene glycol as additives. The average pyramid size is 1-2µm to ensure good light coupling and minimal loss of silicon material. After cleaning in RCA #1 and then diluted-HF solutions, a layer of high quality SiON, is grown in a plasma enhanced chemical vapour deposition (PECVD) tool at 400°C. This provides good passivation to the surface, hydrogen to the bulk and anti-reflection coating (ARC) to the device. The front contacts are patterned and doped by a 532nm continuous-wave laser with the assist of spin-on dopant [3.3.1.2.4]. Then a stack of Ni and Cu forms the fingers and busbars using self-aligning light induced plating technology [3.3.1.2.5]. The edges of the device are then isolated with a combination of laser cutting, mechanical trimming as well as chemical etching.
3.3.1.2.4 Results and discussion

The SiONₓ film produced by the PECVD process has a consistent refractive index of 2 to 2.1; however, the deposited film thickness varied across the sample surface. This was caused by sample warping under heat, a result of thermal mismatch between the device layer (Si) and the substrate layer (steel). The film uniformity was optimized by varying PECVD gas ratios and measuring the deposition rate at different locations in the chamber. To characterize this shift of uniformity, Light Beam Induced Current (LBIC) is used to scan the cell surface with a 404nm laser. The tool measured and plotted the corresponding percentage reflection as shown in Figure 3.3.1.2.2.

![Figure 3.3.1.2.2: Reflection measurement with a 404nm laser on LBIC shows performance of the SiONₓ film before (left) and after (right) optimization](image)

The I-V characteristics were measured in a h.a.l.m. cetisPV-Celltest3 tester at UNSW. Table I summarizes some of the milestone results of the large UTSi solar cell fabrication project.

<table>
<thead>
<tr>
<th>Area</th>
<th>UNSW V oc(mV)/Jsc (mA/cm²)/η</th>
<th>NREL V oc(mV)/Jsc (mA/cm²)/η</th>
</tr>
</thead>
<tbody>
<tr>
<td>50cm²</td>
<td>569 28.2 11.9%</td>
<td></td>
</tr>
<tr>
<td>50cm²</td>
<td>616 33.7 15.6%</td>
<td></td>
</tr>
<tr>
<td>100cm²</td>
<td>593 31.7 14.4%</td>
<td></td>
</tr>
<tr>
<td>100cm²</td>
<td>609 35.0 16.2%</td>
<td>612 33.9 15.8%</td>
</tr>
<tr>
<td>612</td>
<td>33.9 15.8%</td>
<td></td>
</tr>
<tr>
<td>90cm²</td>
<td>632 35.0 16.5%</td>
<td>632 33.7 15.9%</td>
</tr>
</tbody>
</table>

TS833 is the cell with highest efficiency, measured as 16.5% at UNSW and 15.9% by NREL (Figure 3.3.1.2.3). The device was shunted at two fingers after the standard fabrication process, and the problem was rectified using a mechanical shear (Figure 3.3.1.2.4). The effective cut with this shear confirms the robust nature of the UTSi structure. It also allows cutting over laser doped fingers and busbars without causing shunt problem. The initial results show a 1-3% fill factor loss compared to a good-clean laser isolation.

Note that Jsc in the NREL measurement of TS833 was via multi-point probes which introduced some shading losses. Using a Kelvin probe on the same device, NREL measured Jsc of 34.5mA/cm², an increase of 0.8mA/cm². This allows an extrapolation to a no-shading efficiency value of 16.34%, close to the 16.5% efficiency measured by UNSW.
Figure 3.3.1.2.3: IV measurement of the 90cm² ultra-thin Si cell

![IV Measurement](image)

- $V_{oc} = 0.6316$ V
- $I_{sc} = 2.9705$ A
- $I_{oc} = 33.652$ mA/cm²
- Fill Factor = 74.99 %

- $V_{max} = 0.5224$ V
- $P_{max} = 1.4068$ W
- Efficiency = 15.94 %

Figure 3.3.1.2.4: Photoluminescence image of TS883 before (left) and after (right) a mechanical cut to remove two shunted fingers.
The reflection and internal/external quantum efficiency (IQE/EQE) of TS883 are shown in Figure 3.3.1.2.5.

**Figure 3.3.1.2.5:** IQE/EQE/Reflection measurement of the champion ultra-thin Si cell with device area of 90cm$^2$

Summary

This paper discussed the design, fabrication process and progress in the development of large area (100cm$^2$) ultra-thin Si on steel solar cells. Improvement in the fabrication process has enabled a 90cm$^2$ champion cell with measured efficiency of 16.5% to be developed.

References


3.3.1.2.3 Zhao, Jianhua, Aihua Wang, and Martin A. Green. "24.5% Efficiency silicon PERT cells on MCZ substrates and 24.7% efficiency PERL cells on FZ substrates." Progress in Photovoltaics: Research and Applications 7.6 (1999): 471-474.


3.3.1.3 III-V on Silicon Cells

**Research Team:**
- **University Staff**
  - Martin Green
  - Stephen Bremner
  - Gavin Conibeer
  - A. Ho-Baillie
  - Xiaojing Hao
  - H. Mehrvarz

**Postgraduate Research Students and Research Assistants**
- Sammy Lee
- Ziheng Liu
- Ibraheem Al Mansouri
- Shinyoung Noh

With the 25% UNSW lab result providing a likely cap on what can be achieved in production with conventional approaches, much higher efficiency is possible if tandem stacks of cells are used, with the ultimate thermodynamic efficiency potential increased by a factor of 2-3. Silicon is a clean and low-cost substrate and it is possible to grow high bandgap material on it. The limiting efficiency for tandem solar cell using Si as bottom cell is quite close to the efficiency limit for tandem solar cell with unconstrained material choice, which indicates Si is an excellent choice for the bottom cell. Equally impressive to the progress with Si technology has been the rapid improvement in Group III-V cell efficiency, driven by the use of these much more expensive cells in space and in systems with sunlight focused 300-500 times. Efficiency has increased rapidly recently with 36% efficiency demonstrated under standard sunlight, increasing to over 43% with strongly concentrated sunlight. The preferred substrates for these cells are Germanium (Ge) wafers. Even though much cheaper than III-V semiconductor wafers, Ge wafers are over 100 times more expensive than Si, providing the fundamental limit on achievable III-V cell costs.

Tandem stack III-V technology provides a significant opportunity to improve efficiency but is expensive in its usual form since Ge is a perfect match to the III-V group, but is over 100 times more expensive than Si. If the lattice spacing difference between Ge and Si is taken up near the interface with a thin, essentially perfectly crystalline Ge layer formed above this interfacial layer, the Si wafer can be converted into a “virtual Ge” substrate, suitable for the subsequent deposition of a III-V cell stack, see Fig. 1.

![Diagram](image)

**Figure 1:** Possible cell stack grown on Ge coated Si wafer
3.3.1.3.1 Cyclic thermal annealing on Ge/Si epitaxial films

In 2014, cyclic thermal annealing is investigated as an option to reduce the threading dislocation density (TDD). The high TDD in the Ge film due to the lattice mismatch between Ge and Si induces high TDD in the III-V material and therefore degrades the cell performance. The TDD is reduced by two orders of magnitude after 6-cycle-annealing. The mechanism of the TDD reduction is investigated revealing formation of dislocation loops and dissociation of dislocations into planar defects at the interface.

The cyclic annealing was conducted in a furnace and each annealing cycle includes 900 °C for 10 min and 750 °C for 10 min. After cyclic annealing, the Ge peak intensity increases and the full width at half-maximum decreases indicating improved crystallinity as shown in XRD (Fig. 2a). The XRD reciprocal space mappings (Fig. 2b) reveal that the Ge peak becomes steeper after a 6-cycle annealing owing to improved crystallinity and a tail is observed suggesting the diffusion of Si near the interface. In addition, the peak shifts in XRD and Raman spectra (Fig. 3) indicate the in-plane strain in the Ge film changes from compressive to tensile after annealing.

TEM images in Fig. 4 show that the TDD reduces after cyclic annealing. During annealing the dislocations within the Ge film are thermally activated to glide towards the edges and the interface. The possible reactions between dislocations include annihilation, fusion, and dissociation. The annihilation may happen between dislocations with opposite Burger vector when they glide within an annihilation radius. In a fusion reaction, two dislocations may react to form a new dislocation as evidenced by the loops observed near the Si - Ge interface in Fig. 4(d). The close-up view of the interface shown in Fig. 4(f) reveals that the defective layer at the interface contains planar defects which could be generated by the dissociation of dislocations.

Figure 2: XRD results of (a) 2θ-Ω profiles around (004) order of the Ge samples before and after 1-cycle; 3-cycle; and 6-cycle annealing. (004) reciprocal space maps of the Ge films (b) before annealing and (c) after a 6-cycle annealing.
3.3.1.3.2 Diode laser annealing on Ge/Si epitaxial films

Cyclic thermal annealing could effectively reduce the TDD of Ge, although the process requires relatively high temperature and long annealing time. Diode laser annealing (DLA) is investigated as a simple, fast and low-cost alternative. A patent application on this approach has been filed through NSi, UNSW.
By laser scanning the Ge film, the top Ge layer is melted and the dislocations could glide towards
the Si and Ge interface. The TDD of the Ge film could be reduced by three orders of magnitude.

As shown in Fig. 5, the normalized peak temperature sharply rises with laser dose increasing and after
that peak temperature saturates at a maximum value indicating partial melting of the film and
absorption of latent heat. The partial melting of top layer is confirmed by the TEM images in Fig. 7.

Raman spectra (Fig. 6) show the full width at half maximum of the Ge films after DLA decreases
significantly revealing the crystallinity improvement in the top Ge layer. After DLA, a quite clean top
layer and a defective bottom layer are observed in the TEM images (Fig.7). The TDD of the top layer
in DLA Ge film is reduced by three orders of magnitude to low $10^7$ cm$^{-2}$ and the surface dislocation
density might be even lower. Ongoing work to be carried out to improve the uniformity of DLA.

![Graph](image)

**Figure 5**: Normalized peak temperatures of the Ge sample surface at different laser doses.
Figure 6: Raman spectra of the Ge samples before and after diode laser annealing at laser doses of 2 a.u and 2.4 a.u.

Figure 7: Cross-sectional TEM images of Ge samples before annealing in (a) bright and (b) dark field; and after diode laser annealing with an optimized dosage in (c) bright and (d) dark field.
3.3.1.3.3 Publications


Liu, Z., Hao, X., Ho-Baillie, A., Li, W. and Green, M.A. “Laser annealing for Ge epitaxial film on Si wafer, a cost-effective virtual Ge substrate for high efficiency III-V solar cells”, application submitted to be filed (NSi Ref: 14_2945).

3.3.1.4 High Performance, High Voltage GaAsP on Silicon Solar Cells

Research Team
Allen Barnett
Ivan Perez-Wurfl

Postgraduate research students:
Martin Diaz
Li Wang
Dun Li
Brianna Conrad
Xin Zhao
Anastasia Soeriyadi

3.3.1.4.1 Abstract
Lattice matched GaAsP/SiGe dual-junction solar cells have been grown directly on silicon substrates. This structure has the potential of achieving tandem efficiencies of 40% by utilizing the high performance of the III-V top cell while maintaining the cost advantages of silicon solar cells. It is the SiGe graded buffer grown on the silicon substrate that ultimately allows for lattice matching of the top and bottom cell while providing a low dislocation interface between the silicon substrate and the device layers. The two-step growth process of these structures is accomplished using reduced pressure chemical vapor deposition followed by metal organic chemical vapor deposition. Fabrication is concluded with the application of a double layer anti-reflection coating. Initial tandem structures have reached open-circuit voltages and short-circuit current densities up to 1.5 V and 18.4 mA/cm² with anti-reflection coating, respectively. Efficiencies of 18.9% have been achieved and near term improvements to 25% under AM 1.5G have been determined.

3.3.1.4.2 Introduction
Though III-V multi-junction concentrator technology holds the record for solar cell efficiency, crystalline silicon has continued to dominate the solar energy market with over 85% of the market share and the most efficient commercial modules [3.3.1.4.1][3.3.1.4.2]. The highest efficiency for silicon substrate based solar cells is 25.6% under 1-sun [3.3.1.4.2]. The efficiency limit for a two-junction unconstrained tandem structure is 45% and is 42.5% for a structure constrained to a silicon bottom cell [3.3.1.4.3]. To realize the higher efficiencies from multi-junction tandem solar cells, high voltages and high quantum efficiencies must be demonstrated by the top solar cells [3.3.1.4.4]. III-V materials have been proven to meet these requirements as the highest photovoltaic efficiencies are those from III-V multi-junction solar cells [3.3.1.4.2].

The aim of this research is to combine the high performance of III-V multi-junction solar cells with the developed silicon wafer based technology for a potential efficiency of 35%. However, the difficulty with this process lies with the large lattice-mismatch between the silicon substrate and the III-V epitaxial layers resulting in an increased threading dislocation density (TDD). This higher TDD affects the minority carrier lifetime and reduces the open-circuit voltage ($V_{oc}$) of the device [3.3.1.4.5]. By lattice matching the top and bottom cells, the voltage loss due to threading dislocations is minimized. The lattice-matched GaAsP/SiGe tandem structure from which this research stems has been studied by Schmieder et al.
3.3.1.4.3 Approach

The key technology behind this structure is the metamorphic SiGe graded buffer developed by AmberWave which allows for this lattice matching and low dislocation interface between the silicon substrate and the device layers resulting in high performance from the top cell. This tandem structure utilizes GaAsP for the top cell and SiGe for the bottom cell to achieve both lattice matching and current matching for maximum performance. Figure 3.3.1.4.1 shows the basic two-terminal tandem structure design. A more detailed diagram of the GaAsP/SiGe on Si tandem structure and cross-sectional SEM is shown in Figure 3.3.1.4.2.

![Diagram](image)

**Figure 3.3.1.4.1:** Two-terminal GaAsP/SiGe on Silicon tandem solar cell device

<table>
<thead>
<tr>
<th>Layer</th>
<th>Material</th>
<th>Energy</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Contact</td>
<td>GaAs$<em>{0.84}$P$</em>{0.16}$</td>
<td>1.67eV</td>
<td>n+</td>
</tr>
<tr>
<td>Window</td>
<td>In$<em>{0.3}$Al$</em>{0.7}$P</td>
<td>2.4eV</td>
<td>n</td>
</tr>
<tr>
<td>Emitter</td>
<td>GaAs$<em>{0.84}$P$</em>{0.16}$</td>
<td>1.67eV</td>
<td>n</td>
</tr>
<tr>
<td>Base</td>
<td>Ga$<em>{0.59}$In$</em>{0.41}$P</td>
<td>1.67eV</td>
<td>p</td>
</tr>
<tr>
<td>BSF</td>
<td>GaAs$<em>{0.84}$P$</em>{0.16}$</td>
<td>2eV</td>
<td>p</td>
</tr>
<tr>
<td>Buffer</td>
<td>GaAs$<em>{0.84}$P$</em>{0.16}$</td>
<td>1.67eV</td>
<td>p</td>
</tr>
<tr>
<td>TJ</td>
<td>GaAs$<em>{0.84}$P$</em>{0.16}$</td>
<td>1.67eV</td>
<td>p/n+</td>
</tr>
<tr>
<td>Buffer</td>
<td>GaAs$<em>{0.84}$P$</em>{0.16}$</td>
<td>1.67eV</td>
<td>n</td>
</tr>
<tr>
<td>Nucleation</td>
<td>Ga$<em>{0.59}$In$</em>{0.41}$P</td>
<td>2eV</td>
<td>n</td>
</tr>
<tr>
<td>Si$<em>{0.18}$Ge$</em>{0.82}$</td>
<td>SiGe</td>
<td>0.86eV</td>
<td>i</td>
</tr>
<tr>
<td>Emitter</td>
<td>Si$<em>{0.18}$Ge$</em>{0.82}$</td>
<td>0.86eV</td>
<td>n</td>
</tr>
<tr>
<td>Base</td>
<td>Si$<em>{0.18}$Ge$</em>{0.82}$</td>
<td>0.86eV</td>
<td>p</td>
</tr>
<tr>
<td>Graded Buffer</td>
<td>Si$<em>{0.18}$Ge$</em>{0.82}$</td>
<td>1.1-0.86eV</td>
<td>p</td>
</tr>
<tr>
<td>Si Substrate</td>
<td>SiGe</td>
<td>1.1-0.86eV</td>
<td>p</td>
</tr>
</tbody>
</table>

**Figure 3.3.1.4.2:** Simplified GaAsP/SiGe on Si device structure.
3.3.1.4.4 Material Growth

The growth of this tandem structure is completed using a two-step growth process of the epitaxial layers and fabrication is finalized with the aid of photolithography. The first growth step involves the growth of the SiGe layers while the second growth step produces the III-V layers.

AmberWave uses reduced pressure chemical vapor deposition (RPCVD) to carry out the growth of SiGe on (100) 6° offcut CZ silicon. Threading dislocation densities (TDD) as low as $2\times10^5$ cm$^{-2}$ have been realized with this growth process [3.3.1.4.7]. Ge concentrations of 82-86% for the SiGe bottom cell are achieved with the SiGe graded buffer.

Veeco then completes the lattice-matched III-V growth using metal organic chemical vapor deposition (MOCVD) while keeping the thickness to a minimum <3µm. Contributing to the thickness of these layers is the tunnel junction for these n+/p structures, however it will be beneficial to have the SiGe material contain the tunnel junction in future tandem device structures. These III-V layers have exhibited a TDD of $6.2\times10^6$ cm$^{-2}$ on SiGe [3.3.1.4.8]. Figure 3 shows the SEM cross section of the full growth structure with the corresponding epitaxial growth layers.

![Figure 3.3.1.4.3: Cross-sectional SEM and structure design.](image)

3.3.1.4.5 Fabrication

The primary process used for fabrication in this research is photolithography, which provides all necessary processing requirements for the quick turnaround devices shown in Figure 3.3.1.4.4 with few disadvantages. The rear Al metal and front Ni/AuGe metal is deposited using thermal evaporation. The contacts are then annealed using rapid thermal processing (RTP). Isolation of the devices is performed using a combination of wet and dry etching resulting in devices of 0.01 mm$^2$, 1.0 mm$^2$, 9.0 mm$^2$, and 1.0 cm$^2$ in size. The SiGe bottom cell is not isolated in these early devices as it has not yet been optimized to match the current of the GaAsP top cell. The final step is the application of the double layer anti-reflection coating (DLARC) deposited by plasma-enhanced chemical vapor deposition (PECVD).
3.3.1.4.6 Results

The fabricated two-terminal solar cell devices are tested indoors with a solar simulator. These latest devices contain a SiNₓ/SiO₂ DLAR C and demonstrate a short-circuit current density (JSC) improvement of 10.4% over previous best devices resulting in a JSC of 18.1 mA/cm².

The improvement in the quantum efficiency (QE) of each cell due to the DLARC can be seen in Figure 3.3.1.4.5. With the DLARC minimizing the reflection to less than 10% between 350 nm and 1050 nm the external quantum efficiency (EQE) has improved by 21.6% and 30.2% for the GaAsP top cell and the SiGe bottom cell, respectively. This improvement in JSC has contributed to the 1.7% absolute improvement in efficiency over previous best results. Table I summarizes and compares the latest best device results with the previous best. With an open-circuit voltage (VOC) of 1.45 V and a fill factor (FF) of 72% the best efficiency achieved for this tandem device structure is 18.9%. The current density-voltage (J-V) curve is shown in Figure 3.3.1.4.6.

Further analysis shows the devices suffering from a low FF due to series resistance. Figure 3.3.1.4.7 compares a measured J-V curve with the measured JOC-VOC curve which removes the effect of series resistance. Without the effect from series resistance the FF improves from 71.4% to 81.5% which near the calculated intrinsic FF of 82%. With the VOC and JSC remaining the same the device performance approaches an efficiency of 21.5% as the FF is improved to 82%. As the VOC is improved to the best voltage measured of 1.5 V and the current is improved to match the best top cell measured JSC of 20.1 mA/cm², the overall tandem efficiency approaches 25%.
Figure 3.3.1.4.5: Quantum efficiency of GaAsP/SiGe on Si tandem device with and without ARC.

Figure 3.3.1.4.6: IV performance for GaAsP/SiGe tandem solar cell with ARC.
Lattice matched GaAsP/SiGe tandem devices are grown on silicon substrates and fabricated with an ARC resulting in an improved efficiency of 18.9%. The QE of the sub-cells shows an improvement of 21.6% and 30.2% for the GaAsP top cell and the SiGe bottom cell, respectively, with the addition of the ARC. This two-terminal tandem structure continues to show promising results although the SiGe bottom cell remains the current-limiting cell as it is not fully optimized. Furthermore, high series resistance significantly effects the device performance and contributes to the low FF measured.

With further optimization to the SiGe bottom cell and the addition of surface texturing and a rear back contact reflector for light trapping such that the current of the SiGe bottom cell matches the current of the GaAsP top cell, the potential efficiency of this early tandem structure approaches 25.0%.

3.3.1.4.7 Conclusions

Figure 3.3.1.4.7: GaAsP/SiGe on Si measured light I-V and measured $J_{SC}$-V$_{OC}$ curve

3.3.1.4.8 References


3.3.2 INDUSTRY COLLABORATIVE RESEARCH AND COMMERCIALISATION

3.3.2.1 Introduction

UNSW has a strong track record in developing and successfully commercializing photovoltaic (PV) technology. Approximately half of the new silicon-based PV technologies successfully developed and commercialised internationally in the last 30 years have originated from UNSW, with four distinct technologies having been successfully implemented into large-scale manufacturing with a fifth currently in pilot production with several companies. Of these five technologies, three are based on plated metallization, one on screen-printing of the metal contacts and one on the sputtering of the metal contacts. Screen-printing strongly dominates current commercial devices but with experts in general predicting that plated contacts will eventually dominate in the future. UNSW has arguably the strongest initiative internationally on both the science of plating to solar cells and also the commercialization of plating technologies with the team focusing on the former headed by Dr Alison Lennon while the team working on the latter is headed by Assoc Professor Ji. Figure 3.3.2.1 shows commercial plating baths based on light induced plating (LIP) designed by Prof Ji based on UNSW plating technology and installed in SIRF at UNSW to demonstrate this innovative technology. More than ten of these sets of baths have already been manufactured and sold commercially for use in high throughput solar cell manufacturing.

UNSW is in a particularly strong position if the use of plating technology expands, particularly since LIP is becoming the international standard and UNSW has been recently awarded two key patents that appear to cover all the approaches being used by plating bath manufacturers [3.3.2.1, 3.3.2.2] around the world. These patents are nicely complemented by an additional two patents [3.3.2.3, 3.3.2.4] that cover the design of the plating baths. The latter being “method” patents are not as powerful as the first two “concept” patents, but in combination form a strong portfolio that would appear to necessitate any plating tool manufacturers for photovoltaics needing to license the technology from UNSW. Even the simultaneous plating to both n-type and p-type contacts appears to be covered by new UNSW patent applications although final patent review is not yet complete. In relation to UNSW wafer-based research, most innovative technologies are based on plated contacts due to their potential for both superior performance and lower cost by eliminating silver consumption.
Figure 3.3.2.1: Plating baths suitable for large-scale manufacturing, designed by world expert Dr Ji for forming solar cell contacts based on the UNSW developed plating technology. (d) shows a cross-section of the plating (left) and a top surface view of a plated cell using these plating baths.

3.3.2.2 Industry Collaborators and Licensees of Technology

In recent years, increasing interest from industry in the Centre’s commercially significant technologies has led to a substantial increase in the number of the world’s leading cell manufacturers choosing to directly fund, support and engage in collaborative research with the Centre. A new model for interfacing with industry was adopted in 2014 where a consortium approach was preferred over the establishment of independent collaborative research agreements with individual companies. It appears that for a number of reasons, many of the largest companies are now willing to work together in developing and commercialising the Centre’s technologies rather than as previously in isolation. The changed attitude has in part been contributed to by tougher times following the world financial crisis, although several companies have indicated that their determination to have access to the latest generation of Centre technology has become more important to them than who they have to team up with. The net result is a very positive one for the Centre with industry funding now being able to be pooled in support of a larger core research program rather than being split into many smaller parcels with corresponding isolated but overlapping projects.

The new ARENA project 1-060 has a large number of industry partners including eight of the world’s largest solar cell manufacturers, seven leading tool manufacturers and six material suppliers, with most of the latter being silicon producers. In return for funding the core research associated with the new advanced hydrogen passivation technology, automatic licences are provided to the contributing manufacturers.

In addition, the Centre has a large number of other collaborators and licensees including many other cell manufacturers of various sizes, working with the Centre to improve or develop new solar cell technology for commercialisation. Some of these fund the Centre quite generously and are seen as being partners to NewSouth Innovations (NSI), the commercial arm of the University that manages the entire intellectual property portfolio for the Centre. Interest from companies wanting to become commercial partners with the Centre or license technology grew rapidly during the last five years despite the world financial crisis in late 2008 and subsequent international financial turmoil. This appears to be due in part to the perceived world leadership of UNSW in this area, but also due to the growing long-term importance placed on photovoltaics by a world struggling to deal with climate change, diminishing resources and increasing energy requirements. Collaborators with the Centre in the first generation photovoltaics area come predominantly from China, Germany, the United States, Australia, South Korea and Taiwan and include Suntech-Power, Roth and Rau, Guodian Solar, Centrotherm, Tianwei New Energy, Optomec, Sunrise Energy, Sunergy, E-ton Solar, Spectraphysics,
Hyundai Heavy Industries, China Light, Corum Solar, Advent, Shinsung, Apollon Solar, 1366, Trina Solar, LG Electronics, Dupont, Heraeus and Yunnan Tianda. Several of these companies are amongst the world’s largest solar cell and equipment manufacturers.

3.3.2.3 Commercially Relevant Technologies

3.3.2.3.1 Introduction

With screen-printed solar cells continuing to dominate commercial manufacturing with well over 50% market share, the broad aim of this work has been to develop, in conjunction with several industry partners, the next generation of screen-printed solar cell. In particular, the fundamental limitations of the conventional screen-printed solar cell that have limited its performance for the last 30 years have been identified, and innovative approaches to redesigning the emitter and front metal contact have been devised, developed and analysed in this work. In addition to overcoming the current and voltage limitations imposed by the design shown below, a further aim of this work has been to retain compatibility with existing equipment and infrastructure currently used by our industry partners for the manufacture of screen-printed solar cells.

Despite the dominance of this technology, this solar cell design has significant performance limitations that limit the cell efficiencies to well below those achievable in research laboratories around the world. In particular, the front surface screen-printed metallisation necessitates a heavily diffused emitter to achieve low contact resistance and also to achieve adequate lateral conductivity in the emitter since the metal lines need to be widely spaced compared to laboratory cells to avoid excessive shading losses. Such cells therefore typically have emitters with sheet resistivities in the vicinity of 80 ohms per square, which inevitably give significantly degraded response to short wavelength light. Good work in recent years by partners Dupont and Heraeus has improved paste formulations, allowing ohmic contacts to be formed to more lightly doped emitters in the vicinity of 80 ohms/square while simultaneously lowering the bulk resistivity of the fired paste. To further raise this sheet resistivity to above 100 ohms per square, as required for near unity internal quantum efficiencies for short wavelength light, serious resistive losses are introduced, both in the emitter and through the contact resistance at the metal to n-type silicon interface. Furthermore, the metal/silicon interface contributes increasing dark-saturation current densities as the emitter sheet resistivity is increased when using a homogeneous emitter.

Furthermore, the conventional design for screen-printed solar cells has quite poor surface passivation in both the metallised and non-metallised regions. Even if good ohmic contacts could be made to more lightly doped emitters, the large metal/silicon interface area would significantly limit the voltages achievable due to the high levels of recombination in these regions and the corresponding contribution to the device dark saturation current. These voltage limitations are not of major significance at the moment due to the limitations imposed by the substrates. However, in the future as wafer thicknesses are reduced to improve the device economics and improved rear surface passivation is introduced, the cells will have the potential for improved open circuit voltages, but only provided the surfaces, including under the metal, are well passivated.

Despite the limitations of the standard screen-printed solar cell, UNSW is working in conjunction with numerous industry partners to make improvements through improving the wafer and surface passivation quality. This is through an innovative hydrogen passivation technology that has demonstrated its ability to passivate virtually any recombination mechanisms including crystallographic defects, metal contaminants and surface states. Recombination that cannot be eliminated is that associated with metal/silicon interfaces which by necessity must approach infinite surface recombination velocities for such interfaces to act as ohmic contacts. Unfortunately, the application of the new hydrogen passivation processes following metal contact formation can lead to the partial passivation of the metal/silicon interfaces with resulting increases in contact resistance. Despite this, Figure 3.3.2.2 shows PL images of a standard screen-printed cell on a low quality cast wafer. Figure 3.3.2.2(a) corresponds to immediately following completion of standard screen-printed
processing where the efficiency was 16.7% and Figure 3.3.2.2(b) corresponds to following the application of the advanced hydrogenation technology to increase the efficiency to 18.0%, even though the fill factor fell to about 73%. The advanced hydrogenation process is implemented through the use of high intensity light of the right wavelength to control the charge state of the hydrogen atoms within the silicon to enhance both the mobility and reactivity of the hydrogen.

![Figure 3.3.2.2: (a) PL image of a standard screen printed multicell of 16.7% which following application of the advanced hydrogenation gives the PL image of (b) with efficiency of 18.0%](image)

### 3.3.2.3.2 Advanced Hydrogenation Technology

The advanced hydrogen passivation technology, developed originally as part of the ARENA project 1-082 and owned by UNSW, has been heralded as one of the major breakthroughs in recent years in silicon photovoltaics. It has been recognized through the awarding of the 2013/14 A F Harvey Engineering Prize, and the 2014 James N Kirby Award, widely regarded as leading Engineering Prizes internationally in any field. A large number of media interviews and articles have been conducted in relation to this technology and the various prizes that have originated as a result.

This work recognizes the importance of controlling the charge state of the hydrogen atoms within the silicon, affecting the mobility of the hydrogen atoms by as much as a factor of one million while also having a major impact on the reactivity of the hydrogen in terms of its ability to bond to and passivate crystallographic defects and contaminants within the silicon that would otherwise create recombination that degrades the efficiency of the solar cell. Perhaps more importantly, the 1-082 project developed innovative ways for controlling the hydrogen charge state, leading to large and demonstrated improvements in the ability to passivate the silicon and surfaces. This has facilitated amazing improvements in the quality of commercial grade wafers, demonstrating the potential for p-type commercial devices in the future to achieve open circuit voltages well above 700mV provided the advanced hydrogenation techniques can be incorporated into device processing so that its benefits can be retained at the completion of device fabrication.

This breakthrough, although achieved as part of the ARENA 1-082 project, will be a major ongoing focus in any projects involving silicon wafer-based projects such as ARENA 1-060 and ARENA RND068 as it appears applicable to all cell technologies. As an example, Figure 3.3.2.3(a) below shows the PL count for a low quality silicon wafer that has been coated on both surfaces with hydrogenated silicon nitride. The wafer was subsequently heated to 250degC while the circular region received the localised application of the advanced hydrogenation process where localised control of the hydrogen charge states appears to have passivated virtually every defect and contaminant to transform the material into being of
similar quality to the highest quality of p-type silicon wafers that are typically more than ten times the price. To quantify the improvements, minority carrier lifetimes are increased by more than two orders of magnitude to above 1ms with corresponding \( \text{iV}_{\text{oc}} \) values above 720mV. Following this important innovation in ARENA 1-082, the new project ARENA RND068 represents the perfect project for the development and integration of this breakthrough into high efficiency cell technology for manufacturing companies. In combination with other innovative enhancements it appears that both plated and screen-printed cell technologies have the potential to take commercial cell efficiencies to levels well above those previously thought possible, particularly in conjunction with suitable rear surface passivation that also doubles as a second hydrogen source.

Figure 3.3.2.3(b) shows a multi wafer that has received conventional hydrogen passivation at 700degC following being coated with SiNx front and rear for surface passivation and to provide hydrogen sources. This was followed in Figure 3.3.2.3(c) by the use of the advanced hydrogenation process that was optimised for CZ wafers by controlling the hydrogen charge state. This was followed in Figure 3.3.2.3(d) by the use of the advanced hydrogenation optimised for grain boundary and crystallographic defect passivation. The latter was particularly effective at eliminating non-uniformities throughout the multi wafers arising from recombination associated with the crystallographic defects, leading to the PL response revealing minimal resulting impact from grain boundaries and other defects. With multi wafers predicted to dominate future photovoltaic manufacturing, industry partners are particularly interested in this technology and applying it to their respective cell technologies.
3.3.2.3.3  Semiconductor Finger Solar Cells

To accommodate a top surface emitter sheet resistivity of at least 100 ohms per square, metal fingers need to be spaced no more than 1mm apart to avoid excessive sheet resistivity losses. Due to the large width of screen printed metal lines of 50 microns or more, such a close spacing is not possible without shading well over 5% of the cell surface. The concept of semiconductor fingers is therefore introduced as shown in Figure 3.3.2.4(a), with (b) showing the superiority of a typical corresponding spectral response. These semiconductor fingers are formed by laser doped the silicon surface while simultaneously patterning the dielectric layer to expose the heavily doped silicon surface. Developmental work with the laser doping process allows sheet resistivities as low as 1 ohm/square to be achieved while simultaneously forming laser doped lines of only 8 microns width. Spacing such lines 0.8mm apart avoids significant resistive losses within the lightly doped emitter which can be diffused to 100 ohms/square, ensuring excellent response to the short wavelengths of light. In the laser-doped regions, approximately half of the incident light is lost due to absorption within the heavily doped semiconductor fingers.

This is defined as a 50% effective shading loss of the semiconductor fingers. Using this design, the effective shading loss of the semiconductor fingers is only 0.5%, while the effective emitter sheet resistivity of the emitter is 50 ohms/square. This latter figure results from the emitter sheet resistance of 100 ohms/square in parallel with the laser doped lines which cover 1% of the area with a sheet resistivity of 1 ohm/square and therefore also effectively contribute 100 ohms/square. This allows the screen-printed lines to retain their normal spacing, but with 99% of the emitter being lightly doped and therefore able to achieve near unity internal quantum efficiencies for short wavelengths of light. In addition, the passivating dielectric layer not only passivates the lightly diffused surface so as to give near unity internal quantum efficiencies for short wavelength light, but it also isolates the metal from these same regions to minimise the device dark saturation current. Importantly, the silicon is only exposed at the semiconductor fingers, with the screen-printed metal having been shown to make excellent ohmic contact to the heavily phosphorus diffused silicon in these regions. Both thick oxides and silicon nitride layers, when used with appropriate pastes, appear to provide adequate protection to the lightly diffused surface regions, preventing the screen-printed metal from contacting the silicon.
Figure 3.3.2.4: (a) Screen-printed fingers running perpendicular to the heavily diffused semiconductor fingers where electrical contact is made. A dielectric/AR coating passivates the top surface and isolates the metal from the lightly diffused top surface. (b) gives the corresponding spectral response curve showing the excellent response to short wavelength light.

A typical cell design based on this concept uses semiconductor fingers 8 microns wide of sheet resistivity 1-2 ohms/square and spacing of 0.8mm. The top surface sheet resistivity is typically 100 ohms/square, with the effective sheet resistivity in the direction parallel to the semiconductor fingers typically 50-60 ohms per square. The screen printed metal lines are printed perpendicular to the semiconductor fingers with a width of 100 microns and spacing of 2.2mm. The overall effective shading loss of the combination of the semiconductor fingers and the screen-printed metal lines (not counting interconnect strips) is therefore 5%, comprising 4.5% from the metal plus 0.5% from the semiconductor fingers. This is typical of conventional screen-printed cells, but with the greatly enhanced short wavelength response of these cells giving about a 3% advantage in short circuit current.

This design also has the advantage of being the equivalent of a self-aligned selective emitter design with the metal only contacting the silicon in heavily doped regions. This gives the cell top surface structure much higher voltage capability although improved rear surface passivation will be necessary to capitalise on this. The biggest challenge in turning this into a robust technology for large scale production is the very small metal/silicon interface area which is less than 0.1% of the top surface. This is sufficient for suitably low contact resistance to facilitate high fill factors provided everything works properly. However, despite approaching 19% efficiency being achieved in pilot production, variability in this contact resistance is a weakness in the design causing efficiencies in production of the technology to vary from 17 to 19%, with the average being below 18%.

The processing sequence for this technology is easily retrofitted onto a standard screen-print line and is as follows:
1. Surface texturing
2. Emitter diffusion (100 ohms per square)
3. Rear surface etch plus edge isolation
4. SiNx deposition by PECVD (top surface)
5. Semiconductor fingers by laser doping
6. Rear metal plus front metal screen-printing
7. Firing of metal contacts

Only step 5 deviates from standard homogeneous emitter screen-printed solar cell fabrication, with the overall fabrication appearing to be simpler and shorter than those sequences proposed for introducing selective emitter designs for screen-printed solar cells.

The best semiconductor finger solar cells have fill factors of 79%, demonstrated with this structure on large area devices of approximately 150cm$^2$, verifying the effectiveness of this contacting scheme for minimising resistive losses. These cells also have near perfect response to short wavelength light as shown below, leading to $J_{sc}$ values of 37mA/cm$^2$. Even though commercial p-type substrates are not capable of voltages above about 640mV, $V_{oc}$ values approaching this have been achieved in pilot production with this technology, with corresponding efficiencies approaching 19%.

This concept of semiconductor fingers does not appear to have been used in large-scale commercial solar cell production, and has considerable appeal as it facilitates good conductivity within the emitter, but without the normal trade-off found in screen printed cells. Normally, such regions of good emitter conduction are located at the top surface and therefore degrade the cell spectral response and current generating capability due to the corresponding extremely short minority carrier diffusion lengths in such regions. This technology is particularly well suited to multicrystalline silicon wafers that normally degrade when exposed to prolonged thermal treatments.

Another possible implementation of this technology would appear to be the incorporation of the laser chemical processing (LCP) techniques developed by the Fraunhofer Institute in Germany in conjunction with the laser company Synova. This would allow the superior performance of the laser grooved semiconductor finger solar cell to be combined with the simplicity and low cost of the laser doped semiconductor finger solar cell. Both institutions have intellectual property that would appear to provide significant benefits in combination.

As part of the core research of the Centre of Excellence funded previously by the ARC and UNSW and more recently by ARENA and industry partners, an enhanced version of the semiconductor finger solar cell was designed and developed to overcome the limitations of the standard semiconductor finger solar cell described in section 3.3.2.3.2. This involves plating 2 microns of silver (or Ni/Ag or Ni/Cu/Ag) to the screen-printed metal at the end of processing, which simultaneously plates a similar thickness to the semiconductor fingers when using light induced plating as shown in Figure 3.3.2.5.

The application of this plated metal has several benefits. Firstly, it makes good ohmic contact to both the heavily doped silicon and also the screen-printed metal, overcoming the high contact resistance sometimes experienced by the standard semiconductor finger solar cell. This makes high fill-factors routinely achievable while solving the yield problems of the original implementation. Secondly, the increased conductivity of the semiconductor fingers facilitates increasing the screen-printed metal line spacing to typically 2-3cm. Although the corresponding width has to be increased to 400 microns, it has the benefit of allowing both tapering and increased height to above 50 microns. This reduces the shading loss of the screen-printed metal fingers from 5% down to about 1%, with the corresponding $J_{sc}$ increase taking efficiencies to above 19%. Interestingly the effective shading loss of the semiconductor fingers was expected to increase by 0.5% although in reality, the plated laser doped surface appears rough enough to scatter the reflected light so that almost half is totally internally reflected at the glass/air interface and returned to the solar cell surface. Therefore the effective shading loss of the semiconductor fingers remains virtually unchanged. Importantly, by avoiding the contact between the screen-printed silver and the lightly doped silicon, the top surface design of this
A solar cell behaves very differently to standard screen-printed contacts and appears to have the potential to achieve open circuit voltages approaching 700mV.

Figure 3.3.2.5: Photo of a hybrid screen-printed and plated solar cell showing the three levels of metallisation. Each of the two busbars effectively collect current from 8 small solar cells, each with a tapered screen-printed line that carries the current from the narrow plated lines to the respective busbar/interconnect.

The development of this technology has formed part of the ARENA 1-082 project involving Suntech. It is particularly well suited to multicrystalline silicon wafers due to the avoidance of prolonged high temperature thermal processes. Based on small area test devices, the inclusion of rear surface passivation is expected to take efficiencies on multi material to over 18% with corresponding open circuit voltages in excess of 650mV while on mono, efficiencies of 21% are anticipated with open circuit voltages exceeding 680mV.

3.3.2.3.4 Advanced N-type Screen-printed Solar Cells
3.3.2.3.4.1 N-type Screen-Printed Cells with Homogeneous Top Surface Diffusion

Increasing interest is being shown in n-type CZ material as a means for avoiding the widely reported defects associated with the high boron and oxygen concentrations in p-type CZ material. In particular, screen-printed aluminium has been used as a simple and cost-effective way to create an Al-alloyed rear emitter for such n-type CZ material, especially in the n’np+ cell design with rear junction. However low voltages for such structures reported in the range 617-627mV appear to be a severe limitation of this approach since n-type CZ wafers should be capable of achieving much higher open circuit voltages.

Discontinuities in the p+ layer have been identified as the main cause for such performance degradation of this device. These discontinuities, as seen in Fig. 4.3.2.6 (a), are isolated points where the junction fails to form, usually created by non-uniform wetting of the silicon by the Al during the alloying process. Although their presence can be minimized by optimizing the firing process so as to allow uniform wetting of the surface to occur, they cannot be completely avoided. In small quantities, such non-uniformities have almost negligible influence on the performance of the back surface field.
in conventional p-type cells. However, they can significantly degrade the quality of the Al-alloyed emitter in n-type wafers by allowing Al to locally bypass the p+ region and directly contact the n-type bulk via a Schottky barrier causing a non-linear shunt. A new and modified firing process has therefore been developed to avoid the damage from such non-uniformities. In this method, a patented low temperature solid phase epitaxial growth process is employed after the conventional standard spike firing to minimize the impacts of these junction discontinuities so that a uniform and good quality junction as illustrated in Fig.3.3.2.6 (b) can be achieved.

![Cross-sectional SEM photos](image)

**Figure 3.3.2.6:** Cross-sectional SEM photos show: (a) discontinuities in the Al-doped p+ layer; (b) a deep and uniform Al-doped p+ layer.

These improvements have facilitated a 15-20mV increase in Voc relative to those reported in the literature and efficiencies over 17% for standard screen-printed solar cell technology with homogeneous n-type emitter (front surface field) applied to n-type wafers.

A common problem with the manufacture of conventional screen-printed solar cells is minute amounts of aluminium paste accidently coming into contact with the cell front surface. This can happen when wafers are face down during the printing of the rear or during wafer transfer/handling. Aluminium paste contamination of such surfaces and transfer belts happens relatively easily in a production environment such as through a broken wafer that has been Al printed, operators’ contaminated gloves, tiny holes in the screen-printing screen etc. However such contamination with the current rear junction n-type technology creates unusual photoactivated shunts that are not present in the dark. This is because a p-n-p transistor structure is formed when the unwanted aluminium on the top surface is fired into the n-type surface (with the second p-n junction of course being at the rear of the device). In this phototransistor, the lightly doped wafer forms the base of the transistor, and despite the base being very thick, approaching 200 microns, the high lifetime of the CZ n-type material allows the transistor to achieve moderate gain levels and therefore conduct large currents when illuminated by light that generates the necessary base current for the transistor. The unusual consequence is that the apparent shunt resistance of the cell is very poor (low) when illuminated brightly, increasing to high values in the dark or even low illumination levels. The ramifications of this for cell efficiency and fill-factor are that values fall with reducing light intensity as is normally the case for shunted cells, but with values increasing again for low illumination levels as the shunt problems disappear as the phototransistors are deactivated.

Even without such phototransistor shunting, analysis of such homogeneous emitter n-type devices indicates that even higher voltages are potentially achievable if not for the large dark saturation current contribution from the heavily doped phosphorus diffused top surface. This emphasises the importance of moving to the equivalent of a selective emitter design for the front surface to facilitate both improved short wavelength response as well as increased device voltages.
3.3.2.3.4.2 N-type Screen-Printed Cells with the Equivalent of a Selective Emitter

Until recently, the Centre held the world record (jointly with Stanford University) for the most efficient n-type silicon devices with 22.7% efficiency. The cell design was based on the inverted form of the PERL (Passivated Emitter and Rear Locally diffused) solar cell developed at UNSW and is shown below. In this work, the cell design has been adapted to accommodate the use of low cost screen-printed solar cell processes involving the alignment of the screen-printed front metal lines to the heavily doped n+ regions to form the equivalent of a selective emitter on the front surface and the use of a screen-printed aluminium grid pattern on the rear to form the localised p+ regions during the spike firing of the Al.

Figure 3.3.2.7: Inverted form of the PERL (Passivated Emitter and Rear Locally diffused) solar cell developed at UNSW based on the use of N-type silicon.

This approach enables the achievement of 19.5% efficiency but requires a quite complicated processing sequence.

For comparison purposes, the screen-printed front contacts were replaced with laser doped contacts. With a top surface homogeneous emitter diffused to about 200 ohms per square, the self aligned metalisation with heavy doping beneath the metal contact was formed by melting the silicon through the silicon nitride anti-reflection coating in the presence of an n-type dopant source. This laser doping process automatically damages the overlying silicon nitride layer, facilitating direct plating of metal to the heavily doped regions as a self-aligned top surface metal contact. The cell structure is shown below. This approach appears to have significant advantages over the screen printing technique such as self alignment to the locally diffused top surface, narrower metal lines and corresponding significantly lower shading losses. Despite being a significantly simpler process than the screen-print selective emitter design, excellent cell efficiencies of 19.2% have been achieved on large cell areas of 148.6cm² using commercial grade CZ n-type wafers. Commercial partners have demonstrated even higher efficiencies, exceeding 19.8% while simultaneously using only industrial equipment.
In this work, the cells were fabricated using industrial sized (125x125mm) phosphorus-doped CZ n-type wafers of 3ohm-cm resistivity and ~180µm thickness. A texturing process was performed in a NaOH/Isopropanol based solution to form random pyramids. A thin phosphorus diffused n⁺-layer with a sheet resistivity of 200 ohm/sq serving as the front surface field was created by a thermal diffusion at 850°C using liquid POCl₃ source in a conventional tube furnace. A chemical etch containing HF and HNO₃ was then applied to the back of these wafers to remove the unwanted n⁺-layer from this surface. A silicon nitride layer with a refractive index of 2.05 and thickness of 75nm was subsequently deposited using a commercial Roth & Rau remote plasma PECVD system to simultaneously form an anti-reflective coating and provide passivation for the front surface as well as the bulk material. After screen-printing with a selected Aluminium paste on the entire back surface with a gap of around 2mm from the edges, the wafers underwent an alloying process at 860°C in a conventional conveyor belt furnace to produce the rear Al-alloyed emitter. A phosphorus dopant source was then spun onto the front surface, followed by the laser doping process using a 532nm wavelength Q-switch diode laser to create locally heavily diffused lines. The wafers were rinsed and submerged in 1% HF solution for 30sec to remove the dopant source and any native oxide from the laser doped lines. Lastly, light induced plating (LIP) was subsequently performed to deposit Ni, which was sintered at 375°C, followed by Cu plating to form the front contacts.

The performance improvement relative to the selective emitter screen-printed counterparts arises primarily from the reduced shading losses by the top surface metalisation although slightly higher voltages as high as 650mV, fill-factors and yields are also achieved, apparently due primarily to the reduced metal/silicon interface area and superior alignment with the laser doped contacts.

A spectral response measurement was performed to investigate different regions in the cell. A very high value of more than 95% was maintained for internal quantum efficiency (IQE) from 580nm to 960nm. However, there was a slight drop in the short wavelength range, indicating that the front surface passivation can be further improved.
3.3.2.3.5 Buried Contact Solar Cells

Despite this technology being commercialised more than a decade ago, it remains a key technology for collaborative research with industry and continues to do well commercially with close to $1 billion of product now deployed in the field and many new companies interested in its commercial potential. New developments at the Fraunhofer Institute in conjunction with the laser company Synova make the groove formation and doping a much simpler and lower cost process than incorporated into the original technology implementation. The German company Rena is offering a turn-key production line for this technology although it appears at this stage that significant laser induced damage is making the achievement of high efficiencies difficult.

Nevertheless, this is expected to create significant new interest in the Buried Contact technology, particularly with the apparent growing acknowledgement of the benefits of the technology over existing screen-printed solar cell technology. In the 2006 European Inventor of the Year Awards, the Buried Contact technology contributed to Green and Wenham receiving a Top 3 Ranking (out of more than 200,000 inventions world-wide in the period 1990-2000) for inventors outside Europe. A further distinction for this technology is its listing amongst Australia’s Top 100 Inventions of the 20th Century as determined by the Australian Academy of Technological Sciences and Engineering. The original design for this solar cell has the buried metal contacts on the top surface as shown in Figure 3.3.2.10 (a) although in more recent years the interdigitated rear contact design applied to n-type wafers shown in Fig. 3.3.2.10 (b) has become particularly popular and a focus of UNSW research. Efficiencies of 20% have been demonstrated on small area devices with efficiencies of 21% eventually believed achievable on large area CZ material.

A newer implementation of this technology is under development in a collaboration between UNSW and Tianwei in China. Efficiencies approaching 19% have already been demonstrated by using the laser to simultaneously pattern the SiNx layer, ablate some silicon to form the groove and dope the remaining side walls of the groove heavily with phosphorus. To study the performance potential of this front surface design, cells were fabricated with a photolithographically defined PERL rear surface with 20.8% efficiency being achieved.

Figure 3.3.2.9: Spectral response of a typical laser doped n+np+ solar cell.
The primary aim for this UNSW and Tianwei New Energy (TWNE) project in the first 1-2 years has been to develop a new hybrid solar cell technology based on the use of the buried contact concept for the front surface, and an amorphous silicon passivation layer for the rear surface. The buried contact concept has been previously shown to be capable of achieving very high efficiencies, but not in a commercially viable way. The world’s first 20% efficiency silicon PV module was achieved this way more than a decade ago, but with the use of photolithographically defined rear contacts equivalent to those used by the record laboratory cells from UNSW. The lower cost laser-grooved commercial implementation by BP Solar under license to UNSW, although producing close to $1 billion of product, has not been as successful as hoped for several reasons that are being addressed in the present project with TWNE. Firstly, a 25% power loss was sustained by replacing the rear surface photolithographically defined contacts with standard full metal contacts. Secondly, UNSW’s implementation of the technology for BP required lengthy high-temperature processes, particularly for the groove diffusion, making the technology unsuitable for the most commonly used p-type multicrystalline and Czochralski (CZ) wafers used by the industry. Thirdly, the BP implementation of the technology makes it incompatible with the use of PECVD deposited dielectric layers which provide superior surface passivation and hydrogenation and are therefore necessary for the new lower cost cast wafer types being developed by TWNE and other companies for future use and cost reductions.
Excellent progress has been made in addressing the above key issues. Firstly, compatibility with PECVD deposited dielectrics has been achieved by depositing them after the formation of the heavily doped grooves so that they do not need to withstand the high temperatures associated with the groove diffusion. This has been achieved by using the geometrical differences created by the grooves whereby the subsequently deposited PECVD dielectric creates a much thinner coating within the grooves that can be easily removed chemically to expose the groove walls to light induced plating while leaving the top surface protected. The success of this has already been demonstrated with device efficiencies above 19% having already been demonstrated, well above the typical efficiencies achieved by BP Solar of 17-18%. Secondly, the substrate and dielectric damaging high temperature processes associated with diffusion of the groove walls and surface oxidation have been eliminated by changing the groove formation approach. Rather than ablating the silicon during groove formation, silicon to a depth of 5-10 microns is melted in such a way that some of the molten silicon flows from the molten region across the wafer surface, leaving insufficient silicon within the molten region to fill the groove. This leaves a residual groove as shown in Figure 3.3.2.11(a). Importantly, such grooves have an excellent aspect ratio (depth to width ratio) well suited to achieving the differential in dielectric thickness following PECVD necessary for facilitating selective plating of the grooved regions as shown in Figure 3.3.2.11(b).

![Figure 3.3.2.11: Laser groove in the silicon surface (a) formed using new techniques that facilitate the creation of grooves of only 2-3 microns in width while being 10-20 microns in depth. These provide an attractive option in conjunction with copper plating that nucleates from within the grooves as shown in (b). Such metal lines can be as narrow as 2-3 microns and have improved adhesion due to the anchoring provided by the metal within the groove.](image)

Furthermore, the subsequent diffusion of the groove walls is eliminated by melting the silicon in the presence of a dopant source that allows simultaneous heavy doping on the molten silicon. During cooling, this molten silicon regrows epitaxially in the walls of the groove creating the necessary heavy doping. This represents a significant simplification over the BP process while simultaneously avoiding the high temperatures that damage the common commercial grade wafer types.

Thirdly, initial devices using the amorphous silicon stack for rear surface passivation have been fabricated, showing clear improvements in rear surface passivation with the achievement of Voc values in excess of 650mV using standard solar grade p-type CZ wafers. Such Voc values are not achievable with conventional Al alloyed rear metal contacts used by a large majority of commercial cells.

### 3.3.2.3.6 Laser Doped Selective Emitter Solar Cells

The benefits of a selective emitter have been well known and quantified for many years. The benefits of heavy doping beneath the metal contacts contribute significantly to the high performance levels achieved by technologies such as the Buried Contact Solar Cells, the semiconductor finger solar cell, the point contact solar cells and the world-record holding Passivated Emitter and Rear Locally
diffused (PERL) solar cell. The heavy doping not only facilitates reduced contact resistance between the metal and the silicon, but probably more importantly it shields the high recombination velocity metal/silicon interface from the active regions of the cell. In addition, by restricting the heavily doped material to the immediate regions beneath the metal contact, little light absorption takes place in such regions thereby avoiding problems with carrier collection from heavily doped regions where the minority carrier diffusion lengths are very short.

Despite the commercial success of the Buried Contact Solar Cell described above, a potentially more effective and simpler way of achieving a selective emitter is by using laser doping to produce the heavily doped regions beneath the metal contacts as shown in Fig. 3.3.2.12. Following top surface emitter phosphorus diffusion to about 100 ohms per square and silicon nitride deposition, an n-type dopant source is applied or can even be incorporated into the silicon nitride layer. A 532 nm NdYAG laser is used to melt the silicon to a depth in the vicinity of a micron while simultaneously releasing the n-type dopants into the molten region. The molten silicon subsequently regrows epitaxially, heavily doped with phosphorus. Just as importantly, the overlying silicon nitride layer is removed from the silicon surface in isolated regions, facilitating direct plating to the exposed n++ surface. Electroless plating of Ni and Cu provides a particularly effective self-aligned metalisation scheme to provide metal lines wherever the laser doping was effected. The laser doped regions are typically 12 microns wide, leading to metal lines of only 20 microns width after plating.

![Figure 3.3.2.12: Laser doped selective emitter solar cell with self aligned plated contacts.](image)

Innovative light induced plating techniques have been developed that facilitate the achievement of very high aspect ratios for the plated Nickel and Copper. Using conventional electroless plating techniques which tend to plate conformally with a uniform plating rate in all directions, the 10 micron wide laser doped line plates to a width of about 30 microns for a plating height of about 10 microns as shown in Figure 3.3.2.13 (a). In comparison, the new light induced plating techniques achieve line widths of only 24 microns for even greater metal height as shown in Fig. 3.3.2.13 (b).
Figure 3.3.2.13: (a) electroless conformal plating of Cu onto a laser doped region and (b) Improved aspect ratio for metal plated by the new light induced plating techniques where the height is 12 microns while the width is 24 microns. (c) FIB photo of Cu plating using the new light induced plating techniques as for (b).

Contact resistances below 0.001 ohmcm$^2$ have been demonstrated, leading to fill factors as high as 80% being achieved on devices of approximately 150cm$^2$ in area. This has facilitated the achievement of efficiencies above 19% on commercial-grade CZ p-type silicon. Of particular importance has been the defect generation accompanying the laser doping process, particularly in conjunction with dielectric-coated, textured silicon surfaces. Planar surfaces present minimal challenge in terms of achieving near defect free regions in the vicinity of the laser melted regions. Textured surfaces however, particularly in conjunction with dielectric coatings of significantly different thermal expansion coefficient, have provided a significant challenge to match the low defect densities achievable with planar devices. Important processing parameters in the optimization of the laser doping process for textured surfaces have included laser pulse envelope shape, pulse duration, pulse frequency, laser light frequency, laser power, beam focus as well as the type of dielectric and dopant source being used.

The technology transfer team has had significant success helping various companies get this technology into pilot production, often achieving higher efficiencies and on larger area commercial wafers, than has been achieved at UNSW. For example, 19.0% efficiency or higher has been achieved in pilot production at several companies, four of which have chosen to do joint publications with
UNSW documenting the achievements including Sunrise Global Energy in Taiwan, Roth and Rau in Germany, Centrotherm in Germany and Shinsung in Korea.

The preferred implementation of the laser doping selective emitter (LDSE) technology also uses an equivalent laser doping/plating combination on the rear surface using a boron doping source. In this cell design, the majority of both the front and rear surfaces is well passivated using silicon nitride although the preferred rear surface passivation of the undiffused p-type surface uses somewhat different deposition parameters for best results. Implied Voc values above 730mV at one-sun demonstrate the near perfect passivation achieved with such surfaces. Following laser doping of the rear surface, even though plated contacts can be used similarly to on the front surface, the preferred rear contact is achieved through depositing aluminium over the entire surface followed by a low temperature sinter used to form good ohmic contact with the boron laser doped regions. In this cell design, the aluminium layer provides an excellent rear surface reflector. Even with full-size standard commercial grade p-type CZ wafers, based on pilot production, this technology has achieved independently confirmed efficiencies of 20% with pseudo efficiencies exceeding 23% therefore showing the future potential of the technology once parasitic resistive losses are minimised. Impressively, open-circuit voltages as high as 686mV have been achieved by these devices.

The simpler version of the LDSE technology equivalent to the pilot production established at Sunrise with aluminium alloyed rear surface, is far simpler to retrofit onto existing screen-printed production lines, with 90% of existing equipment retained. For several manufacturers such as Shinsung in South Korea, this new technology whereby the laser doped selective emitter combined with light induced plating of the metal contacts are used to replace the front surface screen-printed metal is achieving significantly higher efficiencies well in excess of 19% compared to 18% for conventional screen-printed cells with minimal if any cost increase per cell. Roth and Rau have also secured the rights from UNSW to develop and sell turn-key production lines based on the LDSE technology world-wide. This is expected to make it far simpler for many companies, particularly new manufacturers, to take up the new LDSE technology in large scale production.

Two other popular implementations of the laser doping technology with industry collaborators are the bifacial structure using laser doped self-aligned contacts of opposite polarity on both surfaces and the interdigitated rear surface laser doped contacts for rear junction n-type devices. Collaborative research projects based on these cell designs have been established with the aim of developing the technologies to take cell efficiencies on n-type CZ also to above 20% in large scale commercial production at some stage in the future.

Another use of the laser doping technology was described in Section 3.3.2.3.4.2 as a replacement for screen-printed contacts with n-type CZ wafers in conjunction with aluminium alloyed rear contact and junction. As reported above, excellent efficiencies in the vicinity of 19% have also been achieved with this cell design on 148.6cm² n-type CZ wafers. A simpler patented version of this technology has also been developed which requires no diffusion processes, no edge junction isolation and no thermal processes above 450 degrees Celsius except for the aluminium alloying process for several seconds. Nevertheless, the technology is still able to achieve efficiencies above 18% on full-sized commercial substrates. The processing sequence used is:

1. wafer texturing
2. silicon nitride deposition
3. aluminium rear surface printing and firing
4. laser doping front surface
5. Ni/Cu light induced plating
3.3.2.3.7 Inkjet Technology for Solar Cell Fabrication

3.3.2.3.7.1 Resist Based Method

Inkjet technology has been an area of rapid development over the last decade, particularly for printing. In recent years, its application has been spreading to other fields, but as yet has had only minimal impact in photovoltaics. The first company apparently to commercialise a photovoltaic technology incorporating inkjet technology was CSG Solar who during 2006 commenced production of a thin-film technology that uses inkjet printing of a corrosive material to etch patterns in a resist layer to facilitate metal contacting to the underlying silicon. In the present work, the use of inkjet technology has been expanded to encompass a range of solar cell fabrication processes including texturing, grooving, patterning of dielectric layers for metal contacting, localized diffusions, etc. The techniques developed to carry out these processes are uniquely different to those used before. A non-corrosive plasticizer is inkjet printed onto a low cost resist layer, altering the chemical properties of the resist layer in these localized regions to make them permeable to etchants such as hydrofluoric acid (HF). This facilitates the patterning or etching of underlying dielectrics or semiconductor material to facilitate a range of semiconductor processes. Importantly, the change in resist permeability is a reversible process making it feasible to return the resist to its original state after carrying out processes on the underlying material. This also opens the option to partially reverse the permeability to reduce the hole or feature size produced in the underlying material.

A particular exciting application of this inkjet technology work is for very high efficiency silicon solar cells. The University of New South Wales has held the world record for silicon solar cell efficiencies for the last 15 years, initially with the Passivated Emitter solar cell (PESC) and more recently with the Passivated Emitter and Rear Locally diffused (PERL) solar cell. Despite the performance and achievements of these two technologies, neither has been used commercially, apart from for space cells, primarily due to the sophistication, cost and complexity of the processes involved. The photolithographic based processing is probably the main contributor to this. In this work, inkjet printing techniques have been developed for patterning low cost resist layers as a simple, much cheaper alternative to photolithographic based processing. These new approaches appear capable of achieving similar device performance levels but with the greatest challenge being to match the dimensions of features in the resist patterning achievable with photolithography. Test devices to date based on inkjet technology have achieved feature dimensions such as holes of 30-40 microns diameter as shown in the matrix of holes below. However, these dimensions need to be reduced to about 10 microns diameter to fully match the performance levels demonstrated with photolithographic based processing. New and innovative inkjet printing techniques have been recently developed for further reducing the resist patterning dimensions. This work is being greatly assisted by the recent availability of the new 1 picolitre inkjet heads.
The described dielectric patterning capabilities via inkjet patterning can not only be used for defining localized diffusion regions and locations for metal contacts, but also for the formation if textured surfaces and light trapping schemes. Examples of the latter are shown below as well as corresponding reflectance curves.

Figure 3.3.2.15: (a) Optical Microscope photograph of ink jet patterned holes in a SiO$_2$ layer and (b) Scanning Electron Microscope photograph of the inverted pyramids formed in the silicon surface following KOH etching of (a).
Figure 3.3.2.16: (a) Optical Microscope photograph of ink jet patterned lines in a SiO₂ layer and (b) Scanning Electron Microscope photograph of the grooves formed in the silicon surface following KOH etching of (a).

Figure 3.3.2.17: Reflectance of silicon wafers with different surface finish (i) inverted pyramids formed by photolithography, (ii) inverted pyramids patterned by ink jet printing and (iii) v-grooves patterned by ink jet printing.

Figure 3.3.2.18: (a) Reflectance of silicon wafers with different surface finish (i) laboratory fabricated random, upright pyramids, (ii) inverted pyramids patterned by ink jet printing and (iii) v-grooves patterned by ink jet printing and (b) SEM of (iii).
Significant interest is also being shown in developing high efficiency approaches for multicrystalline silicon wafers. Record performance multicrystalline silicon cells have in the past benefited from photolithographically defined “honeycomb” texturing using an acidic isotropic etch. Such structures have also been demonstrated recently using inkjet technology as shown in Figure 3.3.2.19. Such techniques appear to have significant commercial appeal.

3.3.2.3.7.2 Direct Etching Via Aerosol Jetting

The key to high-efficiency silicon solar cells is the ability to form small-area metal contacts to the silicon through dielectric passivating layers. In this work, a new method for patterned etching of SiO$_2$, SiO$_x$N$_y$ and SiN$_x$ dielectric layers has been developed and patented. The method uses Optomec’s M$^3$D aerosol jetting device to deposit a solution containing fluoride ions, according to an etching pattern, onto an acidic water-soluble polymer layer formed over the dielectric layer as indicated in the schematic of Figure 3.3.2.20. The deposited solution reacts with the polymer layer, at the locations where it is deposited, to form an etchant that etches the SiO$_2$ and SiN$_x$ under the polymer layer to form a pattern of openings in the dielectric layer. After the pattern of openings is formed, the acidic water-soluble polymer and the etch residue are easily removed by rinsing in water. The method involves fewer steps than photolithography and is safer than existing immersion etching techniques in that the corrosive etchant HF is only formed in-situ on the surface to be etched. Furthermore, the method uses small amounts of inexpensive chemicals and produces significantly less hazardous fluoride waste than existing immersion etching methods.
Aerosol jet printing is a new deposition technology being pioneered by Optomec, Inc. The technique enables the finely-controlled deposition of an aerosol, which is generated from a liquid, by using a sheath gas to constrict the aerosol into a fine jet which is directed to the substrate. The technique has been previously used in applications such as printed electronics, fuel cells and displays.

The aerosol etching method has been used to etch groove structures in SiO$_2$ which have been thermally grown on polished silicon wafers. By varying the aerosol and sheath gas flow rates the geometry and depth of etching can be varied. For example, grooves (see Figure 3.3.2.21) were cleanly etched in a 260 nm thick SiO$_2$ layer using aerosol and sheath gas flow rates of 21 and 50 cm$^3$/min respectively and depositing 10 layers of aerosolized 10% NH$_4$F solution. These grooves were ~35 microns wide at the surface but only ~20 microns wide at the Si/SiO$_2$ interface.

![Image](a) Optical image, and (b) Dektak profile of a groove etched in a 260 nm thick thermal oxide grown on a polished Si wafer by deposition of 10 layers of aerosolised 10% (w/v) NH$_4$F solution onto a polyacrylic acid polymer layer of thickness ~ 2.2 microns. The aerosol and sheath gas flow rates were 21 and 50 cm$^3$/min, respectively. The process velocity of the stage was 10 mm/s and the platen was heated to 45ºC. The groove width at surface ~35 microns.

Even narrower structures can be etched by reducing the aerosol flow rate and increasing the sheath gas flow rate. Figure 3.3.2.22 shows the formation of central, more deeply, etched grooves which are 200 nm deep and ~10 microns at the Si/SiO$_2$ interface. It is anticipated that the use of an even lower flow rate for the first, wetting layer will largely eliminate the wider, shallow etched region at the surface thus enabling very narrow grooves to be etched to a depth of at least 200 nm.
Figure 3.3.2.22: (a) Optical image of grooves etched in a 260 nm thick thermal oxide grown on a polished Si wafer by deposition of 25 layers of aerosolised 10% (w/v) NH₄F solution onto a polyacrylic acid polymer layer of thickness ~ 2.2 µm. The aerosol and sheath gas flow rates were 18 and 55 cm³/min, respectively. The process velocity of the stage was 10 mm/s and the platen was heated to 45°C. (b) Dektak profile of a section of the grooves shown in (a).

We have also been able to etch grooves 20-25 microns wide in 75 nm thick SiNx layers on chemically-textured silicon surfaces. The etched grooves can be used to form front or rear metal contacts for silicon solar cells using metal plating, screen printing or evaporation deposition methods. Compared to current inkjet implementations of this direct etching method, aerosol jet etching results in faster etching (fewer layers required to be deposited), smaller etched features and less variation in etched groove width over large etching patterns. Although the current etched feature sizes are sufficiently small for many current front-contact and rear-contact silicon solar cells, it is anticipated that the feature sizes can be further reduced in the near future with refinement of the jetting parameters and modification of the surface polymer layer composition. Replacing the thermal oxide or SiNx layer with SiOₓNᵧ also has beneficial consequences for the dimensions of the feature sizes formed such as shown by the etched lines of 15-20 microns width shown in Figure 3.3.2.23. These further reductions in etched feature size may enable high-efficiency silicon solar cell designs, such as the PERL cell, to be commercially realised.

Figure 3.3.2.23: Aerosol jet-etching of a silicon oxynitride layer to form lines of only 15-20 microns.

This area of work has attracted significant interest and funding from industry, including being awarded a 3-year ARC Linkage grant for the design and fabrication of high efficiency solar cells through the use of the described patented inkjet technology from UNSW.
### 3.3.2.3.8 PLUTO Technology

The Pluto technology is a low cost implementation of the UNSW PERL (Passivated Emitter and Rear Locally diffused) solar cell developed at UNSW. The PERL technology currently holds the world-record for silicon solar cell performance with 25% efficiency being recorded as the new world record for silicon solar cell efficiency during 2008. Through collaborative research with Suntech, two generations of Pluto technology have been developed. The first uses the standard front surface design of the PERL cell but with a screen-printed rear aluminium alloyed rear metal contact that simplifies the technology and allows it to be easily retrofitted onto existing screen-printed solar cell lines. In comparison to standard screen-printed solar cells made on the same production line, Pluto cells achieve an increase in performance of more than 10% by taking average efficiencies from about 18% to 19.6%. These efficiencies have been independently confirmed by the Fraunhofer Institute in Germany. The main contributors to these increased efficiencies are: reduced shading loss (2-3%); improved short wavelength response due to selective emitter (2-3%); improved Voc due to lightly diffused emitter and well passivated surfaces (2-3%); and improved fill-factor due to reduced resistive losses (2%).

In comparison to the semiconductor finger technology, many of the losses associated with the screen-printed metal contacts (shading, contact resistance, metal resistance, dark saturation current from the metal/silicon interface, etc.) have been minimised through the Pluto technology, facilitating an efficiency increase by about 1% in absolute terms. The spectral response and corresponding performance spread in production are shown in Figures 3.3.2.24 and 3.3.2.25 respectively.

![Figure 3.3.2.24: Spectral response curve of a 19% efficient Pluto solar cell.](image)
Figure 3.3.2.25: Solar cell efficiencies of commercially manufactured first generation Pluto solar cells (a) in chronological order and (b) as a histogram.

In comparison to the laser doping technology, the main advantage is the elimination of most of the defects and associated recombination that exists in the resolidified laser doped regions or in locations immediately adjacent to these. Consequently, Pluto cells achieve reduced junction recombination and therefore higher fill factors and Voc's leading to a performance increase of about 5%.

This technology is unique to Suntech with some of the intellectual property being owned solely by Suntech. Intellectual property arising from the collaborative research is jointly owned by UNSW and Suntech, but with the latter having the right to use it in its own production. In recent years Suntech has increased the manufacturing capacity of the Pluto technology to 0.5GW. This was planned to be further scaled during 2012 with the full 2GW production capacity to be retrofitted to the Pluto technology during 2013. However the severe down-turn experienced by the industry during 2012 made it near impossible for any companies to expand the production of any technologies. Figure 3.3.2.26 shows a photo of a Pluto cell juxtaposed to a standard screen-printed solar cell.

Figure 3.3.2.26: Pluto production cell (right) with significantly reduced reflection losses compared to standard screen-printed solar cells (left).

The second generation of Pluto technology uses the full PERL cell design by eliminating the rear screen-printed aluminium layer and replacing it with a localised metal contact. An independently confirmed world-record efficiency for commercial grade p-type CZ wafers of 20.3% was achieved during 2012. Further already identified mechanisms for reducing losses is expected to take these efficiencies to the 21-23% range over the next 1-2 years. It does however avoid the use of vacuum deposition processes and photolithographic techniques, thereby avoiding the expensive fabrication costs associated with most laboratory technologies. This technology is expected to follow the first generation of Pluto technology into large-scale production.
The PLUTO technology has been also successfully applied to multicrystalline silicon wafers and implemented into large scale production with efficiencies of 18-19% also independently confirmed by the Fraunhofer Institute. In mid 2009, Suntech beat the 15.5% multicrystalline silicon module world-record efficiency held by Sandia National Laboratories in the US for 15 years. This was followed later in the year by Suntech’s achievement of another world-record of 16.5% (aperture area) for a multi module, this time beating the recently achieved ECN world record in the Netherlands. During 2010, this module efficiency was further increased to 17% and again confirmed by the Fraunhofer Institute. Further improvements during 2014 focussed on improving the rear surface passivation and incorporating the advanced hydrogen passivation with efficiencies in the range of 19-20% and an independently confirmed module efficiency of 18.9%.

3.3.2.3.9 Photoluminescent Imaging for Device and Material Characterisation

With the current growth in the photovoltaic industry and the trends towards higher cell efficiencies, generally achieved on lower quality and thinner silicon wafers, there is an increasing demand in research laboratories and in industrial manufacturing for fast and easy to use characterisation tools. Recent research at UNSW has established photoluminescence (PL) techniques as extremely fast and useful tools for the characterisation of silicon wafers and of silicon solar cells.

In particular, this work has shown that luminescence imaging techniques give two dimensional high resolution images of electrical parameters such as localised series resistance values and the minority carrier lifetime shown below for a multicrystalline silicon solar cell. The data acquisition times for such measurements are of the order of typically only one second per wafer, which is orders of magnitude faster than any competing experimental techniques. High resolution images of other electrical parameters such as the shunt resistance are also feasible.

**Figure 3.3.2.27:** Luminescence image of a completed multicrystalline silicon solar cell.

A prototype bench-top system established at the Centre three years ago was in such heavy demand by various UNSW research groups and for consultancy projects that a new state-of-the-art system was purchased recently from BTI. It has helped identify a variety of unexpected processing problems and in developing new processing sequences much more quickly than previously possible. In many cases the two dimensional information contained in PL images has given easy to interpret clues about the origin of specific problems. The ability to measure a large number of samples in a short time is very beneficial in this context.

Collaboration with various industrial partners has also identified various processing problems previously unknown to the manufacturers. In addition, recent research at UNSW has shown how the luminescence imaging technique could be used for in-line process control, for example to remove the
influence of shunts. Other potential industrially relevant in-line applications for luminescence imaging that are under investigation include crack detection, spatially resolved series resistance monitoring, quality control of raw material and process control of individual key processing steps such as the emitter diffusion. The collaborative work with various industry partners and several journal and conference publications have resulted in significant interest worldwide in the technique, specifically in a commercial PL imaging system.

A start-up company BT Imaging Pty Ltd has been formed by Centre researchers Robert Bardos and Thorsten Trupke in 2007 with commercial sales of the system taking place during 2008. The company has developed commercial off-line and in-line luminescence imaging tools, with healthy sales to research groups and cell manufacturers throughout the world during 2012.

In summary, photoluminescence techniques have proven particularly useful for the characterisation of various aspects of the screen printed solar cell process. Photoluminescence imaging was applied to the study of belt furnace processing, while photoluminescence imaging with current extraction was applied to the characterisation of n-type solar cells with printed metallisation to identify failure mechanisms in the metallisation. The accuracy, high speed and non-destructive nature of PL techniques make it an attractive candidate for use in high-throughput screen printed solar cell production lines.

3.3.2.4 Pilot Production

Many of the above technologies have been implemented or are in the process of being implemented into pilot production. The following table summarises the performance of each of the technologies in pilot production using standard commercial wafers with commercial processes and equipment.

<table>
<thead>
<tr>
<th>Technology</th>
<th>ARC</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (mV)</th>
<th>FF (%)</th>
<th>Effic %</th>
<th>Area (cm$^2$)</th>
<th>Wafer type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 BCSC (Tianwei)</td>
<td>SiN</td>
<td>38.0</td>
<td>636</td>
<td>78.7</td>
<td>19.1</td>
<td>148.6</td>
<td>(p-type CZ)</td>
</tr>
<tr>
<td>1 BCSC (Tianwei)</td>
<td>SiN</td>
<td>37.2</td>
<td>633</td>
<td>78.2</td>
<td>18.1</td>
<td>156</td>
<td>(p-type multi)</td>
</tr>
<tr>
<td>2 IBBC</td>
<td>SiN</td>
<td>37.1</td>
<td>675</td>
<td>79.4</td>
<td>19.8</td>
<td>46</td>
<td>(n-type CZ)</td>
</tr>
<tr>
<td>3 Screen-print</td>
<td>SiN</td>
<td>37.1</td>
<td>632</td>
<td>78.8</td>
<td>18.5</td>
<td>148.6</td>
<td>(p-type CZ)</td>
</tr>
<tr>
<td>3 Screen-print</td>
<td>SiN</td>
<td>33.3</td>
<td>614</td>
<td>75.5</td>
<td>16.0</td>
<td>156</td>
<td>(p-type multi)</td>
</tr>
<tr>
<td>4 SCF</td>
<td>SiN</td>
<td>37.8</td>
<td>641</td>
<td>78.6</td>
<td>19.0</td>
<td>148.6</td>
<td>(p-type CZ)</td>
</tr>
<tr>
<td>5 LDSE (Sunrise)</td>
<td>SiN</td>
<td>37.8</td>
<td>638</td>
<td>79.0</td>
<td>19.0</td>
<td>225</td>
<td>(p-type CZ)</td>
</tr>
<tr>
<td>5 LDSE (UNSW)</td>
<td>SiN</td>
<td>38.6</td>
<td>642</td>
<td>79.4</td>
<td>19.7</td>
<td>148.6</td>
<td>(p-type CZ)</td>
</tr>
<tr>
<td>5 LDSE (Centrotherm)</td>
<td>SiN</td>
<td>38.4</td>
<td>638</td>
<td>78.9</td>
<td>19.4</td>
<td>148.6</td>
<td>(p-type CZ)</td>
</tr>
<tr>
<td>5 LDSE (Roth &amp; Rau)</td>
<td>SiN</td>
<td>37.8</td>
<td>635</td>
<td>78.4</td>
<td>18.8</td>
<td>225</td>
<td>(p-type CZ)</td>
</tr>
<tr>
<td>5. LDSE (Shinsung)</td>
<td>SiN</td>
<td>38.6</td>
<td>640</td>
<td>79.3</td>
<td>19.6</td>
<td>148.6</td>
<td>(p-type CZ)</td>
</tr>
<tr>
<td>5. DS-LDSE (UNSW)</td>
<td>SiN</td>
<td>40.1</td>
<td>680</td>
<td>75.4</td>
<td>20.3</td>
<td>148.6</td>
<td>(p-type CZ)</td>
</tr>
<tr>
<td>5 DS-LDSE (Hyundai)</td>
<td>SiN</td>
<td>40.2</td>
<td>676</td>
<td>78.0</td>
<td>21.2</td>
<td>148.6</td>
<td>(p-type CZ)</td>
</tr>
<tr>
<td>5 DS-LDSE (a-Si rear)</td>
<td>SiN</td>
<td>40.3</td>
<td>670</td>
<td>75.8</td>
<td>20.3</td>
<td>148.6</td>
<td>(n-type CZ)</td>
</tr>
<tr>
<td>5 DS-LDSE (IMEC)</td>
<td>SiN</td>
<td>39.9</td>
<td>684</td>
<td>80.7</td>
<td>22.0</td>
<td>156</td>
<td>(n-type CZ)</td>
</tr>
<tr>
<td>5 DS-LDSE (IMEC)</td>
<td>SiN</td>
<td>38.2</td>
<td>653</td>
<td>78.5</td>
<td>19.6</td>
<td>156</td>
<td>(p-type multi)</td>
</tr>
<tr>
<td>6 Pluto</td>
<td>SiN</td>
<td>38.7</td>
<td>638</td>
<td>79.5</td>
<td>19.7</td>
<td>148.6</td>
<td>(p-type CZ)</td>
</tr>
<tr>
<td>6 Pluto 2</td>
<td>SiN</td>
<td>40.9</td>
<td>670</td>
<td>74.2</td>
<td>20.3</td>
<td>148.6</td>
<td>(p-type CZ)</td>
</tr>
<tr>
<td>6 Pluto</td>
<td>SiN</td>
<td>36.6</td>
<td>633</td>
<td>79.6</td>
<td>18.5</td>
<td>156</td>
<td>(p-type multi)</td>
</tr>
<tr>
<td>7 PERL</td>
<td>ZnS/MgF$_2$</td>
<td>41.7</td>
<td>704</td>
<td>82.5</td>
<td>24.2</td>
<td>46</td>
<td>(p-type FZ)</td>
</tr>
</tbody>
</table>
3.3.2.5 Core Research

The distinguishing feature of core research is that it is funded by UNSW, the ASI, ARENA and the Centre of Excellence or other Government funding schemes. The priorities for the work are therefore set by the Centre rather than by industry. Any IP is therefore wholly owned by UNSW, but with any such developments made available at no cost to industry partners of the Centre such as those funding collaborative research programs or else licensing Centre technology. Such core research is therefore of great importance in the initial stages of development of a new technology to take the development to the point where industry interest is gained and industry is willing to fund the ongoing development. An example of this is the Advanced Semiconductor Finger Solar Cell described in Section 3.3.2.3.3 where core research has facilitated the development and demonstration of the concept, to the point where test structures can show that efficiencies above 19% are achievable, making these the most efficient screen-printed cells world-wide on standard commercial grade p-type CZ wafers. This work is now to continue as an industry funded project in conjunction with the ASI and ARENA, with the industry partner being Suntech.

Other important areas of the core research are where problems are tackled and the solutions can be used for the benefit of all or most industry partners. A primary example is the new advanced hydrogenation technology that appears to have benefit for all silicon wafer types and also corresponding solar cell technologies. This work is being generously supported by ARENA with funding in excess of $4 million from 2012-2016 with similar levels of funding coming from a large number of industry partners that include many of the world’s largest solar cell and equipment manufacturers. Other examples of core research include improvements in the light induced plating techniques, reducing the laser induced defects during the laser doping process, reducing feature sizes during inkjet patterning of dielectric layers, improving surface passivation techniques, adapting processes to suit low cost silicon etc. The Centre has a large number of very talented PhD students contributing to this core research, the achievements from which are significantly accelerating the progress for most industry collaborative research projects. This represents a major benefit to companies that engage in funding photovoltaic research at UNSW.

Some core research however is conducted in conjunction with companies, but where the companies are not funding the work at UNSW and have no claim over any resulting IP from the work at UNSW and cannot exercise any restriction regarding its use. An example of this is the collaboration with Centrotherm to evaluate the compatibility between the LDSE technology and the standard Centrotherm screen-printing technology. Cells from a standard Centrotherm screen-printing line for producing homogeneous emitter solar cells of 18% efficiency were fabricated without front silver metal. The emitter sheet resistivity was the only processing variation, being raised to 120 ohms per square. After laser doping and plating at UNSW, the finished 5 inch cells were sent to the Fraunhoffer Institute in Germany where they were confirmed to be 19.4% efficiency. At the time, this was believed to be the highest ever independently confirmed for industrial solar cells fabricated on standard commercial grade p-type CZ wafers. This record however was shortly after broken through collaborative work with Shinsung where similar devices fabricated using similar wafers were measured to be 19.8% efficiency. This was followed by further world records with 20.3% being achieved for Suntech’s second generation Pluto cells developed collaboratively with UNSW and more recently, 21.0% by Hyundai, also based on the UNSW laser-doping selective emitter technology.

References


3.3.2.3 J. Ji, et alia, Chinese patent CN100541730C, US Patent US2010307540A1,

3.3.2.4 J. Ji, et alia, Chinese Patent CN102083717A (WO2010135850A).
3.3.2.6. Patterning for Plated Heterojunction and Back Contact Cells

Research Team (UNSW):
Alison Lennon
Zi Ouyang
Xi Wang

International Collaborators:
Stuart Bowden (Arizona State University, USA)
Joost Hermans (Roth & Rau, Netherlands)
Pierre Papet (Roth & Rau, Switzerland)
Yu Yao (Meyer Berger, Switzerland)

Postgraduate Research Students:  Research Assistants:
Zhongtian Li     Wei Zhang
Vincent Allen     Derwin Lau
Pei-Chieh Hsiao

3.3.2.6.1. Overview

Contact formation typically requires the patterning of a surface to expose regions for metallisation. This section describes a potentially low-cost, patterning method called inkjet chemical lithography which can be used to form a pattern in a polymer layer on asurface thereby enabling masked etching and metallisation. The application of this patterning method to the plating of heterojunction cells and contact formation on back contact cells is described in Sections 3.3.2.6.2 and 3.3.2.6.3, respectively. The method, depicted in Figure 3.3.2.6.1, requires the use of an inkjet printer to deposit a functional fluid onto a novolac polymer surface such that cross-linking is inhibited at the printed regions in a subsequent heat treatment. The printed regions can then be removed by rinsing in a solvent forming an acid-resistant mask on the surface. Circular hole openings of diameter 20-25 μm and lines as narrow as 20 μm can be formed (see Figure 3.3.2.6.2). As little as a single 1 μL droplet is required to form a hole opening, consequently fast processing rates can be achieved if the method is implemented using industrial inkjet printers that can process 2400 wafers an hour [3.3.2.6.1].

**Figure 3.3.2.6.1:** Flow chart depicting the patterning a novolac polymer using a functional ink (inkjet chemical lithography) (from [3.3.2.6.2]).
3.3.2.6.2. Masking for Plated Heterojunction Cells

Open-circuit voltages of up to 750 mV have been achieved for amorphous silicon heterojunction (HJT) cells [3.3.2.6.3] due to the excellent passivation provided by intrinsic amorphous silicon. However, this passivation is temperature-sensitive and so low-temperature metallisation methods are required. Metal-plated contacts can be formed at room temperature and have the potential to be low-cost. Bifacial metal plating has been reported for laser-doped p-n junction cells [3.3.2.6.4], however plating a bifacial grid to cells coated with transparent conducting oxides, such as indium tin oxide (ITO) requires that the area to be metallised is defined using a metallisation mask. Plating masks can be formed by printing a masking material (e.g., hot melt wax) leaving openings in the mask for metal contacts to be plated [3.3.2.6.5]. The need to print the majority of the cell area can place a limit on how fast the masking process can be performed. Consequently it can be preferable to form the masking layer over the entire surface and then only pattern the regions where openings are required. The inkjet chemical lithography patterning method was used to form a plating mask with an array of line openings over the alkaline-textured surfaces of 156 mm HJT cells [see Figure 3.3.2.6.2(b)]. Copper and then tin were plated on the ITO surface through the exposed line openings using bias-assisted light-induced plating (LIP) [see Figure 3.3.2.6.3 (b)] and field-induced plating (FIP) [see Figure 3.3.2.6.3 (a)] resulting in metal fingers with a height of ~ 5 mm. The polymer acts to constrain the lateral growth of the plated fingers enabling metal fingers as narrow as 20-25 mm to be formed (see Figure 3.3.2.6.4).

Figure 3.3.2.6.3: (a) Plating arrangement for using FIP to plate to the p type ITO surface; and (b) bias-assisted LIP to plate to the n type ITO surface (from [3.3.2.6.2]).
The bifacially-plated cells were then interconnected using Meyer Burger’s SmartWire Connection Technology (SWCT) [3.3.2.6.6] to form mini-modules with a glass-backsheet configuration (see Figure 3.3.2.6.5). Future work will evaluate the possibility of spray-coating the resist instead of spin-coating as used for this study. Also the possibility of using a polymer that can be retained as part of the encapsulation will be investigated.

**Figure 3.3.2.6.5:** Digital image of SWCT-encapsulated mini modules (from [3.3.2.6.2]).

### 3.3.2.6.3. Contact Formation for Back Contact Cells

Industrial production of high efficiency back contact cells requires that: (i) the metal-silicon contact area is minimised to reduce contact recombination; and (ii) metallisation grids are insulated from the device whilst minimising electrical shading and maximising electrode area. These requirements need to be satisfied with a consideration of industrial alignment tolerances. The inkjet chemical lithography process has been used to form small point openings for back contact cells [3.3.2.6.7], however rather than remove the polymer as for the plating mask application described in Section 3.3.2.6.2, in this case the polymer was retained as a rear insulating layer for the cell. A metal layer deposited on the surface of the polymer acts as both an electrode and a rear reflector (see Figure 3.3.2.6.6) and a metal coverage area exceeding 80% can be achieved. One of the advantages of this approach is that the cell and the metallisation grid can be optimised separately and the metal can be deposited without highly accurate alignment.
Figure 3.3.2.6.6: Schematic showing a back contact cell after metallisation with the polymer acting as the insulation layer (from [3.3.2.6.7]).

Provided that the polymer was heated at 130 °C for 10 min before metal deposition and was at least 3 mm thick, its area-normalised resistance exceeded $1 \times 10^{10}$ Ω cm$^2$. This is significantly higher than the value $2 \times 10^8$ Ω cm$^2$ reported as being required in [3.3.2.6.8] for back contact cells. Ellipsometry measurements of the refractive index ($n$ and $k$) showed that if the polymer was heated at 130 °C for 10 min, it would not significantly absorb light that reached the rear surface of the cell and light reaching the polymer would be reflected back into the cell by the rear metal reflector. However, as the temperature of the heat treatment increased, the $n$ and $k$ values both increased which indicated more absorption of light in the polymer layer presumably due to increased cross linking of the polymer at higher temperatures. The expected photocurrent for 180 mm thick cells with a polymer heated at different temperatures was simulated using the angular distribution matrix (see Section 3.3.2.7) and the results are shown in Figure 3.3.2.6.7. The simulated photocurrent decreased for cells with a polymer layer heated at higher temperatures, however for higher metal coverage percentages, the simulated photocurrents for cells with the polymer layer exceeded that of a cell with only with 200 nm SiNx (i.e., no polymer). This is due to the thicker insulation layer (polymer and SiNx) acting to minimise parasitic absorption in the rear metal (in this case aluminium) layer [3.3.2.6.9].

Figure 3.3.2.6.7: Simulated photocurrent as a function of aluminium rear reflector coverage for 180 µm thick cells with a 4 mm thick polymer layer heated at different temperatures for 10 min. The simulated photocurrent is compared with a cell without a polymer layer (i.e., just 200 nm SiNx; black line). (from [3.3.2.6.7]).

These initial results demonstrate that a novolac polymer layer can act both as reliable patterning mask, an insulating layer for back contact cells and can enhance the optical performance of back contact cells. A further advantage of the proposed cell metallisation scheme, which incorporates the polymer layer as part of the rear insulation layer, is that the alignment tolerance can be much larger.
Furthermore, the metal series resistance can be reduced since the metal area fractions for the n and p type metal electrodes can be the similar and maximised. With these benefits and the higher metallisation alignment tolerance, new contact separation and interconnection methods are made possible which exploit the fine patterning resolution achieved by the inkjet chemical lithography process.

REFERENCES


3.3.2.6.2 Z. Li, et al. "Pattern for plated heterojunction cells." 5th Metallization Workshop of Crystalline Silicon Solar Cells, Konstance, Germany, 2014


3.3.2.6.7 Z. Li., et al. "Electrical and optical analysis of polymer rear insulation layers for back contact cells." 5th International Conference on Crystalline Silicon Photovoltaics 2015 Konstance, Germany.


3.3.2.7. Angular Matrix Framework for Optical Analysis of Solar Cells

Research Team (UNSW):
Alison Lennon
Zi Ouyang
Postgraduate research students:
Yang Li

3.3.2.7.1. Overview

Complex light trapping structures make it challenging to simulate the optical properties of solar cells accurately. Recently, a new Angular Matrix Framework (AMF) was proposed where matrices are used to describe the transition of the angular distribution of the light when it is reflected, transmitted or absorbed. The matrices can be computed using a range of different simulation methods and when parts of a complex structure are to be optimized, or the incident light is altered, the pre-computed matrices can be used with the potential benefit of saving computational time. Examples are provided to demonstrate the effectiveness and benefits of this framework in Section 3.3.2.7.2.

System-oriented optical modelling of solar cells is introduced in Section 3.3.2.7.3 as an important application of the AMF. By combining the angular distributions of the solar spectrum at different times and places into the AMF, a fast estimation of the system power output over a period of time at a particular location and environment can be achieved. This method can be used to accurately guide the development of customised PV products for specific geographical locations or environments.

3.3.2.7.2. Angular Matrix Framework

Optical design and optimization is essential if the energy conversion efficiency of solar cells is to be maximized. As wafer thicknesses are reduced to achieve cost reduction and potential voltage gains [1], optical modelling and optimization of solar cells become more critical. There are several methods currently available to model the optical performance of solar cells. However, it is often difficult to identify a single modelling method for solar cells employing hybrid light-trapping schemes, as each method has strengths and limitations for particular applications. Computational electromagnetics methods, like Finite Difference Time Domain (FDTD), can be used for an arbitrary structure [2]. However, high computational complexity makes it difficult to simulate thick devices over large areas, a capability which is required for silicon wafer-based solar cells.

An angular matrix framework was proposed for simulating the optical performance of solar cells based on separated modelling of the capability of surfaces and the substrate to redistribute the light intensity across different angles in the device [3]. The angular redistributions of reflection, transmission and absorption of the surfaces and bulk region are modelled with matrices, which can be assembled using different methods. The optical performance of devices can then be efficiently calculated using these matrices. When suitable methods are used to estimate the matrices for different regions of a solar cell, hybrid simulation can be effectively performed. In addition, the framework enables the reuse of the established model for angular response. Once the matrices for particular light-trapping structures have been determined, the reflection, absorption and transmission for different incident angles can be calculated by changing the incident energy distribution without reconstructing these matrices.

Reflection of an acidic-textured multi-crystalline silicon wafer [see Figure 3.3.2.7.1 (a)], an alkaline-textured mono-crystalline silicon wafer [see Figure 3.3.2.7.1 (b)], and an alkaline-textured mono-crystalline silicon wafer with an anti-reflection coating [see Figure 3.3.2.7.1 (c)] were measured with a spectrometer and compared with simulations [see Figure 3.3.2.7.1 (d)]. The angular matrices in this case were calculated with an in-house two-dimensional ray-tracer. Simulated reflections were in good agreement with the measurements. In addition, the non-absorbed fraction of the light for the alkaline textured wafer was measured at 0° and 30° in a center mount setup of the spectrometer. The simulated results of the combination of transmission and reflection for these two incident angles were performed by multiplying the angular distribution of incident light at two angles, E_0° and E_30°, with the
matrices constructed for the previous simulation. The simulated results in Figure 3.3.2.7.2 are consistent with the measurements.

Figure 3.3.2.7.1: Schematics for: (a) an acidic-textured silicon wafer; (b) an alkaline-textured silicon wafer; and (c) an alkaline-textured silicon wafer with a 75 nm SiNx ARC. (d) Experimental (symbols) and simulated reflection (solid lines) for an acidic-textured silicon wafer (green), an alkaline-textured silicon wafer (blue), and an alkaline-textured silicon wafer with one-side 75 nm SiNx (red).

Figure 3.3.2.7.2: Schematics showing illumination at an: (a) incident angle of 0° and corresponding incident distribution E_0°; and (b) incident angle of 30° and corresponding incident distribution E_30°. (c) Experimental (symbols) and simulated (solid lines) reflection plus transmission for alkaline-textured silicon wafer at incident angle of 0° (blue) and 30° (green).

To demonstrate the benefit of using hybrid simulation, an earlier proposed thin silicon solar cell with a metal nano-grating was simulated [2]. The schematic of the structure is shown in Figure 3.3.2.7.3 (a). The substrate was a 10 μm thick silicon absorber with a silver nano-grating and rear reflector having a pitch and pillar width of 500 nm and 300 nm, respectively. It was challenging to model the structure with only ray-tracing or FDTD. With AMF, ray-tracing and TMM were used to generate the angular matrices for the front surface, while the structures on the rear surface were simulated using the FDTD method. The reflection and absorption for the proposed device, with and without a silver nano-grating, are shown in Figure 3.3.2.7.3 (b) and (c). As expected, the device...
with the nano-grating demonstrated higher absorption in the silicon absorber and lower reflection for wavelengths exceeding 700 nm, due to the enhanced effective light path length from the wider scattered angle of the grating.

Figure 3.3.2.7.3: Schematics for a device: (a) with a silver nano-grating; and (b) without the silver nano-grating. (c) Simulated absorption (solid lines) and reflection (dashed line) for the device with the nano-grating (blue) and without the nano-grating (red).

3.3.2.7.3. System-oriented Optical Modelling of Solar Cells

As solar PV-generated power becomes more cost-effective, it can penetrate more markets and be distributed in more diverse geographic locations. To maximise the power generation for different locations, it can be beneficial to customise aspects of the optical design for both the cell and module so that the module performs optimally for specific geographical locations and/or environments (e.g., including solar insolation spectrum, weather and shading).

A method to realise System-Oriented Optical Modelling (SOM) of solar cells was developed. In this method, absorption was calculated at the cell level using the AMF described in Section 3.3.2.7.2, which provides native support to the calculation of the wavelength-resolved angular-dependent absorption. The local solar irradiation was then calculated using the SPCTRAL2 [4]. The output of each of the two calculations was represented in a matrix, which when combined in a matrix product, elegantly modelled the PV system operating in the specific environment over a period of time. In this approach, which is depicted schematically in Figure 3.3.2.7.4, the contributions of the module and environment are clearly separated, thereby avoiding the need for repeated calculations. Using this method, the parameters of solar cell, related to the cell’s optics, can be optimised for a particular geographical location and/or environment.

Figure 3.3.2.7.4: Structure of proposed method of combining AMF and SPCTRAL2 to achieve SOM.
The SOOM method can be used to estimate the power generation of a PV system. Simulations of the power output of a rooftop PV array predicted the measured time-based power output of the array with a reasonable accuracy. It can also be used to optimise the optical design of cells according to the target system location. As a demonstration, the method was used to estimate the energy production of modules installed in two different geographical locations where the cells were fabricated with different ARC thicknesses. The simulations used the local solar spectrum at the two locations (Brisbane, Australia and Hamburg, Germany) and the angular absorption properties of the cells. Figure 3.3.2.7.5 shows the normalised energy produced of the solar cells as a function of ARC thickness at the two geographical locations over a period of one year. It can be seen that the optimal ARC thicknesses are ~ 75 nm for Brisbane and ~ 78 nm for Hamburg. Due to the higher latitude, the air mass in Hamburg is significantly larger than in Brisbane, which results in a flatter solar spectrum due to the higher scattering and absorption for short wavelength light by the atmosphere.

![Figure 3.3.2.7.5](image)

**Figure 3.3.2.7.5:** Normalised energy production for solar cells with varying ARC thickness in Brisbane, Australia (black line) and Hamburg, Germany (red line) over a period of one year.

The asynchronous implementation of modelling and simulation of this method makes a vertically-integrated optical simulation possible. The different optimal ARC thicknesses demonstrated the performance advantage of cell optical optimisation for localities and the effectiveness of this method. The approach can be extended to determine the performance advantage of different module components (e.g., encapsulant, module glass texturisation and alternative frontsheets) for installations at different geographical locations or environments.

REFERENCES


3.3.2.8. Durability and Reliability of Plated Metallisation

Research team (UNSW):
Alison Lennon
Xi Wang

Collaborating Partners:
Matthew Stocks (ANU)
Shengzhao Yuan (Trina Solar, China)

Postgraduate research students:  Research assistant:
Pei-Chieh Hsiao     Wei Zhang
Xi Wang
Zhongtian Li
Vincent Allen
Jack Colwell

3.3.2.8.1. Overview

By replacing screen-printed silver metallisation with plated copper, silicon PV manufacturers can reduce material costs, but perhaps more importantly they can: (i) minimise material cost volatility that comes from using an investment metal; and (ii) develop a metallisation platform that can enable higher efficiencies in the future. Although new silver screen printing pastes are eroding some of the efficiency potential of plated copper metallisation, challenges remain for the pastes in that their fire-through properties require the use of glass frits that place limits on the achievable contact resistances. Furthermore, as the width of screen printed fingers is reduced it becomes increasingly difficult to ensure continuous metal lines which have sufficient cohesive strength.

However despite the often acknowledged benefits of copper plating for silicon solar cells, plated metallisation has so-far to gain traction in silicon PV manufacturing [3.3.2.8.1]. Concerns regarding durability of the contacts, possible copper penetration into the cell and poor adhesion of plated metal to silicon have limited the uptake of plated metallisation. This research activity aims to address some of these concerns. It is supported in part by the ARENA-funded project “RND000 – Advanced Surface and Contact Technologies for Industrial Silicon Photovoltaics” and Trina Solar.

3.3.2.8.2. Copper Penetration through Plated Barrier Layers

Plated copper metallisation schemes typically include the plating of thin nickel layers under the plated copper to act as a barrier to copper diffusion into the cell. However, copper can penetrate through grain boundaries of diffusion layers [3.3.2.8.2] and plated nickel layers typically contain many grain boundaries because when nickel is plated directly to silicon it deposits at nucleation sites and then proceeds to “grow” out from these sites. So the question remains, “does the copper get into the cell and if so then why have module IEC tests not detected any reliability issues associated with the copper penetration?” Furthermore testing of BP Solar Saturn modules that have been in the field for 20 years have not demonstrated any unexpected degradation, and in fact have outperformed screen-printed modules of similar vintage in some studies [3.3.2.8.3].

Recently Flynn detected copper precipitates in laser-doped cells that had been plated with nickel and then copper which were subsequently heated at 200 °C for 5 hrs and then quenched [3.3.2.8.4]. The precipitates (see Figure 3.3.2.8.1) were detected in transmission electron microscope (TEM) cross-sectional images of the regions immediately under the metal contact (i.e., in the laser-doped region). However, precipitates were only detected with quenching. They could not be detected in cells that were cooled naturally. She concluded that copper may penetrate through plated nickel barrier layers, however if the cell is allowed to cool naturally after heating, the copper out-diffuses to the surface where it does not impact the device performance. In fact Flynn was able to demonstrate that if a cell was heated and quenched the average PL intensity was reduced, but then if the same cell was re-heated and then allowed to cool naturally the PL intensity was returned to close to its pre-heated
values. This finding suggests that copper precipitates that form during quenching may be able to be re-dissolved in a subsequent heat treatment and then out-diffuse on ambient cooling. Although this may be perceived as “fortunate” for the silicon solar cell, an improved understanding of the behaviour of copper in cells and the ability of barrier layers to impede copper ingress is required.

Figure 3.3.2.8.1: Transmission electron microscope images of Cu particles in a LIP Ni barrier layer sample annealed at 200°C for 5 hours followed by fast quenching (from [3.3.2.8.4]).

Recent work [3.3.2.8.5] has examined the possibility of using laser ablation inductively-coupled plasma mass spectroscopy (LA-ICPMS) to detect copper ingress in cells on heating, as the TEM analysis used by Flynn was time consuming and therefore limited to fortuitous discovery of the precipitates. The LA-ICPMS method enables systematic measurements to be made and therefore may shed light on where in the cell copper, and indeed nickel, may go in the cell if the metals penetrate during heat treatment. Almost all studies on plated metal diffusion into the cells have focussed on what occurs when the cell is heated, but studies are also required to establish what may happen when a cell is reverse-biased (e.g., when a module is shaded) or subject to potential-induced degradation.

3.3.2.8.3. Metal Finger Adhesion Measurements

Plated metal adhesion has been typically assessed using pull-tests [3.3.2.8.6], however these measurements do not take into consideration possible poor adhesion of metal fingers. Stress can evolve in plated metal depending on the plating chemistry and process used and, for this reason, thin metal fingers can act like wires with high levels of tensile stress. This can make them prone to peeling, an effect that can be distinct from metal-silicon adhesion at the busbar. Young et al., recognised this difference and developed a stylus-based testing method which could be used to measure the force required to dislodge metal fingers [3.3.2.8.7].

Subsequent work performed at UNSW using an adhesion tester similar to the tool developed by Young (see Figure 3.3.2.8.3), has shown that two distinct failure modes can arise when fingers are impacted by the moving stylus [3.3.2.8.8]. Fingers can be dislodged by the stylus and can be extended momentarily before breaking. Alternatively, if the silicon-metal adhesion is much stronger in comparison to the cohesive strength of the fingers, then the stylus will “cut through” the metal finger. The latter mode is typically observed for screen-printed cells as their cohesive strength typically is comparatively less than their adhesive strength. However, plated metal fingers can either be “cut-off” or “dislodged” depending on how the patterning and plating is done. Figure 3.3.7.2.1 shows these different modes. These measurements can assist process development however future research will attempt to correlate the measured forces with physical properties of the plated metal fingers (e.g., tensile/compressive stress) so that more reliable plating processes can be developed. Additional correlations between the measured forces and known metrics such as the pull strength of busbars and performance on the different IEC module tests will help establish this new testing method as being an acceptable metric for plated metal adhesion.

A useful feature of the adhesion testing method is the ability to perform a number of scans across a wafer recording the cut-off or dislodgement force across a series of fingers. This data, which can be
visualised as a contour plot as shown in Figure 3.3.2.8.4, can highlight processing non-uniformities. For example, in Figure 3.3.2.8.4 (b) the significant difference in dislodgement force across the wafer was attributed to variations in the laser doping process across a wafer. Contour maps can also be used to detect non-uniformities in plating due to non-ideal plating tool design. Although the final reliability metric is successful completion of the appropriate IEC tests, the ability to track plated finger adhesion can enable production problems to be detected and addressed earlier in the production flow.

Figure 3.3.2.8.2: The stylus-based adhesion tester developed at UNSW based on the design by Young et al.

Figure 3.3.2.8.3: Images of the stylus tip: (a) cutting through a screen-printed silver finger; and (b) dislodging a nickel/copper plated finger (from [3.3.2.8.7]).
Figure 3.3.2.8.4: Contour maps of cut-off force and dislodgment force for: (a) a screen-printed cell; and (b) a laser-doped cell, respectively (from [3.3.2.8.7]).

REFERENCES


3.3.2.8.8 R. Chen, W. Zhang, X. Wang, X. Wang, and A. Lennon, "Failure modes identified during adhesion testing of metal fingers on silicon solar cells," in 5th Workshop on Metallization of Crystalline Silicon Solar Cells, Konstance, Germany, 2014.
3.3.2.9. Anodic Oxides for Tunable Dielectrics and Contact Layers

Research team (UNSW):
Alison Lennon
Dirk König
Zi Ouyang

Postgraduate research students:
Zhong Lu
Xi Wang
Jingnan Tong
Yu Jiang
Daniel Lambert

3.3.2.9.1. Overview

Anodisation is an electrochemical method for forming metal oxides. If a silicon surface is anodised, thin anodic silicon oxide layers can be formed on the surface of the wafer. Alternatively, metal layers can evaporated or sputtered on the wafer surface and then anodised to form a metal oxide layer. Earlier work by Lu et al., demonstrated that porous anodic aluminium oxide (AAO) could result surface recombination current densities for phosphorus-diffused p-type silicon wafers as low as 8 fA/cm² [3.3.2.9.1]. Unlike Al₂O₃ deposited by PECVD these layers were shown to contain positive charge, which made them well-suited to passivating n-type silicon surfaces.

Anodic oxides can be formed by directly contacting the silicon or metal layer to the anode of a power supply. However, this anodisation method has a number of disadvantages including incomplete anodisation at the electrode contact and non-uniform anodisation current due to the current passing parallel to the surface being anodised. Alternatively, it is possible to direct the current perpendicular to the surface being anodised (i.e., through the wafer) using the processes of light-induced anodisation (LIA) [3.3.2.9.2] and field-induced anodisation (FIA) [3.3.2.9.3] [3.3.2.9.4]. These processes, which are simply the anodic equivalents of light-induced and field-induced metal plating (see Section 3.3.2.6.2), can achieve uniform anodisation over large areas without the need for excessively high currents. The properties of anodic oxides can be tuned by varying the anodisation process. This enables their application to surface passivation (see Section 3.3.2.9.2), formation of tunnel oxides (see Section 3.3.2.9.3) for passivated contacts and also semiconducting transition metal oxides for selective-carrier contact layers (see Section 3.3.2.9.4).

3.3.2.9.2. Tuning the Stored Charge in Anodic Oxides

It is generally preferable for a passivating dielectric layer to have stored charge that can induce an accumulation layer in the silicon at the interface. Anodic aluminium oxide layers formed by anodising aluminium under a DC current bias have stored positive charge and therefore will typically result in the formation of an accumulation layer in n-type silicon. Lu demonstrated that if a pulsed current waveform was used to anodise a layer of aluminum formed over a SiO₂ layer, then the magnitude of the effective stored positive charge, Q_{eff}, can be reduced and the polarity can even be reversed at low positive duty cycles [3.3.2.9.5]. The magnitude of the negative stored charge was found to be related to the thicknesses of the intervening SiO₂ and the aluminium layers. Lu was able to show that the more negative stored charge was most effective at reducing the recombination occurring in a boron-diffused surface as shown in Figure 3.3.2.9.1. Measurements were made using symmetrically boron-diffused test structures for the photocurrent (i.e., minority carrier lifetime) measurements and metal-insulator-semiconductor (MIS) test structures for the measurement of Q_{eff} and the density of interface states, D_{it}. 
Figure 3.3.2.9.1: (a) Recombination current density, $J_{0p+}$, estimated for symmetrically-diffused test structures with 400 nm AAO as a function of positive duty cycle; and (b) $Q_{ef}$ and $D_{it}$ as a function of positive duty cycle measured from the MIS structures fabricated with the same SiO$_2$ and AAO thickness (from [3.3.2.9.5]).

The stability of the stored charge in the AAO layers was also assessed. The positive stored charge steadily declined in the first ten months after fabrication [Figure 3.3.2.9.2(a)], however the $Q_{ef}$ of the MIS structures with negative stored charges were relatively stable over the period examined provided that the duty cycle was greater than 30% [see Figure 3.3.2.9.2(b)].

Figure 3.3.2.9.2: (a) Stability of the positive $Q_{ef}$ over time for test structures fabricated at with different AAO layer thicknesses and 100% positive duty cycle; and (b) stability of the negative $Q_{ef}$ over time for test structures with different positive duty cycle (from [3.3.2.9.5]).

Future research will investigate whether the range of $Q_{ef}$ values can be extended by using thinner intervening SiO$_2$ layers (e.g., using the ultra-thin anodic tunnel oxides described below in Section 3.3.2.9.3). Pulsed anodisation will also be trialed using the through-wafer processes of LIA and FIA to see if the $D_{it}$ can be reduced from the values measured to-date. Finally, manipulation of stored charge may prove to be a useful way in which to tune the band bending properties of anodic transition metal oxide selective-carrier contact layers (see Section 3.3.2.9.4).

3.3.2.9.3. Ultra-thin Anodic Tunnel Oxides

 Ultra-thin tunnel oxides are critical for passivated contacts. They need to be sufficiently thin [3.3.2.9.6] and uniform across the wafer surface for carriers to tunnel through to the contact layer, whilst also minimising recombination at the silicon surface. They can be grown using dry thermal oxidation, however the processes require the maintenance of very clean furnaces and suffer from low-throughput and a high thermal budget. Also it becomes increasingly challenging to achieve very thin and uniformly thick thermally-grown oxides on the larger wafers required for commercially-produced
silicon solar cells. An alternative is to grow the oxide using chemical immersion methods, however doubts remain as to whether the required oxide uniformity, in both thickness and electronic quality, can be achieved when scaling up to large wafers.

Anodic oxides represent another alternative. Field-induced anodisation can result in very uniform thin silicon oxides because the anodisation current flows through the wafer in a direction that is perpendicular to the surface being anodised. This enables uniform anodisation over an area that can be scaled to industrial-sized wafers without the use of very high currents. The FIA process can be applied to devices with or without a p-n junction. When a p-n junction exists then the bias voltage or current must be applied to forward bias the junction so current can flow through the wafer. If lightly-doped wafers are used then illumination is required to ensure that a current can flow across depletion regions that can form at the silicon-electrolyte interface.

The thickness of anodic silicon oxides grown by FIA can be controlled by selecting an appropriate bias voltage for the required oxide thickness. Figure 3.3.2.9.3 graphs the thickness of silicon oxide layers grown using FIA in 0.5 M H₂SO₄ on n-type double-sided polished Cz (100) silicon wafers as a function of time for two applied bias voltages. The uniformity of the anodic oxides improves with longer anodisation times because the through-wafer current flows through the paths of least resistance until the applied voltage is insufficient for a current to flow [3.3.2.9.7]. This means that FIA can be used to grow very uniform and controllably thin layers. For each applied bias, the layer thickness saturated at a value that was limited by the resistance provided by the formed oxide. This was 2.34 ± 0.03 nm and 3.37 ± 0.07 nm for the oxides grown with applied voltages of 1.5 and 3.0 V, respectively. The thickness of a chemical oxide, formed by immersion in the same electrolyte, was limited at 1.90 ± 0.15 nm, the larger variance indicating the poorer uniformity of the chemical oxide.

![Figure 3.3.2.9.3](image)

Figure 3.3.2.9.3: Thickness of silicon oxide layers formed by immersion in 0.5 M H₂SO₄ (i.e., chemical oxide) and FIA under different anodisation conditions. The thickness was measured at 5 points across the wafer and is represented as a mean with the error bars representing the standard deviation (from [3.3.2.9.7]).

Figure 3.3.2.9.4 shows the implied open circuit voltage, $iV_{oc}$, measured for a number of selected anodic silicon oxide layers formed by FIA on n-type double-sided polished Cz (100) silicon wafer fragments of thickness of 525 μm and a resistivity of 0.8 Ω-cm and capped with 100 nm SiNx deposited by remote plasma PECVD. A nearly linear increase in $iV_{oc}$ with increasing anodic oxide thickness was observed, with an $iV_{oc}$ of 680 mV being measured for an anodic oxide of thickness of 12.8 nm. A belt furnace anneal at 400 °C after SiNx deposition did not appear to improve the surface passivation. Future work will focus on comparing the anodic oxides with thermal oxides grown over a wider range of thicknesses. With FIA it is expected that with higher applied voltages there would be a higher $D_i$ at the interface due to the larger tunneling current, however this should not be a problem as the thickness of tunnel oxides for passivated contacts is typically in the range of 2-3 nm.
3.3.2.9.4. Anodic Transition Metal Oxides for Carrier-Selective Contacts

There has been interest in exploring the use of transition metal oxides for carrier-selective contacts. Of particular interest is the use of molybdenum oxide, MoOₓ, as a hole contact layer [3.3.2.9.8] [3.3.2.9.9]. Molybdenum oxide is an n-type semiconductor and from band edge data it would be expected to present a significant barrier to holes flowing from the silicon to the contact layer. However, when layers of MoOₓ are formed by evaporation, a sub-oxide transition layer forms at the interface with the silicon. This results in defect states close to the valence band edge which can mediate the transport of electrons from the MoOₓ to holes at the silicon interface. Since sub-oxides can also form during anodisation, it was hypothesised that it should be possible to anodise sputtered molybdenum layers to form anodic MoOₓ with the extent of the sub-oxide layer being controlled by anodisation conditions and subsequent annealing processes.

Initial experiments have demonstrated that it is possible to anodise sputtered molybdenum layers using FIA, however the XPS spectra (see Figure 3.3.2.9.5) indicate a significant fraction of Mo and MoO₂ (peaks occurring at 227.8 and 229.7 eV, respectively) compared to MoO₃ (232.6 eV). This suggests that longer anodisation times will be required.

Figure 3.3.2.9.5: Binding energy spectrum of an anodic MoOₓ layer.

Future research will also investigate the anodisation of tungsten (hole contact) and titanium (electron contact). One of the advantages of forming transition metal oxides by anodisation is that there is the
potential to tune their electronic properties, which is not always possible when the oxides are formed by sputtering or evaporation. The use of pulsed anodisation, as described in Section 3.3.2.9.2 may be able to be used to control the stored charge properties of the layers, and in doing so control the band bending at the silicon interface.

The properties of transition metal oxides are of interest to a range of different applications and so an improved understanding of their properties is of interest. Hartree-Fock density functional theory (HF-DFT) modelling can be used to simulate the configuration and density of states of both the bulk phase and interface regions of different anodic metal oxides formed by through-wafer anodisation. The oxides can be modelled including substitutional, interstitial and vacancy defects which may be created by the anodisation process.

REFERENCES


3.3.3 New Wafer-based Projects

3.3.3.1 Introduction

Significant increases in research funding, particularly from ARENA, has facilitated the initiation of a range of new wafer-based projects during 2014-2015. Summaries of these projects are as follows.

3.3.3.2 Hydrogen Passivation of Contaminants and Crystallographic Defects in Silicon

**Staff and Postdocs**
S. Wenham
M. Abbott,
M. Edwards
C. M. Chong
L. Mai
A. Sugianto
D. Lu
B. Hallam
C. Chan
P. Hamer

**Students**
S. Wang
A. Wenham
L. Song
N. Nampalli

**Summary**
Hydrogen passivation of defects in silicon has been utilized for decades for improving the material and/or surface quality in a range of semiconductor devices such as solar cells. More recently, new techniques have been devised for controlling the charge state of the hydrogen within the silicon. This appears to have significant importance for both the mobility and reactivity of the hydrogen and therefore its ability to passivate or deactivate recombination sites within the silicon material and at the interfaces. These new techniques are being applied to both finished and partially fabricated devices. The challenge for the latter is to then retain the improved passivation quality for the respective device at the completion of processing.

A particular focus for the work is to collaborate with companies producing lower quality grades of silicon that are significantly cheaper to produce such as the UMG material originating from companies such as Apollon Solar, Elkem and Silicor. The aim is to repair defects in the material to produce wafers of equivalent quality to what would be achieved through the use of semiconductor grade silicon. As shown in Figure 3.3.3.2.1, the hydrogenation has facilitated significant improvement in the wafer quality with minority carrier lifetimes increasing from about 1 microsecond to over approaching 1ms, similar to that expected for p-type CZ wafers formed using the highest possible quality of silicon feedstock. The “secret tricks” referred to in achieving this passivation quality refers to controlling the charge state of the hydrogen during the passivation process and subsequent cooling process. This can also be applied on a localized basis to areas as small as 100 microns in diameter. Figure 3.3.3.2.2 demonstrates the application of the passivation process to only half the solar grade wafer with a corresponding increase in implied open circuit voltage (iVoc) for the treated half of approaching 100mV to approximately 700mV.
Figure 3.3.3.2.1: Photoluminescent (PL) images for three identical UMG p-type CZ wafers from Apollon Solar showing large variations in carrier lifetimes as a function of passivation technology applied. All three wafers are coated on both surfaces with identical SiNx layers to provide surface passivation and a source of hydrogen. The use of hydrogen charge state control on the wafer segments to the right facilitated the achievement of greatly improved carrier lifetimes and corresponding iVoc values in the vicinity of 700mV.

Figure 3.3.3.2.2: PL image of a UMG p-type CZ wafers from Apollon Solar with hydrogen charge state control applied only to the right hand side of the wafer during heating and cooling.

Numerous industry partners, including many of the world’s largest cell manufacturers, have been given demonstrations of the effectiveness of the new defect passivation technology and have signed licence and funding agreements with UNSW for access and development of the technology. Numerous tool manufacturers have also donated pieces of equipment for use in the work and are contributing the expertise necessary for the redesign of such tools for adaptation to the new technology. This work is also forming the basis of a large ARENA grant 1-060 valued at approximately $4 million and contributed significantly to UNSW researchers receiving the 2013 IET H F Harvey Engineering Prize valued at about US$500k.
3.3.3.3 Towards Ultimate Performance Commercial Silicon Solar Cells

The ARENA 1-082 project finishes early 2015 with all milestones achieved including several world record efficiencies for both cells and modules, multi and single crystalline silicon. This new project builds on the developments of ARENA 1-082. During the expression of interest round for ARENA funding in early 2014, this project and corresponding team led by Dr Sugianto received the highest ranking out of more than one hundred applications Australia-wide. The full proposal however was further strengthened through merging with two other highly ranked projects with valuable expertise and technology, one led by Dr Bremner and the other by Associate professor Ji. These three overlapping projects form three subsections of the new ARENA RND068 project commencing in 2015. The ambitious aims include achieving in excess of 23% efficiency on commercial grade p-type wafers.

3.3.3.3.1 New Laser-doping and Metal Contact Formation Technology

Staff
A. Sugianto
S. Wenham
M. Green
J. Jia
L. Mai

Industry Partners
Schmid
Sunrise Global Energy
Suntech
Trina Solar
Tempress

Summary
Since 2011, the collaboration between UNSW and Suntech has significantly bridged the efficiency gap between laboratory-based UNSW world-record 25% efficient PERL solar cells and full-sized commercial cells fabricated using the dominant p-type industrial-grade wafers. Most of this improvement results from integrating high-efficiency attributes of PERL cells into the commercial cell design, known as the Pluto technology, with record efficiencies above 20% surpassing the long-term international efficiency targets set in the International Technology Roadmap for Photovoltaics (ITRPV). Several important innovations from this work have been patented and demonstrated to have the potential to make substantial further improvements to the record efficiencies already achieved by Pluto. In particular, these improvements include a new, superior approach for forming the metal contacts and the integration of an advanced passivation technology that has already demonstrated the potential to improve the quality of low-cost industrial-grade wafers to match that of excellent quality FZ wafers used by the laboratory PERL cells that typically cost more than 10 times more. This project aims to incorporate the potential of this major breakthrough into the commercial implementation of Pluto, raising efficiencies with industrial-grade wafers to over 23%. Work will focus on achieving record efficiencies for various industrial-grade wafers including multicrystalline silicon and fabricating modules to allow full evaluation and certification for commercial readiness.

Research Program
The primary objectives are to implement new innovations into Pluto technology to develop a new generation of record performance, lower cost, solar cells using p-type CZ and multicrystalline wafers and to demonstrate their commercial viability through device and module fabrication and testing in the state-of-the-art UNSW SIRF facilities. In the proposed cell structure, the heavily-doped n-type emitter in screen-printed cells is replaced by a lightly doped emitter but with localised heavily laser-doped silicon stripes that are closely spaced and transport the current from the emitter to the metal fingers. A particularly innovative aspect of forming these heavily-doped stripes is the creation of
narrow grooves only 2-3 microns wide as shown in Figure 3.3.3.1, that are ideal for nucleating the growth of the plated metal contacts. An important aspect is that the groove walls are simultaneously heavily doped while in the molten phase to a depth of typically 5 microns perpendicular to the groove wall surface, making them ideal for selective-emitter formation where heavily doped metal/silicon interfaces achieve low contact resistance and dark saturation current. Such grooves can be formed prior to surface dielectric deposition, avoiding laser-induced defects from the thermal expansion mismatch between the silicon and the dielectric during laser melting. This is particularly important for high voltage cells such as being developed in this project.

Following groove formation, top surface passivation through dielectric deposition creates sufficiently thin coating in the grooves to facilitate metal plating nucleation. Other important aspects to replacing Pluto's metal contacts with this new groove approach are that: firstly, the metal deposition is self-aligned through innovative light-induced plating which is predicted by the ITRPV to displace screen-printing by 2023 as the main metallisation approach; secondly, the grooves create anchor points to greatly improve metal adhesion; and thirdly, metal lines can be 3 microns width up to tens of microns depending on plating duration, providing ideal flexibility for high efficiency cell design and with potentially simple low-cost implementation into the Pluto technology through this project. This approach is very new and in the process of being patented. The rear screen-printed metal for Pluto is to be replaced by high-quality passivating dielectric layers which comprise hydrogen-rich silicon nitride, aluminium oxide or silicon oxynitride depending on technology compatibility, cost and ease of implementation for mass-production. Following laser patterning, rear metal can be screen-printed, sputtered or even plated to create a bifacial cell design. Another innovative development in this project is the incorporation into Pluto of the new hydrogen passivation techniques developed at UNSW using hydrogen charge state control to significantly increase wafer quality. Test structures indicate that greatly improved wafer quality can result with >700mV open-circuit voltages feasible with standard p-type CZ and multi-wafers. These techniques will be implemented into both Roth&Rau and Tempress PECVD systems for comparison and Pluto optimisation.

3.3.3.3.2 Commercial Development of Point-contacting by localized dielectric breakdown (PLBD) process for high performance silicon solar cells

Staff
S Bremner
N. Western
S. Wenham
J. Jia

Industry Partners
Trina Solar
Schmid

Summary
A novel rear contacting approach, Point-contacting by Localised Dielectric Breakdown (PLDB), patented by UNSW, will be developed and potentially implemented in the next generation of commercial high efficiency silicon solar cells. This development is timely, as the industry recognizes that the next 'quantum leap' in performance requires rear surface optimization of solar cells. The PLDB approach allows the formation of rear point-contacts through a passivating dielectric, whilst maintaining other performance advantages, and avoids high temperature processes, giving a significant cost advantage over current approaches. Combining laser doping, developed at UNSW, with bias induced breakdown of the passivating dielectric, repeatable and reliable high performance structures can be spliced into existing solar cell processing sequences. Working closely with industry partners, commercially viable fabricating processes will be determined and tools for accomplishing this on industrially relevant scales will also be designed. Complementing the UNSW developed and increasingly industrially important PERC solar cell, and ongoing ARENA sponsored projects working
to reduce production costs, a pathway for the next generation of high performance low-cost devices will be determined.

3.3.3.3.3 Development of Large-scale High-throughput Plating Baths for n and p-type Solar Cell Contacts

Staff
J. Ji
S. Wenham
M. Green
D. Bagnall

Industry Partners
Suntech
Schmid
Sharesun
Centrotechnics

Summary
Despite Australia’s success developing and commercializing high efficiency photovoltaic technology utilizing plated metal contacts for >20 years with $billions of product in the field, suitable plating tools for large-scale manufacturing have never been developed for wide-spread use. The closest is the single-polarity light-induced plating tool designed and developed by Dr Ji exclusively for the 0.5GW Pluto manufacturing facility. With expected massive increases in demand for plating in the near-future, Dr Ji has developed new and patented state-of-the-art in-line plating technology including the ability to plate both metal contact polarities. To ensure Australian ownership of this new technology and corresponding plating tools, Dr Ji recently transferred them, including IP and prototype tool, to UNSW for evaluation and ongoing development in this project. Scaling the technology to develop, fabricate and evaluate a full-size high-throughput prototype plating tool for location in SIRF at UNSW to ensure these state-of-the-art plating capabilities are available to all Australian research groups and companies is also a priority. Industry partner equipment manufacturers will assist with equipment construction, evaluation and optimization, and following project completion, potential manufacturing. Industry partner cell manufacturers will collaborate with UNSW to adapt the new plating technology for their own devices for demonstration, evaluation and optimization purposes.

Significance
Experts internationally, such as documented in the ITRPV, predict that in several years plated contacts will dominate over the present standard screen-printed metal contacts. However a suitable manufacturing tool based on light induced plating and capable of plating both polarities of metal contacts, does not currently exist in the industry.

UNSW has pioneered the development and use of plated contacts for commercial solar cells ever since the UNSW buried contact solar cell was commercialised by BP Solar in the late 1980’s. By the turn of the century, virtually 100% of plated solar cells in the field were based on UNSW cell technology. This has remained the case even as recently as 2010 with all commercialized UNSW PV technologies such as the Saturn technology, the Laser Doping Selective Emitter technology and the Pluto technology, all capitalizing on the many high performance, low cost benefits of plated contacts.

The major drawback has been the lack of a suitable commercial tool for large scale manufacturing of plated contacts. This has led to each UNSW industry partner such as BP Solar and Suntech needing to develop and patent their own respective plating tools incorporating UNSW technology, but with none of the resulting tools being made available for use by other cell manufacturers. This has greatly restricted the commercial uptake of UNSW advanced pv technologies and more generally, the use of plated contacts by the industry. This project will address this serious need.
Research Project

An in-line prototype plating tool incorporating the latest generation of plating technology that is capable of plating both polarities of metal contacts for full-size cells without requiring contacts to the surfaces being plated, has been designed, built and patented. This tool is being transferred to UNSW and commissioned during the first year of the project. This tool is be an in-kind contribution by industry partners, with the remainder of the first year following commissioning used to test, evaluate and optimize the tool in accordance with various performance, durability, economic and compatibility criteria including:

- Plating uniformity
- Metal to silicon interface resistance
- Throughput/plating rate
- Ability to plate both polarities
- Process repeatability
- Yields
- Metal adhesion strength
- Durability based on copper penetration
- Compatibility with other device materials such as dielectric masking layers
- Compatibility with various cell technologies including from UNSW
- Compatibility with cell interconnection technologies
- Cost of ownership analysis

Given successful performance against the key criteria listed above, phase two of the project in the second year will involve scaling the tool design to facilitate large scale commercial manufacturing. This will be done in conjunction with the industry partners with experience in tool design and manufacturing. Following satisfactory completion of the design, the new commercial plating baths will be constructed with a completion date expected by the end of the second year.

Following the commissioning of the new tool, a range of evaluation and demonstration criteria similar to those listed above for the prototype tool will be implemented during the third year of the project. In particular, industry partners who are cell manufacturers will be given the opportunity to evaluate the tool in terms of compatibility and suitability for their respective cell technologies. Where necessary, the tool design will be modified or adapted to suit the various requirements of the different technologies. In particular, the SIRF will be used to assist with the fabrication of devices such as based on UNSW technology prior to use of the new plating baths to apply the metallization.

Following the fabrication of sufficient suitable devices, cells will be interconnected and several modules fabricated to facilitate a range of additional testing at module level for both performance and durability. In particular, testing equivalent to the relevant IEC standards will be used to verify the quality and durability of the modules.

Given successful completion of the project, the new state-of-the-art plating baths will be included in the tool set in SIRF at UNSW made available for all Australian companies and research groups to be able to use. It will also provide valuable inclusion in education and training programs run in SIRF as well as be available for technology transfers and demonstrations for companies around the world wanting to use UNSW high performance pv technologies.
3.3.3.4 Detailed computational modelling of laser-grooving and laser-doping processes

Staff
S. Chan
E. Hawks
S. Cook
A. Sugianto
S. Wenham

Summary
The aim of the project is to develop fundamental understanding and predictive modelling capabilities for laser material processing, which is used in several UNSW PV technologies. It is motivated urgently by the recent discovery in project ASI-1-A082 of a new laser-based approach to create deep (~15 micro-m), very narrow (~1-3 micro-m), and damage-free grooves in a highly doped region, which will likely be used in front-side metallisation in the next generation of Suntech’s Pluto technology. In addition to the well-known advantages of UNSW’s existing selective emitter technology (low shading loss, improved blue response, etc.), this new approach results in even lower shading loss without increasing resistance in the contacts due to the very high aspect ratio, and with significantly enhanced contact adhesion due to penetration of the metal into the surface. To optimise this new generation of laser grooving, and to protect the intellectual property, the mechanism of groove formation must be understood in detail. The aim of this project is to provide this currently lacking understanding using:

i) detailed computational modelling of the heat transfer, phase change, fluid mechanics, and dopant transport; and

ii) detailed in situ experimental microscopic visualisations of temperature and melt flows during the laser groove formation.

Research Project
The main tasks are:

Task 1: Develop and validate computational model
The required capability does not exist in commercial software. Therefore, we will build the model from source using an open-source finite-volume-based multi-physics framework, OpenFOAM. OpenFOAM is a library of tools for modelling fluid mechanics having the advantage that much of the required architecture is already in place. The governing equations are a system of partial differential equations for conservation of momenta, energy, and species mass, with an elliptic constraint on pressure. At the phase interface, there are jump conditions on density, pressure, and material properties. To deal with these, we will adopt a volume of fluid (VOF) approach, as it conserves mass and is already implemented in OpenFOAM. VOF solves for a phase indicator scalar used to identify the sharp phase boundaries at which the jump conditions are imposed. Radiation is governed by the integro-differential radiative transfer equation, which we will solve via the Monte-Carlo approach, involving ray-tracing an ensemble of photon bundles. While not currently implemented in OpenFOAM, we have recently implemented this in another solver under ARENA project USO-034 (on solar thermochemical reactors).

Task 2: Experimental Measurements
To validate our model and to better understand the laser-material interactions, we will perform both measurements during (in situ) and after (ex situ) the process.

a/ In situ, time- and space-resolved measurements of reflected light. Exploiting the strong change of optical properties of silicon during melting, we will use a fast photodetector to capture the transient reflectivity (~1 ns resolution, ~1 micro-m detection size), and hence phase transformation. We will visualise laser-material interactions using microscopic photography (~5 ns integration time and ~5 micro-m resolution).
b/ In situ, time-resolved (~10 ns), single-point (~1 micro-m) measurements of temperature and emissivity (and thus phase) using spectral pyrometry. This powerful technique provides an accuracy of 3–6%, even with variations of emissivity or geometry.

c/ In situ, spatially semi-resolved (a few micro-m) time-averaged (over ~1 micro-s) temperature visualisations. Single band pyrometry will be conducted using a high-speed IR camera to provide complementary 2D temperature measurement of the sample.

d/ Ex situ measurements. Prof Wenham's group has extensive experience with several techniques including measurements/visualisations of: groove structure using scanning electron microscopes (SEM); dopant concentrations using secondary ion mass spectrometry (SIMS); junctions using electron beam induced current (EBIC); and crystallinity and residual strain using Raman spectroscopy.

Task 3: Knowledge discovery

The modelling will reveal a 3D and time-dependent picture of the process. We will analyse results by visualisations of temperature, flows, dopant concentration, thermal stresses, etc. Similarly, the in situ experiments will reveal considerable new information. The modelling/experimental team will perform analysis jointly with Sugianto and Wenham's group. The resulting deep understanding will enable considerably stronger IP, and further optimisation/adaption of the process.
3.3.3.5 High Efficiency Low Cost Commercial Silicon Solar Cells with Reduced Metallisation and Improved Interconnection Techniques

Staff
M. Edwards
j. Jia
S. Wenham

Industry Partners
Roth & Rau
Schmid
Suntech
United Crystal Technology
Sharesun

Research Project
The purpose of this project is to investigate and develop the Reduced Metal Passivated Emitter Rear Locally-diffused (RM-PERL) photovoltaic cell, and novel, improved interconnection techniques such as the Meyer Burger Smartwire multiple busbar-wire technique and laser soldering. RM-PERL is an Australian technology and was patented at UNSW in 2013, and both RM-PERL and laser soldering were developed by Australian individuals and employees of UNSW. Approximately 40% of this project will take place outside Australia: 20% at investor UCT’s facilities fabricating solar cells, and 20% at Meyer Burger, who will interconnect cells using their Smartwire multiple busbar technique and provide advice and support on module fabrication.

It is currently well known in industry that technologies which reduce cost of ownership not just at the cell but also the wafer and module level are essential to allow the cost of photovoltaics to continue to fall and replace fossil fuel power generation. In conjunction with multiple-busbar interconnection, RM-PERL allows for the removal of over 95% of cell metallisation compared to standard screen print technology and over 90% of cell metallisation compared to the industry standard. Only a thin ~1 micron layer of plated nickel or tin is required on the cell itself to contact the interconnect- no screen printing is required. This allows for considerable truncation of the cell process line and allows a simple path to realisation of a PERL cell structure, with efficiencies up to 23% possible. This vast increase in efficiency (whilst actually reducing cost per unit at the cell level) results in significant cost per watt reductions at the wafer and module level, with total cost of ownership reduction of over 20%. In addition, the concept allows the complete elimination of toxic lead and cadmium (currently subject to temporary EU exemptions) and expensive silver and copper, the latter of which is known to cause reliability issues in solar modules. While advanced interconnection schemes often involve expensive and rare indium, a new laser soldering technique will replace this metal with lead-free tin solder.

Objectives:
The primary aims of this work are to:
1. Optimise the Reduced Metal (RM) solar cell technology with alloyed-Al rear surfaces so fill factors of 78% can be routinely achieved.
2. Transfer the technology to UNSW’s SIRF pilot line where efficiencies of 18-20% on industrial-sized solar grade silicon wafers (or 16 - 18% at module level) will be demonstrated by the end of first year.
3. Develop future implementations of RM technology for a low cost, high yield/throughput manufacturing environment. These technologies include RM-PERL and other commercially-viable cell structures.
4. To develop or identify encapsulant and superstrate materials and processes capable of maintaining the superior response to blue light of these high efficiency cells at the module level. Research will encompass optical, electrical and durability characteristics of module materials and processes.
5. Evaluate or develop a low temperature, lead-free scheme for interconnection of RM and RM-PERL cells with minimal power loss.
6. Evaluate or develop an indium-free, laser soldering scheme for interconnection of RM and RM-PERL cells with minimal power loss.
7. Perform commercial cost-of-ownership and process-flow modelling of fabricated cell structures to aid in research direction and commercialisation of technologies.
8. To assist New South Innovations to evaluate new ideas, assess technologies and carry out IP protection where required. This will also include transfer of technology to UCT and other company production lines.
3.3.3.6 Advanced Recombination-based Loss Analysis Methods for Silicon Wafer and Silicon Solar Cells

**Staff**
Z. Hameiri  
T. Trupke  
S. Wenham  
D. Macdonald (ANU)

**Industry Partners**
Ron Sinton Instrument  
BT Imaging

**Aims**
In order to make solar energy a viable solution for the energy and environmental challenges facing humankind in coming years, the cost of solar cells must be reduced. A key path to reducing cost is increasing solar cell efficiency without significantly increasing the manufacturing cost. The efficiency of commercial solar cells is limited by loss mechanisms, many of which are caused by carrier recombination processes within the silicon wafer and at its surfaces. Improvement in solar cell efficiency requires the ability to identify and quantify these loss mechanisms; hence, advanced loss analysis methods need to be developed. ‘Effective lifetime’ measurements are widely used to identify recombination processes; however, most commercially-available systems are relatively basic and provide only part of the obtainable information. The goal of this project is to investigate recombination processes using an innovative measurement system combined with new simulation tools. More specifically, the research aims are to: (i) characterise the passivation provided by hydrogen for various bulk defects (hydrogenation); (ii) extract electrical parameters associated with surface passivation provided by new dielectric films such as anodic oxides; (iii) investigate and characterise recombination processes at the silicon-metal interface; (iv) investigate and characterise degradation mechanisms of bulk and surface passivation; and (v) develop temperature-dependent models of silicon properties, such as Auger recombination and carrier mobility in compensated silicon wafers.

**Research Methodology**

1. **Electronic characterisation of bulk defects:**
   In order to improve the hydrogenation process, a deeper understanding of its impact on the electronic properties of bulk defects (concentration, energy level and capture cross section) is required. Initial part of this project is focusing on the development of an advanced measurement system. Temperature- and injection-dependent lifetime spectroscopy (TIDLS) method combines the benefits of other methods and therefore was chosen to be used in this study. Extraction of the electronic parameters from the TIDLS measurements requires accurate fitting capabilities. An algorithm is being developed to determine the required set of measurements, while software is being written to extract the electronic properties from these measurements. The electronic parameters are extracted using the Shockley-Read-Hall (SRH) equation. Since SRH recombination dominates the total recombination within the device at low illumination, accurate measurements are required in this illumination range. To improve the measurement precision at low illumination, photoluminescence (PL) sensors will be used instead of the commonly employed photoconductance (PC) detectors. Although lifetime measurements are commonly used in recombination-related studies, the uncertainty associated with the measurement is rarely presented. To further improve the measurement quality, the used software includes a built-in Monte-Carlo-based uncertainty analysis.

The developed system and software will then be utilised to investigate the novel hydrogenation process being developed at UNSW. The impact of process temperature, heating and cooling rate, illumination level, process duration will be evaluated by monitoring the electronic properties of bulk defects before and after processing. A part from evaluation of the hydrogenation process, the obtained
electronic properties will be essential for device simulations in order to predict the improvement in the solar cell efficiency due to the hydrogen passivation.

This project will also reduce the uncertainty associated with the electronic properties of common metal impurities in silicon wafers. High quality float-zone (FZ) silicon wafers will be intentionally contaminated with a known amount of impurity. Front and rear wafer surfaces will be passivated by high quality low-temperature passivation film (such as aluminium oxide), so the measured lifetime will be largely dominated by the metal impurity. The improved sensitivity of the measurement system at low illumination will enable advanced simulations to calculate the electronic properties of these impurities with minimal uncertainty.

Outputs:

- Determination of the electronic properties of bulk defects before and after the hydrogenation process, in order to evaluate the effectiveness of the hydrogenation process and its impact on solar cell performance.
- Minimisation of the uncertainty associated with the electronic properties of metal impurities. These values will then to be used in device simulation to predict their impact on solar cell efficiency.

2. Electronic characterisation of surface passivation:
Surface passivation of silicon wafers can be accomplished either by reduction of the surface defect density or by reduction of the surface concentration of one of the carrier types. Reduction of the surface defect density is obtained by chemical passivation, usually by coating the surface with a dielectric layer that passivates dangling bonds. Reduction of carrier concentration at the surface can be accomplished by electric fields such as that formed by the presence of a diffused layer or by a fixed charge density ($Q_f$) within the coated dielectric. Most of the dielectrics used for PV applications provide both chemical and field-effect passivation. In order to develop passivation methods the electrical properties of these layers need to be investigated.

In addition to temperature control, measurements designed to extract surface passivation properties will use the corona effect to charge the dielectric. Depositing negative (positive) charge on top a dielectric film that contains a positive (negative) $Q_f$ allows the determination of $Q_f$ within the passivation layer. When plotting the measured lifetime as a function of the deposited charge, a minimum value can be identified. The corresponding deposited charge at this minimum point is assumed to be equal to $Q_f$, while the lifetime value at this point represents the quality of the chemical passivation (as the field passivation is negated by the deposited charge). Therefore, integration of a corona charging capability in the measurement system allows investigation of the influence of $Q_f$ and surface state density on the obtained passivation, without the extensive sample preparation required for capacitance-voltage (C-V) measurements.

Outputs:

- Determination of the impact of process conditions on the electrical properties of the silicon-oxide interface.
- Determination of the electronic properties of PECVD dielectrics.

3. Recombination at the silicon-metal interface:
Recombination at the silicon-metal interface is rarely investigated, as metallised samples cannot be measured by standard PC-based systems. The few existing PL-based systems also have a limited ability to measure metallised samples since the PL sensor is located below the sample; in this configuration, the metal reflects or absorbs the emitted PL signal. To overcome this limitation, this project will use an additional PL sensor located on the front side of the sample. In this configuration, the PL signal can be detected even if the rear surface is totally covered by metal. This novel ability opens a wide range of research areas regarding the impact of different metallisation methods.

Samples will be measured before and after metallisation to evaluate the impact of the process on
recombination within the device. Different metallisation methods will be compared, especially the
dominant industrial method – screen printed contacts – versus the plating method commonly used in
various UNSW solar cell structures. Application of anodic oxides as contact passivation layers will be
investigated by growing a thin oxide layer (2–3 nm) beneath the metal contact. This unique
application has not been previously investigated and can offer high-quality contact passivation using a
simple process. Since the presence of metal can impact the optical properties of the samples and
therefore may influence the detection of the PL signal, an analysis method will be developed to
separate the impacts of optical properties and the additional recombination on the detected PL signal.

Outputs:
• Development of the ability to measure the recombination rate at the silicon-metal interface.
• Comparison between the recombination rates due to different metallisation methods.

4. Degradation processes of bulk and surface passivation:
The stability of the bulk passivation obtained by hydrogenation and of surface passivation obtained by
dielectric layers is an important requirement of the industry, since module power stability has a
critical impact on project financing and commercial viability. In this project, the stability of various
passivation methods, especially that provided by the hydrogenation process, will be investigated.
Typical stability tests require a large number of measurements separated by a sufficient time interval.
It is also desirable to perform these measurements at conditions similar to those in the field or even
under conditions that may accelerate recombination processes. In order to perform these
measurements, the system will include a bias light (a constant illumination) that together with the
temperature-controlled measurement stage can simulate field-operation conditions. The combination
of illumination and elevated temperature will also allow investigation of light-induced degradation
processes and a variety of annealing procedures.

Outputs:
• Evaluation of the stability of the bulk passivation offered by the hydrogenation process.
• Evaluation of the stability of the surface passivation offered by anodic oxides and by PECVD
dielectrics.

5. Development of temperature-dependent models of silicon properties:
Although carrier mobility is an important electrical parameter that significantly influences the
performance of crystalline silicon solar cells, the effects of compensating dopants and grain
boundaries have been less studied and there is yet to emerge a coherent model that accounts for these
effects. In this project, the temperature control stage will be used to extend previous mobility-related
studies to a wide range of temperatures. Silicon samples with different compensation levels will be
passivated and will be measured in order to establish a temperature-dependent mobility model that
accounts for compensation.
The temperature control, together with sensitive detection by the PL sensor, will also allow the
development of a temperature-dependent Auger recombination model. High-quality passivated FZ
silicon wafers will be used in this study. In these samples, intrinsic recombination (mainly Auger
recombination) dominates the entire measurement range. Fitting a large set of measurements at
different temperatures will enable the development of a temperature-dependent model; this will fill a
knowledge gap regarding Auger recombination at elevated temperatures. Similarly, the advanced
system will be also used to validate the temperature-dependent model of radiative recombination.

Outputs:
• Development of temperature-dependent model of carrier mobility in compensated silicon.
• Development of temperature-dependent model of Auger recombination.
Initial Results

Figure 1 presents PL images of a multi-crystalline wafer at various temperatures (all images shown on the same absolute colour scale). Two observations can be made: (a) the measured PL intensity decreases with increasing wafer temperature, and (b) the recombination activity of several (but not all) defects is significantly reduced at high temperature [for example, compare the regions within the squares in Fig. 1(a) and in Fig. 1(d)].

![PL images of a multi-crystalline wafer at various temperatures](image)

**Fig. 1** PL images of a representative six-inch mc-Si wafer at: (a) room temperature (298 K), (b) 398 K, (c) 498 K, and (d) 598 K. All images were taken under the same conditions and are presented on the same colour scale.

In order to distinguish between the changes of the bulk lifetime and the expected reduction of the measured PL signal (mainly due to increasing absorption of Si with increased temperature) the PL simulation by Wang et al. was used. Figure 2 provides the simulated spectral PL emission for different wafer temperatures. Simulation parameters are summarised in the figure caption.

![Simulated spectral PL emission](image)

**Fig. 2** Simulated spectral PL emission from a Si wafer at different wafer temperatures. Simulated values: 180 µm thick 1 Ω.cm p-type wafer; bulk lifetime: 250 µs; surface recombination velocity: 100 cm/s (both surfaces); and excitation wavelength: 808 nm.
The simulated emitted PL intensity was then multiplied by the external quantum efficiency (EQE) of the detection system in order to determine the calibration factor $C_T$ that needs to be used to remove the effect of the PL signal variation:

$$
C_T = \frac{\int_{1300}^{\lambda} EQE(\lambda) PL_T(\lambda) d\lambda}{\int_{900}^{1300} EQE(\lambda) PL_{RT}(\lambda) d\lambda},
$$

where $PL_T(\lambda)$ is the emitted PL signal at temperature $T$ and wavelength $\lambda$, while $PL_{RT}$ is the PL signal at room temperature.

This calibration constant was used to normalise the PL intensity of each pixel $PL(x,y)$ of the images of Fig.1 [$PL(x,y)/C_T$]. The normalised images were then used to create differential images that highlight the variation of $\% eff$ [see Fig. 3]. The significant $\% eff$ improvement of the left side of the wafer [see Fig. 3(d)] indicates that $\% eff$ in this region is dominated by shallow-level defects, while the reduction in $\% eff$ that is observed on the right side indicates this region to be dominated by deep-level defects near the mid gap.

![Differential PL images of a representative mc-Si wafer](image)

**Fig. 3** Differential PL images of a representative mc-Si wafer: (a) 348 K image - 298 K image, (b) 398 K – 298 K, (c) 498 K – 298 K, and (d) 598 K – 298 K. Images that were taken above room-temperature were normalised (s)
3.3.3.7 Angle-Resolved Reflection Spectroscopy of Sub-Wavelength Surface Mie Resonators

Research Team
Darren M. Bagnall
David N. R. Payne
Michael Pollard

Summary

The development of techniques that can minimize reflection of semiconductor surfaces is vital in achieving efficiency improvements for a whole range of photovoltaic technologies. Here we investigate, through an experimental study, a relatively new antireflective scheme based on subwavelength Mie resonators and compare it to another class of subwavelength structures, the so-called ‘moth-eye’ array, for its ability to reduce reflectance of the solar spectrum from the surface of silicon. We show that correctly designed Mie resonator arrays have the potential to outperform moth-eye arrays and reduce reflectance to low levels over the wide range of illumination angles and spectral conditions experienced by a fixed solar cell over the course of a day.

1. Introduction

In addition to traditional thin film antireflective coatings (ARCs) [1], [2], reflection from a silicon surface can be reduced by a range of texturing schemes. These include micron-scale pyramidal features [3], [4] and the more recently developed so-called “sub-wavelength-scale” structures, which can be further subdivided into two distinct classes: The biomimetic ‘moth-eye’ schemes of closely packed, tapered pillars [5]-[9] and the Mie resonator arrays, recently highlighted by Spinelli et al.[10] and consisting of less dense arrays of shorter, cylindrical pillars [11]. These latter structures operate through the coupling, by preferential forward scattering, of resonant Mie modes into an underlying substrate. Tapered moth-eye structures, conversely, operate through a graded index mechanism which removes the step change in refractive index at an interface. It has been shown by experiment and simulation that both of these types of subwavelength AR structure have the potential to improve on widely-used thin film coatings and micron-scale texturing for the reduction of reflectance in photovoltaic devices, thereby leading to more efficient solar cells.

In this study, the fabrication and optical characterization of silicon Mie resonator arrays is presented, with a focus on the application of these arrays as an antireflective scheme for silicon solar cells. Structures with a range of periods, heights and pillar diameters are investigated, firstly using an integrating sphere system for near-normal incidence reflectance measurements and then with an angular reflectance spectroscopy system. The results are compared to those from an uncoated, flat silicon surface, several thin film ARCs and a silicon moth-eye array.

Figure 1. SEM images, taken at an angle of 54°, of the best performing (lowest $R_w$) silicon Mie resonator array based on integrating sphere measurements, period = 500 nm, diameter= 180, height = 95 nm.
2. Methods

2.1 Fabrication
Mie resonator arrays were fabricated using a combination of electron beam lithography, lift-off and dry etching as follows: After standard cleaning (RCA) and a HF dip (7:1 for 20 s), 6 inch silicon wafers were spin coated with MMA and PMMA resist layers. Square arrays of holes were patterned into the resist using electron beam lithography (JEOL JBX-9300FS at 100 kV) with a dose of 195 $\mu$C/cm$^2$. The patterned area for each array was 1 cm$^2$ and the period and diameter of the holes were varied in the ranges 400-500 nm and 120-280 nm, respectively, between different array areas. The resist was developed by soaking in methyl isobutyl ketone (MIBK) for 90 s and then isopropyl alcohol (IPA) for 30 s. A 50 nm layer of chromium was then deposited by electron beam evaporation (Lab 700, Leybold Optics). Lift-off was carried out in n-methylpyrrolidone (NMP) at 60° to leave a hard mask of chromium disks on the silicon surface. The samples were then ICP etched (Plasmalab System 100, Oxford Instruments) using a gas mixture of SF$_6$ (25 sccm) and C$_4$F$_8$ (50 sccm). The chamber pressure was 15 mT, the temperature was 15°C, the RF power was 50 W and the ICP power was 800 W. Etch time was varied to achieve different feature heights. The chromium mask was then removed by soaking in Cr etchant for 10 minutes.

To provide a comparison, reflectance results from a good silicon moth-eye sample fabricated using nanoimprinting, lift-off and dry etch processes are presented. The fabrication of this sample is described elsewhere [12], [13]. The sample consists of tapered pillars with a height of approximately 400 nm arranged in a hexagonal array with a period of approximately 270 nm. The base and tip widths are approximately 131 nm and 74 nm, respectively.

2.2 Characterization
The fabricated samples were first imaged using scanning electron microscopy (Carl Zeiss NVision40) with a beam energy of 20 keV, from which the heights, $h$, periods, $p$, and pillar diameters, $d$, of each array were measured.

Hemispherical reflectance spectra of the Mie resonator arrays at an angle of incidence of 8° were measured using an integrating sphere (RTC-060-SF, Prolite (Labsphere)) and supercontinuum laser (Fianium SC450). This technique enables the collection of both diffuse and specular reflected light from a sample mounted at the rear port. A fibre was used to couple a proportion of this light to a spectrometer (BTC112E, B&W TEK, Inc.) for spectral analysis.

The weighted reflectance ($R_w$) was calculated using Eq. (1) where PFD is the AM 1.5 solar spectrum (ASTM173G, global tilt) expressed as a photon flux density (photons/m$^2$/s) and $R(\lambda)$ is the measured hemispherical reflectance of the sample.

\[
R_w = \frac{\sum R(\lambda) \times PFD(\lambda)}{\sum PFD(\lambda)} \tag{1}
\]

Angular resolved specular reflectance spectra were collected using a custom built motorised $\theta$-$\theta$ angular reflectance spectroscopy system. Details of this technique are given in [12]. Collecting data over a wavelength range of 450-850 nm and an angle of incidence range of 5-83° enables a figure of merit termed the weighted specular reflectance (WSR) to be calculated. This gives an indication of how well the antireflective structure would perform over the course of a day if used on a fixed mounted solar cell. Firstly, $R_w$ is calculated (Eq. 2) for each angle using PFD solar spectrum data obtained from SPCTRAL2 model from the National Renewable Energy Laboratory [14]. Details of this can be found in previous publications [2], [15].

\[
R_w(\theta) = \frac{\sum \lambda [R(\lambda, \theta) \times PFD(\lambda, \theta)]}{\sum \lambda \{PFD(\lambda, \theta)]} \tag{2}
\]

Here, $R(\lambda, \theta)$ is the average of the s and p polarisation specular reflectance values of a sample.
measured using the reflectometer system. The WSR is then calculated by averaging over all angles of incidence to give a single percentage figure of merit.

3. Results and Discussion

Scanning electron micrographs of a successfully fabricated array of Mie resonators are shown in Figure 1. The high precision of electron beam lithography resulted in uniform arrays of features and the etch recipe developed produced vertical side walls as desired.

3.1 Integrating sphere measurements

Hemispherical reflectance spectra of Mie resonator arrays fabricated with a range of periods, heights and pillar diameters, collected at near normal incidence (8°), using the integrating sphere method, are presented and compared to that of uncoated, flat silicon in Figure 2. All samples exhibit antireflection with several resonant features appearing across each spectrum, the position and size of which vary considerably between the different samples.

Further insight into the suitability of Mie resonator arrays for photovoltaic applications can be gained by analysing their average reflectance, \( R_w \), weighted to the AM1.5 solar spectrum (Figure 3). The results in Figure 3 reveal that the period, height and diameter of Mie resonator arrays can be tuned to achieve an antireflective effect that exceeds that of traditional optimised thin film antireflective coatings. Furthermore, the best Mie resonator sample in this measurement set (\( p=500 \text{ nm}, d=180 \text{ nm}, h=95 \text{ nm} \)) exhibits an \( R_w \) of only 5.5%, outperforming even the silicon moth-eye structure which has an \( R_w = 6.4\% \). This is further highlighted in the plot in Figure 4a, which compares the hemispherical reflectance spectra of thin film ARCs, the silicon moth-eye sample and the best Mie resonator.

Figure 2. Hemispherical reflectance spectra from Si Mie resonators (MS) with heights of 95 nm, 145 nm and 195 nm collected using the integrating sphere method. The spectrum for uncoated, flat silicon is also shown for comparison: (a) The period, \( p \), is 500 nm and the diameter, \( d \) is varied from 120-280 nm; (b) \( p \) is varied from 400-500 nm and the \( d/p \) ratio held at 0.55.
Figure 3. Weighted reflectance, $R_w$, of the silicon Mie resonators (MS) calculated from the integrating sphere reflectance spectra shown in Figure 2. The $R_w$ values of uncoated, flat silicon, two types of thin film single layer antireflective coating (SLAR), with optimum thicknesses, and the silicon moth-eye structure are included for comparison.

The SEM images of the two types of subwavelength antireflective (the moth-eye sample in Figure 4b, and the best Mie resonator sample in Figure 4c) illustrate that in addition to a lower reflectance the Mie resonators benefit from a shorter feature height and a lower packing density. This is potentially advantageous when considering the relative ease of passivating the silicon surface to keep surface recombination low and also incorporating other layers into a PV device. This also adds to the potential for scaling the patterning to larger areas using nanoimprinting techniques, both in terms of the expense of producing the master stamp and also the ease of printing the pattern.

2.2 Angular Reflectance Spectroscopy

A similar analysis can be performed on reflectance data from the angular reflectance spectroscopy data collected on each of the fabricated samples to yield weighted reflectance values that take into account angular in addition to spectral variations throughout a day. It is important that antireflective surfaces for solar cells perform well for light over a wide range of incident angles as well as over a broad wavelength range because both angular and spectral illumination conditions vary considerably over the course of a day. The resulting WSR values are plotted in Figure 5.
Figure 4. (a) Hemispherical reflectance spectra from integrating sphere method for the best performing Mie resonator and a silicon moth-eye structure. The legend gives the calculated weighted reflectance ($R_w$). Spectra from optimised SLARs and uncoated flat silicon are included for comparison; (b) SEM image of silicon moth-eye sample; (c) SEM image of best performing Mie resonator sample.

Figure 5. Weighted specular reflectance, WSR, of the silicon Mie resonators (MS) calculated from angular reflectance spectroscopy method. The WSR values of uncoated, flat silicon and the silicon moth-eye structure are included for comparison.

The WSR data again demonstrates that the Mie resonator structures with carefully specified dimensions can outperform the thin film SLARs and the silicon moth-eye array. Interestingly, the best
performing Mie resonator sample, when the full angular analysis is performed, is different to that resulting from analysis of the single angle reflectance spectra from section 3.1. The lowest WRS is exhibited by the sample with $p=450$ nm, $d=250$ nm and $h=95$ nm, SEM images of which are presented in Figure 6. This gives a WRS of only 6.5% whereas the sample with the lowest $R_w$ from the integrating sphere exhibits a relatively poor WRS of 11.5%. This indicates that it is important to characterize full angular and wavelength performance when developing optimum Mie resonator antireflective surfaces. For tracking systems which experience only a limited angular variation in incident light throughout a day, the Mie resonator with the best near-normal incidence AR performance (i.e. the sample with the lowest $R_w$, shown in Figure 1) should be used. For non-tracking devices, the Mie resonator that performs best over the full angular range (i.e. the sample exhibiting the lowest WRS, shown in Figure 6) should be employed.

**Figure 6.** SEM images, taken at an angle of 54°, of the best performing (lowest WSR) silicon Mie resonator array based on angular reflectance spectroscopy, period = 450 nm, diameter = 250, height = 95 nm.

The performance of the Mie resonator compared to the moth-eye sample is even more impressive when the full angular characteristics are considered, with the moth-eye sample giving a WSR 10% compared to the 6.5% of the best Mie resonator. The $\theta$-$\omega$ measurement data from both types of subwavelength antireflective structure is displayed in Figure 7. The samples show contrasting behaviour, with the low reflectance region of the Mie resonator sample occurring in the angular range 20-40° and at short wavelengths whilst that of the moth-eye sample occurs at normal incidence. These characteristics are not presently fully understood but confirm fundamentally different AR mechanisms and behaviour for the two types of structure.

**Figure 7.** (a) Angular reflectance spectra (average of s and p incident polarisations) for (a) best performing (lowest WSR) silicon Mie resonator sample (shown in ) and (b) silicon moth-eye sample shown in Figure 4b.
Conclusion

Antireflective Mie resonator arrays have been fabricated on silicon substrates and their AR performance has been analysed and compared to that of a silicon moth-eye array. The results demonstrate that Mie resonators can confer very effective AR to a silicon surface, outperforming a good silicon moth-eye structure, especially when the angular and spectral changes in incident sunlight over a day are taken into account. Furthermore, the performance of the Mie resonators is shown to be highly dependent on the dimensions and spacing of the constituent pillars, features that once tuned for optimal performance for given conditions can be readily produced using nanoimprint lithography. Conversely, the performance of a moth-eye structure is mostly dependent on the exact shape of the tapered pillar, making excellent silicon moth-eyes requires not only complex differential etching techniques and excellent reproducibility, but also increases the surface area of the silicon significantly more than the Mie resonators. Finally, whereas the moth-eye mechanism causes very little light scattering and therefore confers no light-trapping effect, Mie resonators provide effective scattering and therefore light-trapping mechanisms. We can conclude that Mie resonators are a more promising AR scheme for photovoltaics than the moth-eye array, however neither scheme looks likely to replace conventional inverted pyramids until significant performance and cost benefit can be demonstrated.

References


3.3.3.8 Measurement and Simulation of the Scattering from Textured TCOs for Light Trapping in Thin Film Photovoltaics

Research Team
Darren M. Bagnall
David N. R. Payne
Michael Pollard and

Summary
Thin film solar cell technologies typically have the advantage of being lightweight and low cost. However, the thin absorber layer can result in a lack of absorption, leading to the requirement for light trapping. Textured front TCO contacts are often used for this purpose. The scattering effects of textured TCOs have traditionally been optimized empirically with results matched to analytical models. However, the analytical modelling approach provides limited, approximate information and is restricted to particular types of surface texture. We have improved upon this by using numerical FDTD simulation techniques based on imported surface topography information obtained by AFM. This approach has the advantage that arbitrary geometries can be accurately modelled and the resulting optical near field data can be projected to the far-field to determine detailed scattering information. Whilst some groups have numerically modelled textured TCOs as periodic structures, we demonstrate that the periodic approach is only sufficient to obtain near field intensity characteristics and the alternative approach of simulating large surface areas with perfectly matched layer boundaries gives superior agreement for far-field characteristics. Simulated results have been compared to traditional optical measurements as well as novel measurements of wavelength and angular resolved scattering (WARS). This provides strong verification of the modelling technique, validating further investigation through simulation. The effect of geometrically scaling simulated TCO topography has therefore been investigated with increases in the TCO aspect ratio shown to give the best results.

1. Introduction
Thin photovoltaic devices have many advantages but they also have the significant drawback that thinner layers naturally lead to reduced optical absorption. As light is incident on the surface of a solar cell, some of the light is reflected and some is transmitted into the device. With bulk solar cell devices the majority of light that makes it through the front interface of the cell is absorbed in the relatively thick semiconductor layer. For thin film solar cells however, the absorber layers may be so thin that much of the light is transmitted through the semiconductor. The use of a back-reflector ensures that much of the light will make a second pass through the absorber, therefore increasing the chance of absorption, however, a portion of this light may once again transmit through the absorber and escape from the front surface of the cell. This can lead to lower current characteristics and as a result, lower overall cell efficiency. The obvious solution to this problem is to increase the thickness of the absorber layer of the solar cell, but doing this decreases carrier collection and increases the time and costs required to fabricate a device. Solar cells therefore ideally need to be geometrically thin to enable the extraction of carriers and to reduce costs and material waste but optically thick in order to absorb as much light as possible. A popular solution to this problem, particularly in the case of thin film silicon solar cells is to texture the interfaces within the device structure, usually achieved by depositing device layers onto a textured TCO superstrate. The textured interfaces lead to scattering and thus increase the path length of light within the device structure (see Figure 1).
Figure 1: Illustration of light trapping via texturing for an a-Si solar cell.

Textured TCOs are a well established light-trapping technique, particularly in the area of thin film silicon solar cells. However, TCO optimization has largely been empirically carried out a better approach is needed if an ideal match between TCO texture and the subsequent semiconductor absorber is to be achieved. Texture optimization will vary for different device types and determining the ideal texture can be inefficient and costly if carried out experimentally. In the past, analytical models based on scalar scattering theory first developed by Davies in 1954 have been relied upon to help understand and optimize random surface texturing for light trapping [1]. These approaches use the statistically calculated root-mean-square roughness of the texture to predict the total amount of diffuse reflectance or transmittance. Scalar scattering theory and similar approaches are capable of predicting these characteristics reasonable well but they often require additional fitting parameters and are only valid for certain types of surface topographies, for example, those with a Gaussian height distribution, although more recent developments to the theory have attempted to remove this limitation [2,3]. An alternative and potentially superior approach is to use numerical simulation such as finite element method (FEM) and finite difference time domain (FDTD) techniques. In particular, FDTD techniques allow for broadband simulation results in a single run and can be used to model arbitrary structures such as textured TCO surface profiles determined using atomic force microscopy (AFM). For these techniques to be relied upon they must be accurately validated using experimental measurement results. Several groups have shown good agreement between FDTD simulation and measurement of textured TCOs, in particular Bittkau et al have shown correlation between FDTD simulations and near-field scanning optical microscopy (SNOM) measurements [4] and Lacombe et al have used FDTD to achieve reasonable agreement with a textured TCOs total reflectance and transmittance [5]. However, for the investigation of light trapping, information on the scattering of light is key. Therefore, the total simulated haze should also be shown to match experiment and ideally the agreement for the wavelength and angular distribution of scattered light should be determined. Such extensive validation has not previously been carried out, in part because of the significant computational power required for large area simulations and partly due to the complexities of accurately measuring the wavelength and angular distribution of scattered light. In this paper, data gathered from FDTD simulations is directly compared to total transmittance, haze and complete WARS measurement data. This comprehensive model validation demonstrates the potential of the FDTD technique and allows for reliable further investigation of textured TCO scatter through simulation alone.

2. TCO Characterization & FDTD Input Parameters

Optical Constants

Film thickness and wavelength dependent refractive index properties were determined using variable angle spectroscopic ellipsometry (VASE). The specific ellipsometer used was a J.A. Woollam M2000-DI. In order to acquire meaningful refractive index and thickness values, measured ellipsometry data must be correctly fitted to an oscillator model. This is particularly challenging for semi-transparent, semi-absorbing films such as TCOs and the difficulty of model fitting is further exasperated by the surface roughness of the samples. Due to these complexities, the refractive index obtained through ellipsometry in this case should only be used as an approximate indicator and not an accurate, absolute value. The ellipsometry results showed all investigated samples to have similar refractive
index values with a level of variation similar to the expected ellipsometry error. It was therefore decided that that a constant, wavelength independent refractive index would be used for the simulation of each of the TCO samples. The value chosen for the constant was the average of the measured values for all samples. The use of a single, constant refractive index for all TCO simulations has the significant advantage of eliminating effects from refractive index differences in the simulation results, allowing for a more accurate study of the independent effects of surface topography.

**Surface Topography**
The surface topography of each of the textured TCO samples was determined using atomic force microscopy (AFM). Specifically, a Veeco Caliber AFM tool was used in tapping mode with high aspect ratio probes. The use of high aspect ratio probes was found to be essential as comparisons with SEM images showed that standard probes introduced an artificial rounding of surface features for TCOs with sharp peaks and deep valleys.

**Optical Characterization**
Conventional optical characteristics such as specular and diffuse transmittance and reflectance were determined for each of the investigated samples using integrating sphere based measurements. The exact arrangement used for this work consisted of an RTC-060-SF sphere used with a Fianium SC450-2 broadband super-continuum laser and a TE cooled B&W Tek spectrometer, allowing accurate measurement of wavelengths between 460 nm and 900 nm to a spectral resolution of around 1 nm. The Fianium laser provides a spot size of around 1.5 mm diameter with excellent collimation, eliminating the need for lenses within the experiment. For this setup, measurements of diffuse light account for light scattered to angles greater than 5 degrees. All measurements were carried out in ‘double beam mode’ in order to increase accuracy. Measurements were carried out in air, with the light first incident on the glass side of the sample. To gain further information on the exact angles and wavelengths of scattered light, novel wavelength and angle resolved scattering (WARS) measurements were carried out in transmittance for all TCO samples. These measurements were carried out on custom built goniometer system, shown in Figure 2. This measurement essentially maintains the sample at normal incidence to an incoming white light laser beam whilst sweeping a detector from 90 to 0 degrees, taking full spectral measurements in 1 degree intervals, further details can be found here [6]. Samples were orientated such that light was first incident on the glass substrate. The samples were positioned with the textured TCO/Air interface in the central axis of rotation of the system.

![Figure 2: CAD drawing of the custom built WARS measurement system.](image)

**3. FDTD Modelling Approach**
Finite difference time domain (FDTD) simulations were carried out for each of the samples investigated using Lumerical’s FDTD software. When simulating a non-periodic, non-symmetrical structure, a trade-off must be made between the simulated area and available computer resources.
Simulating a larger area will provide a more accurate representation of the sample but can take significantly longer to compute or may not be possible to compute with available resources. To determine the best area size, several simulations were carried out on different area sizes of the same TCO sample. A size of 20 μm x 20 μm was found to give a good balance between result accuracy and an acceptable computation time. All simulations were therefore based on a lateral area of 20 μm x 20 μm. In each case, the structure simulated consisted of a semi-infinite glass layer with a textured TCO layer on top. The TCOs were defined as having a constant, wavelength independent refractive index of 2.1. The refractive index of glass was defined using the default materials database properties built into the FDTD software. The surface texture of each TCO was imported directly from the topography information gathered using the AFM technique. With regards to simulation boundary conditions and illumination sources, there are two alternative simulation approaches that could provide accurate results. Both of these methods were investigated within this work in order to determine which is preferable for this specific case. The first approach uses a plane wave source with periodic boundaries in the X and Y directions. This approach assumes that the TCO structure is periodic, but if a large enough area is simulated then diffraction effects can be minimized and should become negligible. This approach has the advantage that plane waves and periodic boundaries are typically less computationally expensive to simulate than alternative options. However, one important issue that should be noted is that if the randomly rough surface is modelled as being periodic, then there may be large discontinuities in the surface texture at the boundaries as illustrated in Figure 3.

![Figure 3: Illustration of possible discontinuities at periodic boundaries.](image)

To avoid any spurious results developing from these discontinuities, they were removed by using a custom algorithm to smooth out the edges of the topographical data. Another significant issue with this simulation approach is that the far-field projections calculated from the monitor data may not be accurate as the projection methods used in the software are not strictly intended for periodic simulations. The second simulation approach is to illuminate the sample with a Gaussian beam source and set absorbing PML boundaries in every direction. This approach eliminates the problems of discontinuities at the boundaries and should also provide a more meaningful far-field projection. However, having PML boundaries in the X and Y directions means that some of the scattered light will be absorbed at these boundaries and therefore not detected by the monitor. The use of a Gaussian beam also introduces unwanted angles in the incident light. This effect can be reduced by using a wider beam with lower divergence but this requires increasing the overall simulation area and therefore the time and computer resources required. Both of the simulation approaches were thoroughly tested. In each case a frequency-domain field and power (FDFP) monitor was set above the textured TCO layer to collect the transmitted optical data and the source was set to originate in the semi-infinite glass layer of the sample, as illustrated in Figure 4.
The reason for the source location is due to the use of a semi-infinite glass layer which is required to reduce simulation size and runtime. For the experimental measurements the illumination source originates outside of the glass. The extra reflection at the air/glass interface is therefore not simulated and has to be accounted for mathematically post simulation. Transmission data was determined using FDTD’s monitor transmission function and the scattering of light was determined by projecting the monitor data into the far-field using Fourier transform based methods available through the software’s custom scripting language. Example results for each method are shown in Figure 5. The results that both methods simulated the total transmittance well, the second method provided the best overall match with experimental measurements. Particularly for the long wavelength scatter where the periodic approach seems to significantly overestimate the intensity of scattered light. Results for other surface topologies showed similar differences; the second method was therefore selected to be used for all subsequent TCO simulations within this work.

Textured TCOs can be fabricated with a huge range of surface roughness characteristics. For this study, a selection of three different TCO samples were investigated in order to cover a representative range of the types of roughness applicable for thin film solar cell devices. The sample set consists of the commercial textured TCO Asahi Type-U, an experimental fluorine doped tin oxide (FTO) fabricated at the university of Salford [7] and an experimental aluminium doped zinc oxide (AZO) supplied by EPV Solar [8]. The surface topography of each of these samples is shown in the AFM plots of Figure 6. Asahi Type-U was found to have an RMS roughness of 29, whilst the experimental FTO and AZO films have an RMS roughness of 44 nm and 92 nm respectively.
The optical measurement results for the total, specular and diffuse transmittance of each of the TCO samples are shown in Figure 7 with the simulated results shown on the same plot for comparison. The results show a reasonable agreement between measurement and simulation of the total transmittance and crucially also show good agreement for diffuse transmittance characteristics, indicating that the simulations are accurately modelling the scattering effects of the TCO topography.
To further validate the simulated far-field results, comparisons to full WARS measurements were also made. In each case the simulations showed the correct trends with clear similarities in the angular distribution and wavelength dependence measured and simulated scattering. However, the simulated results also showed some diffractive characteristics due to the finite and relatively small simulation area. An example result comparison for the experimental FTO film is shown in Figure 8.

When considering that a constant, wavelength independent refractive index has been used for each sample and that only a small representative area has been simulated, the agreement achieved between simulation and measurement is quite remarkable. This indicates strong validation of the FDTD simulation technique and in particular, the setup approach used within this work.

6. Extending the Simulations

With the simulation approach validated it is possible to extend the investigation through simulation alone. In this case, the effects of geometrically scaling the TCO topography have been investigated. The experimental FTO film topography was selected as an example case as the results for this sample showed the best agreement between measurement and simulation. The measured topography of the FTO film was scaled by a factor of 2, 3 and 4 in two different ways and then re-simulated. In one case the scaling was applied in the X, Y and Z directions and in the other case scaling was only applied in the Z direction, thus increasing the aspect ratio of features. The simulated results for the total transmittance and diffuse transmittance are shown for both scaling approaches in Figures 9 and 10 respectively.
The simulation results show that whilst both scaling approaches lead to a dramatic increase in scattering, the full scaling approach also leads to significant reductions in total transmittance, in some cases to less than 50%. In contrast, increased scaling of just the aspect ratio of features leads to only small decreases on total transmittance and provides substantial scattering enhancement.

7. Conclusions

The validity of the FDTD simulation technique has been confirmed for both the near-field and far-field optical regimes. However, it has been demonstrated that accurate results require care to be taken with regards to simulation source and boundary setup, with absorbing boundaries shown to give the best far-field results. Validation of the simulation technique has allowed for systematic investigation of surface texture characteristics, in this case showing the beneficial scattering effect of increasing the height of surface features without increasing lateral dimensions. However, although high aspect ratio features provide the best scattering, it is widely known that in reality such features could lead to fabrication issues such as cracks when depositing subsequent device layers. Nevertheless, the ability to accurately and systematically investigate scattering properties in ways that are extremely difficult or impossible to perform experimentally have been shown, demonstrating the potential of FDTD simulations for the efficient optimization of light trapping for solar cell devices.

Acknowledgements

Experimental FTO sample provided by H. Yates of the University of Salford and experimental AZO sample provided by A. Delahoy (formerly of EPV Solar). WARS goniometer measurement system developed with assistance from M. Charlton (University of Southampton).
References


3.4 Second Generation: Silicon, Organic and other “Earth Abundant” Thin Films

3.4.1 Silicon Thin Films

University Staff:
Dr Sergey Varlamov (group leader)
Prof. Martin Green

Research Fellows:
Dr Jing Rao
Dr Jialiang Huang
Dr Anthony Teal
Dr Jonathon Dore

Technical Staff:
Dr Patrick Campbell
Mark Griffin
Kazuo Omaki

Postgraduate Research Students:
Kyungsun Kim (Masters)
Chaowei Xue (PhD)
Miga Jung (PhD)
Jonathon Dore (PhD)
Mohd Zamir Pakhuruuddin (PhD)

3.4.1.1 Summary
The silicon thin-film group conducts research on polycrystalline silicon thin-film solar cells on glass. The major focus in 2014 was on a highly promising new technology of diode laser processed liquid phase crystallised silicon films and solar cells funded by the ARENA project 2A014A. Excellent progress and outstanding results were achieved. The laser process parameters were optimised, their effects on the poly-Si film and cell properties were thoroughly studied; new cell fabrication processes were developed; enhanced light-trapping was introduced. The record cell voltages up to 585 mV and the efficiencies up to 11.7%, above the current world record of 10.4%, were demonstrated. Possible approaches to increasing the cell efficiencies above 12% were identified.

3.4.1.2 Introduction
Polycrystalline silicon (poly-Si) on glass is a promising PV material alternative to c-Si wafers which can allow fabrication of solar cells with the performance matching standard Si-wafer cells at a potentially lower cost. However, this potential has not yet been realised. Commercial solid-phase crystallised (SPC) poly-Si on glass solar cells peaked at 10.4% record efficiency [3.4.1.1] (~8% in manufacturing) and were not able to compete with other PV technologies. The poor electronic quality kept the SPC cell efficiency low while a long manufacturing process kept the cost high [3.4.1.2-3]. More recently, a much better electronic quality poly-Si on glass thin films and solar cells were fabricated by liquid-phase crystallisation using either e-beam [3.4.1.4-5] or line focused CW diode laser for melting silicon [3.4.1.6-9]. The liquid-phase crystallised silicon on glass (LPCSG) cell Voc quickly broke above the 500 mV range typical for SPC cells, and, very recently, above 650 mV [3.4.1.10]. The LPCSG cell stable efficiency has reached 11.8% and quickly rising [3.4.1.11].
3.4.1.3 LPCSG solar cell structure and fabrication sequence

A schematic representation of a LPCSG thin film solar cell is shown in Figure 3.4.1.1 and Figure 3.4.1.2 describes the cell fabrication sequence.

![Figure 3.4.1.1: Structure of a LPCSG solar cell (superstrate configuration)](image)

![Figure 3.4.1.2: Process sequence of LPCSG solar cells at UNSW](image)

The superstrate used for the cells is planar 3.3 mm thick borosilicate glass (Schott Borofloat33). After thorough cleaning, the glass is coated with an intermediate dielectric buffer layer made of SiOx, SiCx, SiNx or their combination. Either RF magnetron sputtering or PECVD can be used for dielectric deposition. The buffer layer can be intentionally in-situ doped with boron or undoped. PECVD buffers require annealing at about 600°C to remove residual gasses (hydrogen, nitrogen, water, etc.) which otherwise interfere with the crystallisation process. An about 10 μm thick silicon absorber is then deposited by high rate e-beam evaporation at 600°C nominal substrate temperature and ~500 nm/min. When the buffer layer is B-doped, the Si film is undoped, while for undoped buffers the Si films are doped with B to 1-3E16 cm⁻³. The Si films are crystallised by scanning a line-focus diode laser beam (808 nm, LIM O450-L 12x0.3, 12x0.17 mm² FWHM, Fig 3.4.1.3).
On B-doped buffer layers, during laser melting B diffuses into the Si film to result in the sheet resistance of about 2000 Ohm/sq (B~2E16 cm⁻³ by SIMS). After crystallisation, the exposed Si surface is etched-back to create a light-trapping texture. Next, the cell P-doped emitter (sheet resistance of 200-400 Ohm/sq) is diffused from a spin-on-dopant (SOD) source by either thermal or diode laser annealing. The formed cell structure is finally passivated in a remote hydrogen plasma. Cell metallisation is similar to the one used for CSG SPC cells [3.4.1.1] and relies on forming point contacts on the device rear side by inkjet printing holes in a resin layer and then etching down to the emitter and absorber layers in sequence. Sputtered Al is then used to form contacts to the n- and p-type openings. The insulating resin is impregnated with TiO₂ particles to also serve as a diffuse back reflector.

3.4.1.4 Effects of laser process parameters

The range of laser parameters that allows a successful crystallisation process is limited by the resulting Si crystal structure at the lower energy-dose end, which has to avoid amorphous and/or microcrystalline material, and by dewetting of a Si film from the substrate at the high dose end. Without any intermediate wetting layer, and without substrate heating dewetting and/or delamination occurs at energy doses comparable with the crystallisation limit and no process is feasible. With the intermediate buffer layer, a large-grained crystalline silicon material without dewetting or delamination is obtained at substrate temperatures exceeding the glass softening point of about 550°C and the minimum laser energy dose of about 160 J/cm², which is about the same for different buffers. Fig. 3.4.1.4 shows a process window, laser power versus exposure, in which linear crystal growth is possible on SiOₓ-coated glass [3.4.1.12]. At doses below the liquid-phase crystallisation threshold (black line) the material either stays amorphous or is made up of SPC-like small and defective grains (Fig. 3.4.1.5a), while at doses above the adhesion threshold (red line) dewetting and balling up of the silicon occurs (Fig. 3.4.1.5b). Only at doses between black and red lines large high crystal quality grains are grown (Fig. 3.4.1.5c,d).
3.4.1.5 Effects of intermediate buffer layer

The dielectric buffer layer between the glass and a Si film is of critical importance to the crystallisation process and the cell performance [3.4.1.6-9]. For the superstrate LPCSG cells, this buffer layer should satisfy the following requirements: remain stable at temperatures above the Si melting point of 1414°C; provide good wetting and adhesion of molten Si; have low absorption and high antireflection (AR); prevent impurity diffusion from glass; serve as a dopant source for a Si absorber; ensure low recombination at the Si-glass interface. In practice, a choice is limited to high melting point dielectrics: SiOx, SiCx, SiNx and their combinations.

Laser energy dose window and Si film adhesion

The low dose limit, below which the linear grains are not formed (Fig. 3.4.1.5a), is found to be about 160 J/cm², similar for all dielectrics and bare glass. The high dose limit, above which Si adhesion failure occurs, is mostly determined by the nature of the buffer layer. Three major types of Si adhesion failure were identified, as shown in Fig. 3.4.1.6: diagonal peeling, agglomeration into lines and pinholing.

Table 3.4.1.1 summaries dielectric effects on the failure type and the high dose limit. The process on bare glass has a very small dose window and diagonal peeling starts to occur as soon as linear grains are formed. SiOx increases the high dose limit to about 200 J/cm² after which diagonal peeling starts. SiCx allows the largest process window, up to 250 J/cm² and above this dose the adhesion fails by agglomeration into parallel lines. SiNx leads to pinholing at doses above about 190 J/cm². For composite buffer layers, the adhesion failure type is mostly determined by the dielectric directly next to the glass while the high dose limit can be affected by the nature of intermediate, buried layer, shifting it slightly up or down in direction of the effect of the respective dielectric on its own.
Table 3.4.1.1: Laser crystallisation high energy dose limits and failure types (low dose limit ~160 J/cm²)

<table>
<thead>
<tr>
<th>Buffer</th>
<th>Dose, J/cm²</th>
<th>Failure type</th>
<th>Thickness, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>None (BSG)</td>
<td>163-168</td>
<td>Diag. peeling</td>
<td>-</td>
</tr>
<tr>
<td>SiOₓ sput/pecvd</td>
<td>190-200</td>
<td>Diag. peeling</td>
<td>&gt;30</td>
</tr>
<tr>
<td>SiCₓ sput/pecvd</td>
<td>230-250</td>
<td>Parall. Lines</td>
<td>&gt;15</td>
</tr>
<tr>
<td>SiNₓ sput</td>
<td>190-205</td>
<td>Pinholing</td>
<td>&gt;50</td>
</tr>
<tr>
<td>SiNₓ pecvd</td>
<td>185-195</td>
<td>Pinholing</td>
<td>&gt;50</td>
</tr>
<tr>
<td>SiNₓ R-sput</td>
<td>160-170</td>
<td>Pinholing</td>
<td>&gt;50</td>
</tr>
<tr>
<td>SiOₓ/SiCₓ/SiOₓ sput</td>
<td>207-213</td>
<td>Paral. lines</td>
<td>100/17/22</td>
</tr>
<tr>
<td>SiOₓ/SiCₓ/SiOₓ pecvd</td>
<td>245-255</td>
<td>Diag. peeling</td>
<td>100/20/30</td>
</tr>
<tr>
<td>SiOₓ/SiNₓ/SiOₓ sput</td>
<td>195-200</td>
<td>Diag. peeling</td>
<td>90/45/15</td>
</tr>
<tr>
<td>SiOₓ/R-SiNₓ/SiOₓ sput</td>
<td>175-180</td>
<td>Diag. peeling</td>
<td>90/50/15</td>
</tr>
<tr>
<td>SiOₓ/SiNₓ/SiOₓ pecvd</td>
<td>190-195</td>
<td>Diag. peeling</td>
<td>100/55/20</td>
</tr>
</tbody>
</table>

Buffer layer optics: Absorption and Reflection

Ideally, for the best optical cell properties, the buffer layer should have RI of 2.4 and zero extinction coefficient. As it is shown in Table 3.4.1.2 and Fig. 3.4.1.7, SiOₓ has the lowest absorption but with RI of about 1.5 it offers no AR effect. SiCₓ and sputtered SiNₓ can provide the AR effect but their absorption is too high. PECVD and reactively sputtered nitrides are found to be good low absorption AR candidates but used alone they do not satisfy other BL criteria. An optically optimised stacks of SiOₓ/SiCₓ/SiOₓ (100 nm/20 nm/15 nm) and SiOₓ/SiNₓ/SiOₓ (100 nm/50 nm/15 nm) are developed as acceptable compromise.

Table 3.4.1.2: Measured optical constants of buffer layers at 543 nm

<table>
<thead>
<tr>
<th>Buffer</th>
<th>n</th>
<th>k</th>
<th>Thick., nm</th>
<th>WAA</th>
<th>WAR</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiOₓ sput/pecvd</td>
<td>~1.5</td>
<td>0.000</td>
<td>100</td>
<td>0.00</td>
<td>0.268</td>
</tr>
<tr>
<td>SiCₓ sput</td>
<td>2.96</td>
<td>0.077</td>
<td>19</td>
<td>0.07</td>
<td>0.210</td>
</tr>
<tr>
<td>SiCₓ pecvd</td>
<td>2.73</td>
<td>0.035</td>
<td>20</td>
<td>0.05</td>
<td>0.235</td>
</tr>
<tr>
<td>OCO</td>
<td></td>
<td></td>
<td>100/19/22</td>
<td>0.05</td>
<td>0.128</td>
</tr>
<tr>
<td>SiNₓ sput</td>
<td>2.11</td>
<td>0.007</td>
<td>75</td>
<td>0.02</td>
<td>0.107</td>
</tr>
<tr>
<td>R/pecvd-SiNₓ</td>
<td>1.99</td>
<td>0.001</td>
<td>80</td>
<td>0.00</td>
<td>0.124</td>
</tr>
<tr>
<td>ONO</td>
<td></td>
<td></td>
<td>100/43/16</td>
<td>0.00</td>
<td>0.147</td>
</tr>
</tbody>
</table>

Figure 3.4.1.7: Absorption (left) and reflection (right) of different buffer layers

Impurity diffusion

Borosilicate glass used as a LPCSG cell superstrate has high contents of B, Fe and Al. Metals, Fe in particular, are very harmful for the cell performance and their diffusion into Si during melting has to be avoided. The dielectrics were tested for metal diffusion into Si using SIMS for metal detection. SiOₓ of more than 80 nm thickness prevents excessive Fe and Al diffusion while SiNₓ of the thickness required for AR allows very high concentrations of the metals in the Si films at the depth of
2-4 μm. Besides, a high concentration of N is also detected at the same depth. TEM images (Fig. 3.4.1.8) reveal presence of precipitate-like defects at the same depth. The exact mechanism for metals, nitrogen and related defects concentrating at this depth in the LPCSG film is not established; although a plausible cause could be that it is where two solidification fronts, one advancing from the glass side and another from the air side meet.

![Figure 3.4.1.8: TEM image of LPCSG film with defects at 2-4 μm depth.](Image)

Although B concentration in the Si absorber can be alternatively controlled by in-situ B doping during Si film deposition, in this particular research work more consistent results were obtained by doping Si via B diffusion from the buffer layer during melting. An assessment of B distribution is made by measuring a diffusion ratio of total B present in poly-Si film after crystallisation to total B in the buffer layer before crystallisation (Table 3.4.1.3). While the diffusion ratio for LPCSG films on SiOx are very small, <10%, B is evenly distributed between Si and the SiCx buffer, ~100%. This is consistent with rate limited diffusion from SiOx and dose limited diffusion from SiCx. Consequently, it should be possible to control B diffusion from SiOx by varying laser process condition (temperature and melt duration) while B diffusion from SiCx is expected to be independent from the crystallisation conditions. SiNx has not been tested for B diffusion as the crystallisation process on this buffer layer is not feasible for other reasons.

<table>
<thead>
<tr>
<th>Buffer</th>
<th>Thick., nm</th>
<th>B in buffer, at/cm²</th>
<th>B in Si, at/cm²</th>
<th>Diff. ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiOx:B</td>
<td>80</td>
<td>4.5E20</td>
<td>1.4E16</td>
<td>0.04</td>
</tr>
<tr>
<td>SiOx/SiCx:B</td>
<td>80/20</td>
<td>1.319</td>
<td>2.8E16</td>
<td>1.17</td>
</tr>
</tbody>
</table>

**Table 3.4.1.3: B diffusion ratio for LPCSG films doped from SiOx and SiCx buffers**

**Structural quality**

Most common defects in LPCSG films are twin boundaries and dislocations and both can lead to increased carrier recombination hence poorer cell performance. The fractional content of the defects in the LPCSG films was estimated by measuring an etched fraction. The defects were first revealed by etching the films in a HF:HNO₃ mixture and optical images of the etched surfaces were taken. Then the grey scale images are converted into black and white and a ratio of black to white pixels is calculated. The defect etch fraction of about 0.2 is the smallest for LPCSG films on SiOx-based buffers; the largest of about ~0.4 for SiNx-based buffers; and ~0.3 for the SiCx-based buffers (Fig. 3.4.1.9).

![Figure 3.4.1.9: Mean etched fraction and 95% confidence intervals for samples with different classes of BL. Between seven and nine samples included in each class.](Image)

**Interface passivation and cell performance**

From the aforementioned results it can be concluded that LPCSG cells should have SiOx of about 100 nm thick next to the glass to limit diffusion of impurities. A SiCx or SiNx layer then should be added for antireflection but such that to avoid excessive absorption. I-V curves of the cells on double
SiOx/SiNx (100 nm/70 nm) or SiOx/SiCx (100 nm/20 nm) buffers as well as on SiOx alone as a reference are shown in Fig. 3.4.1.10 and the cell performance are listed in Table 3.4.1.4.

![Figure 3.4.1.10: I-V (a) and IQE (b) curves of LPCSG cells on double layer buffers](image)

**Table 3.4.1.4: Performance parameters of LPCSG cells on different buffers**

<table>
<thead>
<tr>
<th>Buffer</th>
<th>$V_{oc}$, mV</th>
<th>$J_{sc}$, mA/cm²</th>
<th>FF, %</th>
<th>Eff., %</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiOx</td>
<td>525</td>
<td>23.6</td>
<td>62.3</td>
<td>7.72</td>
</tr>
<tr>
<td>“OC”</td>
<td>436</td>
<td>15.3</td>
<td>49.5</td>
<td>3.30</td>
</tr>
<tr>
<td>“ON”</td>
<td>428</td>
<td>13.9</td>
<td>53.4</td>
<td>3.17</td>
</tr>
<tr>
<td>“OCO”</td>
<td>502</td>
<td>25.5</td>
<td>56</td>
<td>7.16</td>
</tr>
<tr>
<td>“ONO”</td>
<td>557</td>
<td>24.2</td>
<td>62.3</td>
<td>8.40</td>
</tr>
<tr>
<td>“R-ONO”</td>
<td>585</td>
<td>28.0</td>
<td>72.4</td>
<td>11.7</td>
</tr>
</tbody>
</table>

The cells with SiNx and SiCx next to Si perform much poorer compared to the cells with SiOx only. In addition to higher defect density for SiNx and SiCx buffers discussed above, the IQE of the cells on SiCx (Fig. 3.4.1.10b) is sloping down at shorter wavelengths indicating a high recombination rate near the Si-glass interface and/or the minority carrier diffusion length less than the cell thickness. In contrast, IQE of the cells on SiOx, with a plateau in the 450-700 nm range is consistent with a low recombination interface and the diffusion length exceeding the cell thickness. From these results, a necessity of having SiOx next to Si can be derived, so further study is conducted with triple layer stacks where an AR SiNx or SiCx layer is sandwiched between two SiOx layers.

The performance of the cell on triple-layer buffers, “OCO” and “ONO”, improves a lot as compared to the cells without thin SiOx next to Si (Fig. 3.4.1.11a vs Fig. 3.4.1.10a, Table 3.4.1.4) proving SiOx ability to reduce recombination near the Si-glass interface. However, despite reasonably high IQE peaks the cells still suffer for poor blue response. PC1D simulations point at parasitic absorption in the buffer as the most likely reason. Although it is not possible to reduce absorption in “OCO” buffers without scarifying AR properties, for “ONO” buffers the absorption can be minimised by replacing directly sputtered, Si-rich SiNx, with reactively sputtered, near stoichiometric SiNx (“R-ONO” buffer). This change allowed further performance gain and led to the best cell efficiency of 11.7% (Fig. 3.4.1.11, Table 3.4.1.4).

![Figure 3.4.1.11: I-V (a) and IQE (b) curves of LPCSG cells on triple layer buffers.](image)
3.4.1.6 LPCSG grain structure and quality.

To obtain LPCSG films, a line-focused diode laser beam is scanned across the surface of the silicon, causing it to melt. Upon directional re-solidification, continuous lateral growth can be achieved, in which the crystal growth front is seeded by the preceding crystallised region, forming parallel grains several mm long and up to a mm wide in the direction of scanning (Figure 3.4.1.5c).

During silicon solidification, cracks usually form through the silicon thickness parallel to the scan direction. An example is shown in Fig. 3.4.1.12. Such cracks may lead to mild short-circuit losses in metallised devices and higher crystal defect density in the region surrounding the crack. Optimisation of the laser process parameters has enabled a significant reduction in crack severity and ongoing work aims to eliminate the problem entirely.

The LPCSG linear grains have been found to be consistently of [101] orientation. The most common boundaries between grains are defect-free, electrically inactive $\Sigma 3$ twin-boundaries as shown in Figure 3.4.1.13.

The grains contain regions with varying defect density. Most laterally grown grains are nearly defect-free on the TEM scale which translates into the defect density of $1 \times 10^5 \text{ cm}^{-2}$ or lower, while the most defect-rich grains can contain dislocations with the density up to $1 \times 10^8 \text{ cm}^{-2}$ (Fig. 3.4.1.14). In particular, such a high defect density is always found near crack edges in the films and it decreases by about two orders of magnitude within 30-50 µm away from the cracks as it can be seen in Fig. 3.4.1.15.
Figure 3.4.1.14: Cross sectional TEM images of (a) a defect free region and (b) a defect rich region.

Figure 3.4.1.15: SEM image of the defective area near a crack in LPCSG film.

The Hall mobility varies between 300 and 470 cm²/V*s, for the carrier concentration of ~10E16 cm⁻³, and resistivity 1~3 Ω*cm. These values are similar to those measured for a reference c-Si wafer: 414 cm²/V*s, 1.6E16 cm⁻³, 0.94 Ω*cm respectively, indicating a high, Si-wafer-like electronic quality of the laser crystallised silicon film, which is far superior to the quality of a reference SPC Si film with the defect density of 1E10 cm² and a mobility of only 50-120 cm²/V*s at the similar boron concentration, Fig. 3.4.1.16, [3.4.1.3].

Figure 3.4.1.16: Hall mobilities in SPC and LPCSG films with a curve for c-Si.

3.4.1.7 Emitter diffusion

Liquid-phase laser crystallisation produces uniformly doped silicon films which need to be turned into solar cells by creating an emitter. It is done by thermally diffusing phosphorous into the rear surface of LPCSG films (after etch-back texturing) from a SOD source. Examples of phosphorous depth profiles in the emitter after diffusion at the peak temperature of 870°C and 900°C are shown in Fig. 3.4.1.17. Etching-back can be applied to the as-diffused emitter if necessary to adjust its sheet resistance to the targeted value of about 200 Ω/√. An alternative phosphorous diffusion process by
Laser annealing is under development using the same line-focus diode laser as for silicon crystallisation.

**Figure 3.4.1.17:** PCOR-SIMS phosphorous depth profiles in LPCSG cell emitter after thermal diffusion from SOD at 870°C (dashed line) and 900°C (solid line); sheet resistances are \(\sim 190 \, \Omega/\square\) and \(\sim 110 \, \Omega/\square\) respectively.

### 3.4.1.8 Hydrogenation effects

Unlike SPC poly-Si thin-film cells, the LPCSG cells do not require thermal defect annealing and dopant activation as the Si has already been exposed to temperatures of at 1414°C during melting. However, hydrogenation was still found to have a significant effect on the LPCSG cell performance. Specifically, for the cells on the triple-layer composite buffers, it was noticed that the hydrogenation effect depends on the nature of the intermediate AR layer in the stack (Fig. 3.4.1.18, Table 3.4.1.5, [3.4.1.8]). \(V_{oc}\) of the cells on SiO\(_x\) does not change after hydrogenation, \(V_{oc}\) of the cells on the “OCO” buffer show small improvement of 10-20 mV, while \(V_{oc}\) of the cells on the “ONO” buffers increases by up to \(\sim 70\) mV. This effect is in agreement with the etched fraction discussed earlier where LPCSG films on SiN\(_x\)-based buffers are found to be the most defective. Hydrogenation is known to effectively passivate extended defects like grain boundaries, so one can expect that a material with more grain boundaries, like LPCSG cells on SiN\(_x\)-based buffers, shows a larger \(V_{oc}\) improvement.

**Figure 3.4.1.18:** \(V_{oc}\) at 1-sun and at 0.1-sun intensity, including 95% confidence intervals for the means, for samples before and after passivation with various sputtered BLs.

Even a larger difference in passivation effects is observed for \(J_{sc}\) (Fig. 3.4.1.19). For the cells on SiO\(_x\)-only \(J_{sc}\) slightly increases from 20 to 22-23 mA/cm\(^2\) while \(J_{sc}\) about triples, from 8 to 25 mA/cm\(^2\) for the cells on the “OCO” buffer. Such large effects of passivation on \(V_{oc}\) and \(J_{sc}\) of the LPCSG cells on the triple-layer buffer can occur if the minority carrier diffusion length in unpassivated cells is significantly less than the cell thickness and it becomes at least comparable to the thickness after passivation.
Figure 3.4.1.19: J_{sc} for cells with and without passivation with various BLs.

Table 3.4.1.5: Effects of passivation on V_{oc} and J_{sc} of LPCSG cell with different buffers

<table>
<thead>
<tr>
<th>Buffer</th>
<th>V_{oc}, mV</th>
<th>J_{sc}, mA/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pre-H</td>
<td>post-H</td>
</tr>
<tr>
<td>SiOₓ</td>
<td>515</td>
<td>512</td>
</tr>
<tr>
<td>&quot;OCO&quot;</td>
<td>460</td>
<td>480</td>
</tr>
<tr>
<td>&quot;ONO&quot;</td>
<td>458</td>
<td>520</td>
</tr>
<tr>
<td>&quot;R-ONO&quot;</td>
<td>478</td>
<td>540</td>
</tr>
</tbody>
</table>

3.4.1.9 Light management in LPCSG solar cells

LPCSG films are currently produced on planar glass and they rely on the front AR layer in the dielectric buffer stack, “ONO” or “OCO”, and the textured rear silicon surface for light trapping. Two types of rear texturing by wet etching have been developed: one is by etching back 200-300 nm of as-crystallised films with HF:K MnO₄ through a porous mask made of a thin spin-on resist; another by etching back 1-3 µm using an alkaline solution (so-called "shallow texture"). The AFM texture profiles, feature angle distributions, and absorption enhancement in LPCSG cells with the rear textures are shown in Fig. 3.4.1.20. The angles are relatively larger for alkaline texturing resulting in higher near infrared light absorption in a LPCSG film.
Additionally, a front glass texture by mechanical glass abrasion followed by wet etching is being also developed, which offers an advantage of a broadband light-coupling effect. Under certain abrasion/etching condition the glass texture features are such that result in a continuous silicon film both after deposition and laser crystallisation (Fig. 3.4.1.21). Because such features are relatively smooth, their own light-trapping effect is less than for typical rough glass textures but with the addition of rear texturing, the combined absorption enhancement is the highest achieved for LPCSG type solar cells (Fig. 3.4.1.20e)

Figure 3.4.1.20: (a, b) AFM surface topography scan of etch-back textured LPCSG films: porous mask acid and alkaline (“shallow”) respectively; (c,d) texture feature angle distribution for (a,b) respectively; (e) absorption in LPCSG films with different textures

Figure 3.4.1.21: Top view SEM image of abraded/etched glass for LPCSG; (b) Cross section SEM of LPCSG Si film on textured glass as shown in (a)

Relative contributions of the AR layer and the rear texture into the cell current are shown in Fig. 3.4.1.22. The AR layer alone improves $J_{sc}$ by about 4 mA/cm$^2$ (~17.5%) due to better broadband
light-coupling. The rear texture alone improves $J_{SC}$ by only 1.3 mA/cm$^2$ (~5.7%) due to light-trapping of the long wavelength light only.

**Figure 3.4.1.22:** Relative contributions of the AR layer and the rear texture into LPCSG cell $J_{SC}$ (as extracted from cells' EQEs); “no LT” is for a cell without ARC and without rear texture.

### 3.4.1.10 Cell metallisation and performance

Standard metallisation of LPCSG cells is shown in Fig. 3.4.1.1. First, the 1 cm$^2$ cell area is defined by laser scribing. The silicon is then coated with a TiO$_2$ impregnated isolating resist. Holes are etched through the resist by inkjet and then through the silicon to expose the buried (absorber) layer. The resist is then exposed to solvent to cause it to reflow over the walls of the emitter, but leave the absorber still exposed. A second round of holes is then etched through the resist to expose the top (emitter) layer. The surface is coated with a thin layer of sputtered aluminium, which makes contact with both the absorber and emitter layers, before laser scribing separates the contacts, which are connected to tabs at either side of the cells. Finally, a 1-hour contact bake at about 150°C completes the process.

The high electronic quality of LPCSG films translates into high cell $V_{OC}$ as compared to SPC poly-Si cells. The $V_{OC}$ of 585 mV is achieved by the cell on the “ONO” triple buffer layer, with the thermally diffused emitter and the silicon etch-back texture [3.4.1.8]. This cell has also the best efficiency of 11.7% which exceeds the previous record results for poly-Si thin-film solar cells fabricated by any approach. The best cell’s I-V curve and the spectral response are shown in Fig. 3.4.1.23.

**Figure 3.4.1.23:** I-V curve (a) and EQI, IEI and R curves of the best 11.7% LPCSG cell.

The cell reflectance (blue) shows that the “ONO” intermediate layer structure is well-optimised for anti-reflection. The IQE is about 86% over the wavelength range of 400-750 nm. It is not as high as it can be for LPCSG cells. The IQE of 93% in the same wavelength range has been reported for a LPCSG cell on the SiO$_x$-only intermediate layer implying the minority carrier lifetime of at least 260 ns and the front surface recombination rate at most 1900 cm/s, which is consistent with efficiencies of over 13% in the optimised device [3.4.1.7].
The 11.7% efficient cell and the identically processed cells experience performance degradation over a few days after fabrication [3.4.1.8]. The cell $J_{SC}$ is unaffected but $V_{OC}$ and $FF$ decrease from 585 mV and 72.4% to about 570 mV and 66% respectively resulting in a lower efficiency of about 10%. $V_{OC}$, $FF$ and the efficiency fully recover, and even can improve, after rebaking the device at about 150°C. For the cells with a slightly higher absorber doping (1.6E16 cm$^{-3}$ vs. 8E15 cm$^{-3}$) repeated rebaking leads to the stable performance, with the highest currently achieved stable efficiency of 10.4%. The degradation is believed to be caused by poor p-type contacts between Al and the lightly doped poly-Si of the cell absorber (circled area S in Fig. 3.4.1.1). An elegant approach using laser firing has been demonstrated that improves the Al contacts to the absorber and stabilises the performance [3.4.1.13]. An improved metallisation is also being currently developed and implemented where the silicon under the absorber contacts is selectively doped with boron, which eliminates the degradation completely [3.4.1.8].

3.4.1.11 PL and EL Imaging of LPCSG films and cells

The improved material quality and thickness of the LPCSG films, allowed Photoluminescence (PL) Imaging to be used as a characterisation technique [3.4.1.14]. There are a number of complicating factors for PL Imaging on thin-film silicon on glass that are not observed in PL Imaging of wafers. A unique thin-film Si PL Imaging tool which allows overcoming those complications has been designed and built (Fig. 3.4.1.24).
Figure 3.4.1.25: (a) Microscope image of a fully-processed poly-Si film and its corresponding PL image. Green arrow: low intensity PL area corresponding to the outlined defective grain in the top image; yellow arrows: poorly crystallised, highly defective SPC-like poly-Si at the edges of the laser crystallised region, and the corresponding low PL intensity; (b) PL image of as crystallised LPCSG film (left) and after emitter diffusion (right) (note the intensity scales).

It has been shown that the PL intensity of samples after phosphorus emitter diffusion increases from as crystallised samples (Fig. 3.4.1.18b). Subsequent hydrogenation increases the uniformity of the material quality across the film, but reduces the average PL intensity over the sample area. It is also found that the PL intensity correlates with the Hall mobility independently measured on the respective sample locations (Fig. 3.4.1.19).

Figure 3.4.1.26: PL image of LPCSG film with measured Hall mobilities: point-1 412 cm²/V*s; point-2: 230 cm²/V*s.
Most recently, a system which can excite and measure the PL decay rate in c-Si with a low carrier lifetime, has been constructed at UNSW. This allowed creating the first implied carrier lifetime image of a thin film Si on glass sample (Fig. 3.4.1.27). The correlation of the PL signal with the measured lifetime points is good resulting in an uncertainty in the implied lifetime of only ±60 ns.

![Image](image1)

**Figure 3.4.1.26:** (a) The measured lifetime and the implied lifetime deduced from the PL image of LPCSG film at multiple points; (b) Implied lifetime image of LPCSG film: the lifetime bar is in nanoseconds

As well as characterising the material quality of the Si at various stages of production, the PL intensity has been shown to be dependent on the excitation wavelengths. The higher PL intensity for shorter WL excitation is consistent with a lower recombination velocity near the well-passivated air-side surface as compared to higher recombination at the Si-glass.

The EL Imaging setup, similar to the previously described PL Imaging system, has also been built. EL image of two different LPCSG cells are shown in Fig 3.4.1.27. The negative and positive contacts are made on the airside of the cells. Thus the luminescence must be measured through the glass substrate. This is similar to the PL imaging setup where the luminescence is also imaged through the glass. The top image (a) of one of the best, 10.5% cell shows that the contacting over the entire area is mostly uniform and optimal. An EL image of an inferior cell with multiple contacting issues is shown below in (b). The cell has a large shunt (top left), multiple poorly contacted fingers, and a crack in the Si film from the crystallisation process (top right).
PL/EL Imaging of c-Si solar cells is typically done with a Si Charged Coupled Device (CCD), which poorly absorbs luminescent light of around 1050 nm. This leads to “photon smearing” where a photon incident on one pixel may be absorbed in another thus reducing the resolution and contrast of image features. An existing method of recovering the original luminescence signal incident on CCD is to deconvolve a Point Spread Function (PSF) with the resultant image. The PSF also corrects quantitative errors present in the raw image. A novel method has been developed for determining the PSF from a measurement of the Edge Spread Function (ESF), which greatly increases the Signal-to-Noise ratio over methods where the PSF is measured directly.

Examples of PL and EL images corrected by deconvolution with PSF are shown in Fig. 3.4.1.28 and 29. The increased contrast in PL image (b) on the right, allows to see greater detail of the different grains compared to image (a) on the left. This gives a more accurate view of the significance of the recombination occurring at grain boundaries. A similar improvement in contrast can be seen in the EL image (b) on the bottom. The most obvious difference is that the haze in the raw data is removed. Also, the crack in the film, at the top right of the image is much clearer after PSF image processing.
PL and EL Imaging has become an important tool for improving Voc of LPCSG material and its ability to characterise the material quality at each step, without interrupting the usual cell fabrication procedure, will help developing a 12% compatible process.

REFERENCES


3.4.2 Organic Thin Films

University Staff:
A/Prof. Ashraf Uddin
Prof. Martin Green
Prof. Gavin Conibeer

Senior Research Fellow:
Dr Dirk König

Postdoctoral Fellow
Dr Shujuan Huang
Dr. Thilini Ishwara
Dr. Murad Tayebjee
Dr. Naveen Kumar Elumalai

Postgraduate Research Students
Matthew Wright
Pengfei Zhang
Rui Lin
Kah Howe Chan (Alex)
Md. Arafat Mahmud
Mushfika Baishakhi Upama
Dian Wang

Undergraduate Thesis Students
Yu Jiang
Wu Heng
Xueting Liang
Yihan Wang
Zhai Shan Ying
Adrian Pang
Shin Suk Ho
Yi Ming Lu
Dun Kang Liu

Taste of Research Students
Xiao Bo Xu

3.4.2.1 Introduction

An organic photovoltaic (OPV) research lab has been established at UNSW with world class research facilities to work on organic semiconductor materials and devices. Today this lab is equipped with facilities supported by an ARC discovery grant (DP10), a UNSW equipment grant, a grant from the Green Family, a Faculty grant and from the support of ARC Photovoltaic Centre of Excellence, UNSW. Currently, the research team consists of three academics, three research fellows, one research assistant, seven PhD, and 12 honours students.

Our research has produced meaningful data over the last four years. Seven journal papers and ten conference proceeding papers have already been published. Several other papers are underway to publish. Our research activities are mainly focusing on the following three areas:
(i) Morphology control of bulk heterojunction organic solar cells
(ii) Light trapping in organic solar cells
(iii) Organic/inorganic nanoparticles hybrid solar cells

We have already designed and developed a new inverted OPV device structure to overcome the challenges of low conversion efficiency and lifetime. We have already achieved 8% efficiency of OPV devices with longer lifetime without any encapsulation. For example: traditional bulk-heterojunction OPV device's lifetimes is around two/three days without any encapsulation whereas our new inverted OPV device lifetime are more than three month.

We are now working on fundamental issues of morphology optimization for organic films for OPV devices such as control of electronic structure at film interfaces, exciton dissociation and carrier transport for photovoltaic operation to achieve our goals. Ab-initio (density functional theory – DFT) methods are a valuable tool to obtain insight into the charge separation (exciton dissociation) and transport process as well as the photochemical stability of organic molecules - a major challenge for organic PV. This helps us to find robust and electronically suitable molecules which determine the morphology of OPV devices. The key issues of polymer design include engineering the bandgap and energy levels to achieve high $J_{SC}$ and $V_{OC}$, enhancing planarity to attain high carrier mobility, and materials process ability and stability. All of these issues are correlated with each other. In the ideal case, all factors should be optimised in a single polymer, but this remains a significant challenge. Furthermore, we have investigated the plasmonic enhancement of bulk heterojunction OPV cells with incorporated thin silver (Ag) nano-particle film. Such films consist of plasmon-active and size-variable Ag nanostructures. Incorporation of plasmon-active Ag nano-material is shown to enhance light absorbance in the photoactive layer. Consequently, enhancements of external quantum efficiency at red wavelengths are observed. This plasmonic enhancement needs to be optimised to further improve the photo conversion efficiency of OPV cells.

Hybrid solar cells are a mixer of nanocrystals (NCs) of both organic and inorganic materials. They combine the unique properties of inorganic semiconductor nanocrystals with properties of organic/polymeric materials. Inorganic NCs such as quantum dots, nano-tubes, etc. have also high absorption coefficients and particle size induced tunability of the optical band-gap. Band-gap tuning in inorganic nanocrystals with different sizes can be used for realization of device architectures, such as tandem solar cells in which the different bandgaps can be obtained by modifying only one chemical compound. A substantial interfacial area for charge separation is provided by nanocrystals, which has high surface area to volume ratios. Thus, the organic-inorganic NCs hybrid concept for PV cells is getting interesting and attractive in recent years.

We are also working on the polymer:metal-oxide solar cells. The aim of the work is to establish reproducible benchmark devices (bilayer and multilayer) against which future improvements can be evaluated. Test novel materials including polymers for improved photon harvesting, improved infiltration properties, or better compatibility with inorganic material, better metal-oxide nanostructures, self-assembled monolayers (SAMs) for surface modification, QDs etc. Increase short circuit current through improved light harvesting, increased interfacial area or reduced charge recombination, and to increase open-circuit voltage through improved energy level alignment at the interface. The hybrid organic-inorganic solar cell combines a metal-oxide with a polymer. The structure has a similarity to the solid state dye-sensitized solar cell but the semiconducting polymer can be used for both light absorption and hole transport. Light absorption in the polymer leads to the creation of an exciton. Following exciton diffusion to the organic-inorganic interface, exciton dissociation results to produce separated charges. Electrons are transported by the metal-oxide and the holes by the polymer. The nanostructure of the metal-oxide can be controlled during growth and the same material can be formed in different structures to create various morphologies. The device is fabricated by depositing the metal-oxide layer on ITO coated glass substrate.

Inorganic-organic hybrid structures have become innovative alternatives for next-generation dye-
sensitized solar cells, because the combine advantages of both systems. Recently, inorganic-organic hybrid solar cells have experienced a dramatically increase of conversion efficiency. Nanocrystalline lead halide perovskite have emerged since 2009 as potential photosensitisers. The performance of a TiO₂ solar cell sensitized with iodide perovskite (CH₃NH₃PbI₃) was optimized further to attain an overall power conversion efficiency of 15% [3.4.2.1].

### 3.4.2.2 OPV Conversion Efficiency

Interest in OPV with increasing conversion efficiency has grown exponentially over recent years. The key development in the OPV device is the bulk heterojunction cells as shown in Fig. 3.4.2.1. Both packaging and cell efficiency had improved by 2006 to the stage where independent measurement of cell efficiency was both feasible and warranted, with subsequent efficiency improvements well documented. Konarka established 4.8% efficiency for a tiny 0.14 cm² cell in July 2005, with Sharp demonstrating 3.0% for a relatively massive 1 cm² cell the following year. Konarka increased this to 5.15% in December 2006 with 5.24% posted for a 0.7 cm² cell in July 2007. In the latter device, P3HT was replaced by lower “bandgap” PCPDTBT. Further benefits have been claimed using C₃₄t-PCBM rather than the usual C₆₁-PCBM. Companies such as Plextronics have reported roughly comparable results using similar materials with 5.4% efficiency confirmed in July 2007. Konarka achieved 6.3% efficiency in a 0.7 cm² device based on the use of PCZ (polycarbazoles) as the donor material.

OPV device developer Solarmer Energy achieved the conversion efficiency record of a plastic OPV champion cell—7.9% in December 2009. In November 2010 Konarka achieved their highest OPV efficiency 8.3%. Mitsubishi reported their highest OPV efficiency around 9.3% in early 2011. University of California has developed 10.6% efficient tandem polymer solar cells in the beginning of 2012 [3.4.2.4]. In January 2013, Heliatek reported the world highest OPV efficiency 12% of their tandem device [3.4.2.5].

![Figure 3.4.2.1: Recent improvements in independently confirmed efficiency for small area (≤1cm²) organic solar cells (extracted from Green et al. [3.4.2.2, 3.4.2.3]).](image-url)
The theoretical conversion efficiency limit of OPV cells is over 22% [3.4.2.6]. The current experimental single-junction OPV cell efficiency is \( \eta \approx 10\% \). This observation directly leads to the question, where this factor of \( \sim 2 \) in efficiency drop originates. There are in principle four reasons for this efficiency drop:

1. Optical losses, meaning that light may be parasitically absorbed in solar cell layers that are not active in charge carrier collection or that the current organic solar cells, have no effective light trapping scheme as most inorganic solar cells.

2. Exciton losses due to insufficient transport of excitons to the donor-acceptor interface or due to inefficient exciton dissociation at the interface.

3. Recombination losses, meaning that only a small part of the carriers recombines radiatively, but most of the carriers recombine nonradiatively at donor-acceptor interfaces or defects in the absorber and at the contacts.

4. Collection losses due to insufficient mobilities only part of the free carriers reach the contacts. In order to quantify the importance of these loss mechanisms, we need to have a simple device model capable of reproducing experimental current/voltage curves.

The cell design improvement, implementation of a range of new ideas relevant to carrier’s recombination reduction and improved light trapping are needed for OPV cells to improve the efficiency. The exploration of the potential of a range of “third generation” options is also needed to improve cell efficiency. This will open the opportunity for fabricating optimised tandem stacks of OPV-based cells, with much higher efficiency. Many new ideas and technology will be required before competitive products eventuate. It is very important to identify the key degradation mechanisms to improve the device lifetime and performance.

4.4.2.3 Inverted OPV structures

The fullerene based acceptor material (PC_{70}BM) with a low bang gap donor polymer, commonly PCPDTBT, with line-bond diagrams for these materials are shown schematic inverted structure of a bulk-heterojunction organic solar cell in Fig. 3.4.2.2(a). From this baseline of device structure, the PV Centre believes it has several strengths that will allow it to contribute to the ongoing cell efficiency evolution documented in Fig. 3.4.2.2 (a) and to the development of more stable and durable devices as shown in Fig. 3.4.2.2 (b). The device fabrication process can be divided into four steps. The first step is the substrate cleaning in which the ITO substrates are sonicated in di-water (15 minutes), acetone (15 minutes) and 2-propanol (15 minutes). Secondly, the sol-gel derived ZnO films are prepared using zinc acetate (Zn(CH3COO)2•2H2O, Aldrich, 99.9%) and ethanolamine (NH2CH2CH2OH, Aldrich, 99.5%) in 2-methoxyethanol (CH3OCH2CH2OH, Aldrich, 99.8%) as a precursor solution. This solution was stirred for 1 hour in air. The precursor solution is then span onto the ITO substrate and subsequently treated at different annealing temperature. After the formation of the sol-gel derived ZnO layer, the active layer (PCPDTBT:PC71BM, PTB7:PC71BM or other polymers) which is stirred on a hotplate at 40 °C overnight in a N2 purged glove box is then cast onto the substrate. Finally, a 10 nm buffer layer of MoO3 and 100 nm silver electrodes are thermal evaporated to form the device. The morphology control techniques are used during this device fabrication process, especially during the active layer solution preparation and the active layer drying process. The effects of sol-gel derived ZnO layer to the donor and acceptor morphology of the active layer is also investigated.
The challenge in the OPV is that absorbing light in an organic donor material produces coulombically bound excitons that require dissociation at the donor/acceptor interface. The energy-level offset of the heterojunction (donor/acceptor interface) is also believed to play an important role for the dissociation of bound excitons in OPV cells. An efficient exciton separation into free charge carriers at the interface of donor/acceptor materials will increase the photocurrent of the solar cell. The transport of excitons to the interface is also limit the conversion efficiency of OPV. The details of the exciton transport mechanism in OPV are still not understood. There is an urgent need for more systematic study to gain in depth understanding of the mechanisms of light absorption, excitons dissociation and charge transport, particularly their relationships with molecular and morphological structures of the materials as well as the nano-scale architectural design of the devices. We believe that the conversion efficiency of OPV can be increased much higher than the reported values for the commercial applications through in-depth understanding of the light harvesting behaviour and mechanisms of organic materials and by selecting suitable materials and new device architectures.

![Figure 3.4.2.2](image1.png)

**Figure 3.4.2.2:** (a) Schematic diagram of inverted structure of a bulk-heterojunction organic solar cell. (b) A verage lifetime of inverted structure OPV devices without encapsulation.

### 3.4.2.4 Ternary blend OPV device

We demonstrate a significant improvement of power conversion efficiency (PCE) by the addition of the polymer Poly[[4,8-bis((2-ethylhexyl)oxy)benzo[1,2-b:4,5-b'] dithiophene-2,6-diyl][3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b] thio-phenediyl]] (PTB7) to a Poly[2,1,3-benzothiadiazole-4,7-diyl [4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene-2,6-diyl]] (PCPDTBT) and [6,6]-phenyl C71 butyric acid methyl ester (PC71BM) host system, to form a ternary blend bulk heterojunction solar cell. This is the first reported investigation using PTB7 in a ternary system. The PTB7 concentration was varied from 1 to 9 wt% in the host system. The addition of only 5 wt% PTB7 caused the highest improvement of average PCE, 28 %, with reference to the binary PCPDTBT:PC 71BM cell. In this ternary blend system, PTB7 works as a sensitisier and greatly enhances the optical performance. We demonstrate that positive charge from PCPDTBT is transferred to PTB7, which acts as an efficient charge transfer matrix. The improved device performance is related to both the sensitised response over a large wavelength region and improved charge carrier transport. The inverted device structure used for this investigation was ITO / ZnO / active
layer / MoO$_3$ / Ag. A schematic illustration of this device structure is displayed in Fig. 3.4.2.3(a) and 3.4.2.3(b) shows the energy band diagram of the device. Charge carrier mobilities were obtained by fabricating hole- and electron-only devices. To make hole-only devices, ZnO was replaced with PEDOT:PSS (Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate), Ossila) as the top contact. The structure used was ITO / PEDOT:PSS / active layer / MoO$_3$ / Ag. PEDOT:PSS was spin coated on the ITO surface and dried on the hot plated at 110 °C for 15 min. The electron-only devices were fabricated using the following structure: ITO / ZnO / active layer / Al. The active layer thickness for both hole- and electron-only devices were carefully controlled at 100 nm.

![Schematic diagram of inverted structure of a bulk-heterojunction organic solar cell and (b) Energy band diagram displaying the electronic structure of the inverted structure solar cell.](image)

**Figure 3.4.2.3:** (a) Schematic diagram of inverted structure of a bulk-heterojunction organic solar cell and (b) Energy band diagram displaying the electronic structure of the inverted structure solar cell.

The absorption spectrum of the three individual materials used in this study are shown in Figure 3.4.2.4(a). Figure 3.4.2.4(b) shows absorbance profiles of films containing varying concentrations of PTB7. The addition of even a small amount of PTB7 leads to an improvement in film absorption for all wavelengths. This enhancement is largest in the region from 550 nm to 760 nm, as PTB7 absorbs strongly in this region. Increasing PTB7 concentration generally leads to increase absorption in this wavelength region, as shown in Fig. 3.4.2.4(a). However, a reduction in absorption is observed for the 9 wt% case. This reduction in absorption, even though the total polymer content is increased, may be caused by a disruption of the PCPDTBT phase due to the presence of PTB7. Similar observations have been presented in other reports [3.4.2.7].
Figure 3.4.2.4: (a) Optical absorbance of pure PCPDTBT, pure PTB7 and PC71BM plotted against the AM 1.5G solar spectrum and (b) Optical absorbance of reference PCPDTBT:PC71BM solar cells and PCPDTBT:PC71BM solar cells with varying concentration of PTB7 from 1 to 9 wt%.

Figure 3.4.2.5 shows AFM images, which provide information about phase segregation in the active layer. An ordered nanomorphology in the active layer can help to reduce the binding energy of charge transfer excitons at the donor - acceptor interface [3.4.2.8]. Enhanced phase separation with suitable donor - acceptor domain sizes are required for efficient charge generation [3.4.2.9]. The PCPDTBT:PC71BM reference cell, shown in Figure 3.4.2.5(a), has
a low surface roughness, with root mean square roughness (R\text{rms}) of 1.56 nm, and small domain sizes. Adding PTB7 to the PCPDTBT:PC\textsubscript{71}BM host system increases the surface roughness (R\text{rms} = 1.92 nm for 9 wt%) and domain size. We propose that PTB7 works as a morphology control agent which influences the phase separation. XRD spectra measured for these films showed no peaks, which indicates that PTB7 alters phase separation but doesn’t seem to influence the crystallinity.

![AFM images](image)

**Figure 3.4.2.5:** AFM image (5 µm x 5 µm) of (a) the reference device and the device with (b) 1 wt% PTB7, (b) 2 wt% PTB7, (c) 3 wt% PTB7, (d) 5 wt% PTB7, (e) 7 wt% PTB7 and (f) 9 wt% PTB7.

We have measured the steady state PL of the PCPDTBT, PTB7, PC\textsubscript{71}BM and different blend mixture. The PL spectra of pristine PCPDTBT, PTB7 and PC\textsubscript{71}BM peak at around 850 nm, 795 nm and 710 nm, respectively are observed as shown in Fig. 3.4.2.6. These peaks indicate that the exciton quenching of the pristine film is strongly related to the position of the highest occupied molecular orbital (HOMO) level and the lowest unoccupied molecular orbital (LUMO) level of the individual material. As shown in Fig. 3.4.2.7, by blending PC\textsubscript{71}BM with PCPDTBT, a red shift of the PL peak, when compared with the PL peaks of pristine films, is observed. The PCPDTBT:PC\textsubscript{71}BM reference cell has a PL peak located at around 960 nm. This red-shifted emissions of the blend can be attributed to the charge transfer recombination between holes located at HOMO level of PCPDTBT and electrons located at LUMO level of PC\textsubscript{71}BM [10]. Introducing PTB7 into the blend film causes a further red shift of the PL peak, to approximately 1020 nm. This red shift occurs, even though there is only a small amount of PTB7 present. The HOMO level of PTB7 is higher than PCPDTBT. So this peak shift to lower energies may be indicative of the transfer of holes from PCPDTBT to PTB7. Whilst positive charge carriers are transported through PCPDTBT in the binary blend, they may be partially transported through the PTB7 phase in these ternary devices, if holes are transferred from PCPDTBT to PTB7. The influence of PTB7 on both positive and negative charge transport was investigated by mobility measurement.
Figure 3.4.2.6: PL spectra of pristine PCPDTBT, PTB7 and PC$_7$1BM are measured at room temperature.

Figure 3.4.2.7: PL spectra of reference PCPDTBT:PC$_7$1BM solar cells and PCPDTBT:PC$_7$1BM solar cells with varying concentration of PTB7 from 1 to 9 wt%.
Figure 3.4.2.8 shows the EQE spectra for devices containing varying concentration of PTB7. For wavelengths lower than 550 nm, the addition of PTB7 generally causes a reduction in EQE, with respect to the reference cell. This reduction occurs despite an increase absorption, owing to the PTB7. We note that the 9 wt% PTB7 device displays the worst spectral response for short wavelengths. Contribution to photocurrent generation in this wavelength region for the ternary blend device is complex, as all three components are able to absorb photons. This reduced performance indicates that the addition of PTB7 into the PCPDTBT matrix influences photocurrent generation, as well as absorption. The EQE profile is significantly enhanced in the wavelength region from 550 to 760 nm with the addition of PTB7. This is to be expected, as PTB7 absorbs strongly in this region, as shown in Fig. 3.4.2.4(a). The enhanced EQE shows that photons absorbed by PTB7 are successfully converted to photocurrent in this ternary device. Small concentrations of PTB7 also cause photocurrent enhancements for wavelengths longer than 760 nm. This additional photocurrent is not generated in the PTB7, as it can not absorb in this region. Evidently, small concentrations of PTB7 have a positive influence on the charge transport characteristics for photocurrent generated in the PCPDTBT phase as it creates more carrier percolation pathway. This may also be related to an increase in hole mobility, as PTB7 has demonstrated higher hole mobility, when compared to PCPDTBT [3.4.2.11]. However, a reduction in EQE is observed for the 9 wt% case in this long wavelength region. This high concentration may cause disruptions of the conducting pathways in the PCPDTBT phase, which hinders charge transport.

Figure 3.4.2.8: The EQE spectra of reference PCPDTBT:PC71BM solar cells and PCPDTBT:PC71BM solar cells with varying concentration of PTB7 from 1 to 9 wt%.
Current density-voltage (J-V) characteristic curves are displayed in Fig. 3.4.2.9. Additionally, characteristic photovoltaic performances of devices with varying PTB7 concentrations are shown in Table 3.4.2.1. Adding small amounts of PTB7 cause an increase in $J_{sc}$, which reaches a maximum of 13.4 mA/cm$^2$ for 5 wt% PTB7. This value is high considering that no processing additives were used in this investigation. This increase in $J_{sc}$ is caused by both additional photocurrents generated in PTB7, as well as an improved long wavelength response. Increasing the PTB7 concentration beyond 5 wt% leads to a reduction in $J_{sc}$. This is due to a disruption of the PCPDTBT phase and the donor-acceptor phase separation, causing reduced charge transport through the active layer. A similar trend is observed for fill-factor (FF). Small concentrations of PTB7 result in improved FF, due to a reduction in series resistance, as shown in Table 3.4.2.2. PTB7 concentrations higher than 5 wt% led to an increase in series resistance and thus a reduction in FF. This is evident from the slope of the J-V curves near $V_{oc}$. Adding PTB7 to form a ternary blend leads to an observable increase in open circuit voltage ($V_{oc}$), when compared to the PCPDTBT:PC$_{71}$BM reference value. Multiple reports have shown that $V_{oc}$ in ternary blend devices is tunable across the composition range of its components, rather than being pinned at a minimum value [3.4.2.12]. Street et al. [3.4.2.13] showed that the properties of the charge transfer state or interface band gap are determined by an averaged composition of the two donor materials. The $V_{oc}$ of our samples shift from ~620 mV for the binary PCPDTBT:PC$_{71}$BM reference to ~670 mV for ternary blend devices. This reinforces the ability for ternary blend OPV devices to achieve higher efficiencies through concurrent optimization of both $J_{sc}$ and $V_{oc}$. The best PCE was achieved by adding 5 wt% PTB7.

Figure 3.4.2.9: Current density-voltage curves of reference PCPDTBT:PC$_{71}$BM solar cells and PCPDTBT:PC$_{71}$BM solar cells with varying concentration of PTB7 from 1 to 9 wt%.
Table 3.4.2.1: Photovoltaic characteristic performance of reference PCPDTBT:PC71BM solar cells and PCPDTBT:PC71BM solar cells with varying PTB7 weight percent.

<table>
<thead>
<tr>
<th></th>
<th>$V_{oc}$ (mV)</th>
<th>$J_{sc}$ (mA/cm²)</th>
<th>FF (%)</th>
<th>$R_s$ (Ω·cm²)</th>
<th>Average PCE (%)</th>
<th>Highest PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference</td>
<td>626.9</td>
<td>11.1</td>
<td>42.2</td>
<td>13.6</td>
<td>2.93</td>
<td>3.21</td>
</tr>
<tr>
<td>1 wt% PTB7</td>
<td>667.1</td>
<td>12.7</td>
<td>43.4</td>
<td>10.3</td>
<td>3.68</td>
<td>3.68</td>
</tr>
<tr>
<td>2 wt% PTB7</td>
<td>663.6</td>
<td>13.2</td>
<td>42.5</td>
<td>10.1</td>
<td>3.72</td>
<td>3.82</td>
</tr>
<tr>
<td>3 wt% PTB7</td>
<td>657.3</td>
<td>13.3</td>
<td>44.5</td>
<td>9.2</td>
<td>3.89</td>
<td>3.91</td>
</tr>
<tr>
<td>5 wt% PTB7</td>
<td>675.4</td>
<td>13.4</td>
<td>45.0</td>
<td>9.1</td>
<td>4.07</td>
<td>4.28</td>
</tr>
<tr>
<td>7 wt% PTB7</td>
<td>676.2</td>
<td>12.2</td>
<td>42.4</td>
<td>11.9</td>
<td>3.49</td>
<td>3.82</td>
</tr>
<tr>
<td>9 wt% PTB7</td>
<td>657.9</td>
<td>12.1</td>
<td>39.1</td>
<td>15.2</td>
<td>3.14</td>
<td>3.58</td>
</tr>
</tbody>
</table>

In conclusion the addition of a small concentration of PTB7 in PCPDTBT:PC71BM host system produced significantly improved photocurrent and $V_{oc}$. These improvement led to 28% increase of PCE by adding 5 wt% PTB7 to the active layer blend.

We have also investigated the effect of P3HT as a sensitizer in Si-PCPDTBT:PC71BM active layer of OPV devices. Poly[2,1,3-benzothiadiazole-4,7-diyl[4,4-bis (2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b’]dithiophene-siloe 2,6-diyl]] (Si-PCPDTBT) is a low band gap donor materials. It was reported that Si-PCPDTBT has higher mobility, better crystallinity and larger phase separation. Si-PCPDTBT contains Si atoms which can be identified throughout the film to understand the vertical phase composition. This low bandgap polymers exhibit an absorption maximum in the 650 - 800 nm range, however, they have low absorption at 500 nm. This limits the maximum obtainable photocurrent. Additionally, a nanometer-scale interpenetrating network with suitable domain sizes smaller than the exciton diffusion length (10 - 20 nm) is necessary for highly-efficient organic solar cells. Generally, these conditions do not occur in OPV devices and which causes poor device performance. We demonstrated ternary bulk heterojunction organic solar cells by incorporating P3HT into a Si-PCPDTBT:PC71BM host system to overcome this limitation. P3HT in this ternary system behaves as a sensitisier and morphology control agent. The absorption, carrier mobility and crystallinity of the active layer film were all improved by adding a small amount of P3HT, thus contributing to an improvement in $J_{sc}$ and FF. Additionally, the $V_{oc}$ of the ternary blend solar cells was improved. The combination of these effects led to a 10% increase in PCE by adding 1 wt% P3HT to the active layer blend. We have proposed that P3HT may act as recombination centres, which caused a reduction in device performance at higher P3HT concentrations. Through the careful optimisation we can suggest that ternary blend photovoltaics can be a simple and effective way to achieve efficient organic solar cells. As an example the J-V characteristics of OPV devices are shown in Fig. 3.4.2.10 for different concentration of P3HT. The average improvements of device performance by adding P3HT for different concentration are concluded in Table 3.4.2.2.
3.4.2.4 Solvent Additive Effects

The concentration of donor and acceptor materials is an important parameter for the operation of an organic solar cell. We have systematically investigated the effects of solvent additive on inverted structure PCPDTBT:PC71BM bulk heterojunction organic solar cells. By incorporating 1,8-ODT into the polymer solution, an ~40 nm red-shift of absorption peak at long wavelengths was observed. The addition of 1 vol% 1,8-ODT greatly enhanced the overall optical absorption of PCPDTBT:PC71BM blend films and EQE spectra of the device. The $J_{sc}$ was increased from 9.89 mA/cm$^2$ to 12.14 mA/cm$^2$ for the 1 vol% 1,8-ODT concentration. A reduction in device performance, caused by the residual 1,8-ODT, was observed as the additive concentration was increased. A vacuum drying process can greatly improve the device performance without changing the optical absorption profile and surface morphology. As an example of the improvement of device performance a $J$-$V$ characteristics is shown in Fig 3.4.2.11. The average improvements of device performance by the solvent
additive for different concentration are concluded in Table 3.4.2.3.

**Figure 3.4.2.11:** Current density (J) – voltage (V) curves of the reference device and the device with 1, 2, 3 and 4 vol% 1,8-ODT concentration.

**Table 3.4.2.3:** The average device performance of the reference device and the device with 1 vol%, 2 vol%, 3 vol% and 4 vol% 1,8-ODT concentration and the device with 3 vol% and 4 vol% 1,8-ODT after drying in vacuum over night

<table>
<thead>
<tr>
<th></th>
<th>Average (J_{oc}) (mA/cm²)</th>
<th>Average (V_{oc}) (mV)</th>
<th>Average FF (%)</th>
<th>Average Efficiency (%)</th>
<th>Best Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference</td>
<td>9.89</td>
<td>550.4</td>
<td>37.7</td>
<td>2.05</td>
<td>2.09</td>
</tr>
<tr>
<td>1,8-ODT 1 vol%</td>
<td>12.14</td>
<td>527.8</td>
<td>38.5</td>
<td>2.46</td>
<td>2.57</td>
</tr>
<tr>
<td>1,8-ODT 2 vol%</td>
<td>11.16</td>
<td>560.6</td>
<td>40.2</td>
<td>2.51</td>
<td>2.63</td>
</tr>
<tr>
<td>1,8-ODT 3 vol%</td>
<td>10.61</td>
<td>562.8</td>
<td>43.6</td>
<td>2.59</td>
<td>2.72</td>
</tr>
<tr>
<td>1,8-ODT 4 vol%</td>
<td>9.95</td>
<td>559.4</td>
<td>41.0</td>
<td>2.28</td>
<td>2.49</td>
</tr>
<tr>
<td>1,8-ODT 2 vol% after drying</td>
<td>11.61</td>
<td>540.3</td>
<td>40.3</td>
<td>2.53</td>
<td>2.64</td>
</tr>
<tr>
<td>1,8-ODT 3 vol% after drying</td>
<td>10.38</td>
<td>552.9</td>
<td>47.2</td>
<td>2.71</td>
<td>2.77</td>
</tr>
<tr>
<td>1,8-ODT 4 vol% after drying</td>
<td>11.32</td>
<td>563.2</td>
<td>44.8</td>
<td>2.85</td>
<td>3.00</td>
</tr>
</tbody>
</table>

**3.4.2.5 Anodic Aluminum Oxide (AAO) Nanoimprinting Mold for Ordered Morphology Control of Organic Solar Cells**

A simple experimental setup as shown in Figure 3.4.2.12 was utilised for the anodic oxidation process. A piece of Nickel alloy plate worked as the cathode metal and the Al sample was clipped to the anode. A constant DC voltage was applied between the two terminals. 0.3M H₂SO₄ was selected as the electrolyte solution. The solution was
continuously agitated by a magnetic stirring ball to maintain a homogenous solution and to release hydrogen generated by the anodic reaction. The first anodisation process could be just full anodisation lasting about 10 minutes or the full anodisation plus an extended anodisation up to 3 hours. After that, samples were etched in 5 wt% H₃PO₄ solution to obtain enlarged pore sizes.

The target of our research is to implementation of this prepared imprinting mold into the proposed self-aligned D/A morphological control technique. The major process to prepare the AAO nanoimprinting mold is to anodise high purity thin film aluminium evaporated on silicon substrate to create a brief porous alumina surface. The anodisation and etching process improve the whole system to an AAO mold with high regularity, which was characterised using high resolution scan electron microscope (HRSEM Hitachi S900). By varying anodic conditions, such as applied DC voltage, electrolyte solution and time of anodisation and each etching step, the pore sizes, pore distribution and packing density can be well manipulated. A highly ordered AAO mold has been successfully fabricated through simple anodisation and chemical etching steps as shown in Fig. 3.4.2.13. This simple, cheap and less time consuming technique provides another path to create well-aligned nanostructures as shown in Fig. 3.4.2.13. The AAO mold process parameters and steps are listed in Table 3.4.2.4. Coupled with the future pattern transfer process (e.g. imprint the AAO mold on the planar organic film), this technique has the great potential in achieving ordered D/A morphology control of BHJ OPV devices. However, a feasible imprinting process needs to be further investigated and developed.

Figure 3.4.2.12: A Schematic diagram of standard anodisation process
Table 3.4.2.4:
AAO thin film on Si wafer or SiO2/Si prepared in phosphorous acid (medium to large pore size nanopattern) - A07-A11

| Experiment | Material: Thermal evaporated 500nm Al on SiO2/Si wafer  
Thermal evaporated 150nm Al on Si wafer (100) |
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Anodisation parameters: single step in H3PO4 with subsequent pore widening etching</td>
<td></td>
</tr>
</tbody>
</table>
| Test factor: 1. H3PO4 vs H2SO4 (A07)  
2. porous alumina forming procedure and PC etching (A08)  
3. vary applied voltage and concentration (A09)  
4. bottom barrier layer removal (A10)  
5. thickness expansion (A11) |
| Findings 1. Anodisation in H3PO4 can produce larger pore size AAO pattern and pore self-organizing in H3PO4 requires higher applied DC voltage.  
2. There are 4 stages for porous alumina to self-organise; TEM images prove the effect of PC etching.  
3. There is a close relationship between applied DC voltages and resultant fully anodisation pore size (pore size proportional to applied) and the effect of electrolyte concentration is minor.  
4. Tipping down voltage during anodisation process is an effective way to reduce the thickness of bottom barrier layer. The subsequent H3PO4 etching will fully remove the bottom barrier layer to reveal underneath substrate surface, which is critical for various photovoltaic applications.  
5. The thickness expansion factor for Al to AAO is about 1.3-1.5. So for precise thickness control, this expansion factor need be taken into account when Al deposition. |

Figure 3.4.2.13: SEM and TEM images of AAO sample on SiO2/Si with 20 minutes subsequent etching.

3.4.2.6 Light Trapping in OPV Devices

The light trapping structure is one of the potential ways to improve the PCE of BHJ by increasing the effective optical path length within the active layer without the need of altering
its physical thickness. Due to the small physical dimensions of the photoactive layer, the ability to absorb a large fraction of the solar spectrum is a crucial parameter in determining the efficiency of OPV devices. Plasmonics is one such technique that involves trapping light inside the cell by exciting surface plasmons on metallic nanostructures [3.4.2.14, 3.4.2.15]. Plasmonic materials are advantageous due to the large electric field enhancement near the metal surface and strong dependence of the resonance frequency on size, shape, material, dielectric environment and location, all design parameters of metal nanoparticles [3.4.2.16, 3.4.2.17]. Additionally, the optical properties of plasmonic materials are electrically decoupled from the cell; hence this light trapping technique does not affect the cell properties or require any major modification to device fabrication. For organic solar cells, the most commonly used plasmonic metals are Ag and Au in spherical shape [3.4.2.18]. It has been proposed that Al could be a good candidate since it supports a good overlap between the plasmon resonance and the natural absorption bands of OPV materials [334.2.19].

Embedding the metal nanostructures near the active layer leads to enhanced electric field near junction which results in more excitons being created within an exciton diffusion length. The purpose of this work was to use the electric field enhancement to increase the number of photogenerated charge carriers which was successfully achieved with a maximum enhancement of a factor of 2.7. The localized surface plasmon resonance (LSPR) induced light absorption enhancement region would be much broader after combining Ag and Au NPs into the PEDOT:PSS buffer layer. This layer had uniform particles, with ~4 nm diameter, and controllable particle spacing. This layer also improved the $J_{sc}$ of P3HT:PC$_{60}$BM organic solar cells, which was attributed to enhanced optical density. Most investigations focus on P3HT as the donor material, however, the spectral response of this polymer is severely limited due to its large band gap.

3.4.2.7 Location of nano-particles

The location of metal nanoparticles is another important parameter when designing a solar cell. The effect of placing the nanoparticle on the front, rear or embedded in the active layer is shown in Fig. 3.4.2.14. The effect of a spacer layer thickness, the location of the metal nanoparticles from the absorbing layer, is also critical in determining the fraction of the coupled radiation into the active layer.

(i) Particles on the Front

The particles are located on the front side of device facing the incident light as shown in Fig. 3.4.2.14. The scattering of light by excitation of surface plasmons can improve the efficiency of solar cells, which is achieved by trapping the light within the active layer to enhance the absorption. The increased efficiencies of the plasmonic OPV devices with the Ag NPs on top of ITO are driven by improved $J_{sc}$ and the low values of device series resistance $R_s$. The enhanced photocurrents indicate that LSPR induces more photogenerated charge carriers by stronger absorption within an active layer, resulting from the stronger enhancement in electric field near the metal nanoparticles. Kalfagiannis et al. found that the saturation current of the device with the Ag embedded in the PEDOT:PSS layer is comparatively higher, indicating lower $R_s$ values [3.4.2.20]. This is because individual Ag NPs may act as hole conductors, transporting hole more efficiently.

Metal nanoparticles generally absorb more light in the shorter wavelength (UV regime) regions. For this geometry any potential absorption in the metal cannot be avoided and can compromise absorption in the cells. Secondly, this geometry leads to a suppression of light absorption in the regions below the resonance wavelength. For wavelengths below plasmon
resonance, Fano resonance effect can cause destructive interference between the transmitted and scattered light, and thus can cause reflection rather than enhanced coupling. In this region the metal nanoparticles would be highly reflective, thereby compensating for the scattered light in the sub-resonance wavelength regime.

![Diagram of light trapping schemes for solar cells using surface plasmons: front, embedded and rear case.](image)

**Figure 3.4.2.14:** Schematic diagram of the light trapping schemes for solar cells using surface plasmons: front, embedded and rear case.

**(ii) Particles on the Rear**
The metal nanoparticles are placed on the side opposite the illuminated side of the solar cell as shown in Fig. 3.4.2.14. The excitation of nanoparticles in this geometry is by the transmitted light through the cell. By placing nanoparticles on the rear any potential absorption in the metal can be ruled out, as shorter wavelength light is absorbed in the cell. Additionally, the suppression of absorption due to interference effects is avoided. This allows tunability of the resonance position over the entire region of interest. However, very few reports investigated this geometry in organic solar cells as the evaporated metal cathode on the rear acts as a back reflector which already provides a good light trapping scheme. Kalfagiannis et al. [3.4.2.20] have compared the performances of P3HT:PC$_{60}$BM bulk-heterojunction organic solar cells when Ag NSs are incorporated in front and rear places. Incorporation of Ag NSs on top of ITO resulted in a better overall performance with an increased efficiency of 17 %. Alternatively, adding Ag NSs on top of the active layer achieved 25 % more photocurrent generation compared with reference cells.

The LSPR of Ag NSs increases the probability of exciton generation and dissociation while high percentage of PC$_{60}$BM on the top of active layer effectively transfers electrons to the cathode. Therefore, placing the plasmonic NPs in direct contact with the active layer plays a key role in the harvesting of the SPR effect. As a result, an increase in the value of short circuit current $J_{sc}$ compared with the Ag NPs located on top of ITO was observed. However, series resistance $R_s$ and overall performance of solar cells with Ag NPs on top of active layer are worse than those of samples with Ag NPs on top of ITO, which imply that the metal nanoparticles inside the photoactive layer could act as carrier traps and decrease cell performance.
(iii) Particles Embedded in the Active Layer

Metal nanoparticles are embedded in a photoactive layer as shown in Fig. 3.4.2.14. Organic materials and metals exhibit good processing compatibility and hence can be easily incorporated into the absorber matrix. It has been found that adding metal nanoparticles into the active layer not only enhances local absorption, it also leads to enhance carrier mobility, since metal nanoparticles are more conductive than organic materials. The incorporated metal nanoparticles modify the nanoscale morphology of the polymer/fullerene blend, especially with high NPs concentration, this makes it difficult to extract carriers before they undergo recombination, and consequently reduce cell performances. Therefore it is necessary to isolate direct contact of the metal nanoparticles with the photoactive layer using a dielectric layer to prevent exciton quenching and charge trapping [3.4.2.21].

The placement of the Ag NSs buffer layer is crucial in determining its impact on the device. There exists a trade-off related to the distance between the buffer layer and the photoactive layer. Placing the buffer layer in contact with the photoactive layer can enhance the LSPR effect of Ag NSs. However, using this geometry would significantly increase the surface recombination. There should be some physical separation between the two. The electric field caused by the excited surface plasmons decays exponentially with distance from the buffer layer [3.4.2.22]. This implies that there is some non-obvious physical separation required, between the Ag NSs buffer layer and the photoactive layer of the device, which allows for the maximum improvement performance. Further optimization of the plasmon enhanced organic bulk-heterojunction devices can be achieved by changing both the diameter of the Ag NSs and the thickness of the PEDOT:PSS buffer layer.

3.4.2.8 Plasmonic effects of Ag nano-spheres

Silver nanospheres (Ag NSs) buffer layers were introduced via a solution casting process to enhance the light absorption in poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C61 butyric acid methyl ester (PCBM) bulk-heterojunction organic solar cells as shown in Fig. 3.4.2.15. In order to improve the performance of P3HT:PCBM bulk-heterojunction organic solar cells, Ag NSs buffer layers were deposited in between ITO and PEDOT:PSS layer. The Ag NSs used for this investigation have average diameters of 20 nm and 40 nm. A thin layer of Ag NSs was spin coated between ITO and PEDOT:PSS hole-conducting layer. Physical film properties were analysed using TEM and optical absorption, whilst electronic characteristics were examined using EQE measurements. These Ag NSs, as surface plasmons, increase the optical electric field in the photoactive layer whilst simultaneously improving the light scattering. As a result, this buffer layer improves the light absorption of P3HT:PCBM blend and consequently improves the external quantum efficiency (EQE) of organic solar cells as shown in Fig. 16. By incorporating plasmon-active Ag NSs, an enhanced optical absorption and improved short circuit current Jsc is observed. The overall optical absorption of P3HT:PCBM blend films in the spectral range of 350-650 nm were increased ~4 and 6 % as a result of utilizing the 20 and 40 nm Ag NSs, respectively. The Jsc increases from ~8.0 mA/cm² to ~ 9.1 and 9.6 mA/cm² for 20 and 40 nm Ag NSs, respectively as shown in Fig. 3.4.2.17. These improvements are due to the light scattering of Ag NSs and the high electric field generated by the excited surface plasmons.
Figure 3.4.2.15: A schematic diagram of OPV device with Ag nano-spheres (NSs) on ITO anode surface for the investigation of plasmonic effects on device performance. The TEM images of (a) 20 nm size Ag NSs and (b) 40 nm size Ag NSs on ITO surfaces [3.4.2.12].

Figure 3.4.2.16: (a) Absorption spectra of P3HT:PCBM films with and without Ag NSs at room temperature. (b) The EQE spectra of P3HT:PCBM blends OPV devices with and without Ag NSs. There is a little effect of Ag NSs on the optical properties of OPV devices, but there is a significant improvement of electrical performance of devices [3.4.2.12].
Figure 3.4.2.17: J-V characteristics of P3HT:PC_{60}BM devices with Ag NSs 20 nm (red solid), 40 nm (blue solid) and control devices (as-cast: black solid, annealed: black dash), recorded under illumination at 100 mW/cm².

Figure 3.4.2.18 shows the uv-vis absorbance spectra of PEDOT:PSS and PCPDTBT:PC_{70}BM blend films with and without Ag NSs buffer layer using cell structure in Fig. 3.4.2.15. The secondary axis displays the enhancements in absorbance, due to the addition of an Ag NSs buffer layer. For the control blend, with no Ag NSs buffer layer (black dashed line), two main absorption peaks at ~400 nm and 760 nm are observed. Both PCPDTBT and PC_{70}BM contribute absorption in the region of the ~400 nm peak, whilst absorption in the region of the ~760 nm peak is attributed only to PCPDTBT. Absorption in the blend film is contributed to primarily by PCPDTBT, especially in long wavelength region. PC_{70}BM has an absorption in the spectral range of 300 nm to 650 nm. The concentration ratio of 2:7 for PCPDTBT and PC_{70}BM was selected, which is due to a balance between light absorption and change transport within the active layer.

Figure 3.4.2.18 Optical absorbance spectra of PEDOT:PSS and PCPDTBT:PC_{70}BM active layer with Ag NSs 10 nm (green solid), 20 nm (red solid), 30 nm (blue solid), 40 nm (brown solid) and control blend (black dash) (primary axis). Enhancements of absorbance for the films with 10 nm (green circle), 20 nm (red up-triangle), 30 nm (blue down-triangle) and 40 nm (brown square) Ag NSs buffer layer (secondary axis).
Incorporation of the Ag NSs buffer layers slightly enhances the absorbance spectra. The optical absorption enhancements of films with Ag NSs buffer layers have peaks around 400 nm, which correspond to absorptions of Ag NSs. And the absorbance displays continuous enhancement after 550 nm, which benefits from plasmonic resonance of Ag NSs. The PEDOT:PSS buffer layer, as a low refractive index media, causes the red-shift of the plasmonic resonance position. The overall absorptions of PEDOT:PSS and PCPDTBT:PC70BM blend films are increased as a result of incorporation of Ag NSs buffer layers. This is attributed to light scattering of the Ag NSs and the increased electric field in the photoactive layer by excited localized surface plasmons around the Ag NSs.

Figure 3.4.2.19 displays the EQE spectra of PCPDTBT:PC70BM devices with and without Ag NSs in cell structure. The secondary axis displays the enhancements in EQE, due to the addition of an Ag NSs buffer layer. For all compared devices, the EQE at wavelengths shorter than 335 nm is identical. This indicates that the measurements were reliable; the condition of the tested devices was stable during the entire study. Although our OPV devices have not been optimized, significant changes in electronic performance as a result of localized surface plasmon resonance (LSPR) have been observed. The EQE profile of the control device (black dashed line) primarily follows the profile of optical absorbance of the PCPDTBT:PC70BM blend film, and has a maximum EQE value of ~40 % at 420 nm. With the presence of an Ag NSs buffer layer, the EQE values increase after 560 nm for different size Ag NSs, this correlates with the plasmonic resonance position in the absorbance spectra. The reason for the EQE enhancements around 340 nm is not fully understood. Similar results have been observed in poly-Si thin film solar cells. It is suggested that the enhancement is related to a higher order plasmonic resonance (quadrupole resonance) [3.4.2.23]. Moreover, EQE decreases due to the absorption of Ag NSs and red-shift of EQE peaks are observed around 400 nm. The calculated maximum EQE enhancements in the spectral range 300-900 nm are 14 %, 18 %, 25 % and 30 % for 10 nm, 20 nm, 30 nm and 40 nm Ag NSs, respectively. The larger-sized Ag NSs led to a larger enhancement of EQE in red wavelength region.

Figure 3.4.2.19: EQE spectra of PCPDTBT:PC70BM devices with Ag NSs 10 nm (green solid), 20 nm (red solid), 30 nm (blue solid), 40 nm (brown solid) and control device (black dash) (primary axis). Enhancements of EQE for the devices with 10 nm (green circle), 20 nm (red up-triangle), 30 nm (blue down-triangle) and 40 nm (brown square) Ag NSs buffer layer (secondary axis).
Figure 3.4.2.20 displays the J-V characteristics of PCPDTBT:PC$_{70}$BM devices with and without Ag NSs. The control device exhibited a $V_{oc}$ of 551 mV, a $J_{sc}$ of 10.16 mA/cm$^2$, and a FF of 0.40, resulting in a PCE of 2.24 %. After the addition of Ag NSs below the PEDOT:PSS layer, the values of $V_{oc}$ and FF remained unchanged, suggesting that the interface between PEDOT:PSS and active layer was not affected by the Ag NSs. Some portion of the Ag NSs surface was probably modified by PEDOT:PSS. The photocurrents, however, were improved as the particle size was increased. For the devices prepared with Ag NSs, the $J_{sc}$ values were ~10.77, 10.97, 11.32 and 11.54 mA/cm$^2$ for 10 nm, 20 nm, 30 nm and 40 nm Ag NSs, respectively. As a result, the PCEs increased to 2.35 %, 2.38 %, 2.45 % and 2.56 %, respectively. This represents an increase of ~5 %, 6 %, 9 % and 14 % for 10 nm, 20 nm, 30 nm and 40 nm Ag NSs, with reference to the control device. The larger-sized Ag NSs led to a larger enhancement of $J_{sc}$ and PCE, which is thought to result from enhanced scattering interactions. With the incorporation of Ag NSs, an additional photocurrent is created due to the enhancement of the photogeneration of excitons associated with enhanced electric field intensity from the localized surface plasmonic resonance. This plasmonic coupling of light is a major contributor to the improved electronic transport through the blend films.

![Reference Cell, 10nm Ag NSs, 20nm Ag NSs, 30nm Ag NSs, 40nm Ag NSs](image)

**Figure 3.4.2.20:** J-V characteristics of PCPDTBT:PC$_{70}$BM devices with Ag NSs 10 nm (green solid), 20 nm (red solid), 30 nm (blue solid), 40 nm (brown solid) and control device (black dash), recorded under illumination at 100 mW/cm$^2$.

### 3.4.2.9 Inorganic-Organic hybrid solar cells

Inorganic-organic hybrid structures have become innovative alternatives for next-generation dye-sensitized solar cells, because the combine advantages of both systems. Recently, inorganic-organic hybrid solar cells have experienced a dramatically increase of conversion efficiency. Nanocrystalline lead halide perovskite have emerged since 2009 as potential photosensitisers. The performance of a TiO$_2$ solar cell sensitized with iodide perovskite (CH$_3$NH$_3$PbI$_3$) was optimized further to attain an overall power conversion efficiency of 15% [3.4.2.1].

The aim of the project of polymer:metal-oxide solar cells is to fabricate and characterize the devices. Establish reproducible benchmark devices (bilayer and multilayer) against which
future improvements can be evaluated. Test novel materials including polymers for improved photon harvesting, improved infiltration properties, or better compatibility with inorganic material, better metal-oxide nanostructures, SAMs for surface modification, QDs etc. Increase short circuit current through improved light harvesting, increased interfacial area or reduced charge recombination, and to increase open-circuit voltage through improved energy level alignment at the interface. The device structure is shown in Fig. 3.4.2.21.

<table>
<thead>
<tr>
<th>Cathode</th>
<th>Electron blocking layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mesoporous metal oxide with polymer or perovskite</td>
<td></td>
</tr>
<tr>
<td>Metal oxide</td>
<td></td>
</tr>
<tr>
<td>ITO or FTO (anode)</td>
<td></td>
</tr>
<tr>
<td>Glass</td>
<td></td>
</tr>
</tbody>
</table>

**Figure 3.4.2.21:** Schematic diagram of Inorganic - Organic base solar cells.

### 3.4.2.10 TiO$_2$ : polymer solar cell

A conjugated polymer is combined with the wide-bandgap semiconductor metal-oxide (TiO$_2$ or ZnO) to form the active layer in these devices. Figure 3.4.2.22 shows the schematic band energy diagram of TiO$_2$ polymer solar cell. Light absorption is achieved in the polymer film while electron transport is carried out by the inorganic layer. The device combines the advantages of the organic and inorganic components, allowing low-temperature solution-processed fabrication, improved stability compared to all-organic solar cells, good electron transport, and the ability to control the nanostructure. Even though this device type exhibits great potential, performance levels are low as this field is still young and further research effort is required for optimisation. The knowledge gained through research of these devices is also of use for tandem solar cells.

**Figure 3.4.2.22:** Schematic band structure diagram of TiO$_2$ : polymer solar cell.
Several collaborations with internal, external groups and an Australian company were established. Collaborations with Dyesol and Dr. Wallace Wong (ASI fellow, University of Melbourne) were established to provide novel organic materials (C106 - Dyesol and FHBC, WW436- Dr. Wong). The preliminary results of these materials are promising. The processing conditions have not yet been optimized and this is required prior to establishing the degree of improvement possible by these materials. A novel ruthenium dye C106 (Ruthenium(4,4'-bis(5-(hexylthio)thiophen-2-yl)-2,2'-bipyridine)(4-carboxylic acid-4'-carboxylate-2,2'-bipyridine)(bis-isothiocyanate)) provided by Dyesol was applied as a surface modifier of the TiO₂ film. The objective is to improve the compatibility of the TiO₂ surface with the polymer film. The polymer used in these studies was P3HT. As the compatibility of the TiO₂ film surface of the porous layer increased, it was expected that more polymer would infiltrate the porous film and result in an increased short-circuit current density (Jₘ). The surface modified device gave a Jₘ of more than double compared to an unmodified device. The open-circuit voltage (Vₘ) was also increased by almost 0.2 V. The increase of Vₘ would be a result of increased spatial separation between the polymer and TiO₂ surface, slowing down recombination of the separated charges. The long alkyl insulating side chains in the dye may increase spatial separation between the polymer and TiO₂ surface, and could be responsible for slowing down recombination, resulting in increased Vₘ. The fill factor is improved by optimizing the processing conditions.

FHBC and WW436 provided by Dr. Wong are Hexa-peri-hexabenzocoronene compounds used as hole transporting solution processable small molecules. As infiltration of the porous film should be easier for small molecules than for long chain polymers such as P3HT, it was expected that these small molecules would result in improved infiltration compared to P3HT. However, their absorption is blue shifted (~400 nm compared to P3HT absorption ~550 nm) leading to lower Jₘ. Therefore these materials were used only for the infiltration film. Subsequently a P3HT film was deposited on the device by spin-coating, to partially coat the top portion of the porous film and as an over layer. Therefore it was expected that by using this technique Jₘ would not be compromised. The resultant devices from both compounds showed increased Jₘ with improvement in Vₘ as well.

In order to investigate different metal-oxide nanostructures in the hybrid structure, collaboration was established with Prof. Rose Amal’s group (School of chemical engineering, UNSW). The group is currently investigating growth of ZnO nanorods on TiO₂ dense films provided. Future projects are planned with the group include growth of TiO₂ nanotubes for the structure.

We have also start worked on fabrication and characterization of perovskite solar cell and try to achieve high efficiency devices by increasing Vₘ, Jₘ and fill factor (FF). We are trying to achieve our goal by studying the exciton recombination mechanism, morphological control of precipitation of the perovskite, develop a sequential deposition method for the control of precipitation, investigation of different metal halides microstructures for the conversion of desired perovskite, etc. As the complexity of solution processed devices increases, controlling and optimizing layer morphology, texture, exclusivity, charge transfer, and thickness becomes difficult. The schematic diagram of our perovskite solar cell structure is shown in Fig. 3.4.2.23. This device use ITO as photo anode, and a layer of compact TiO₂ has deposit on the FTO act as an insolation layer to avoid device shunted by hole transport material; mesoporous TiO₂ is the next layer to contact with perovskite molecules to create electrons and holes; using excessive perovskite layer to create a buffer layer to avoid device
shunted by HTM; use thermal evaporation to deposit gold as the cathode. As an example the SEM image of our device is shown in Fig. 3.4.2.24.

Figure 3.4.2.23: Schematic diagram of perovskite device structure.

Perovskite, a material with superior light absorption was investigated. The structure studied was TiO2/Perovskite/P3HT. With variations to the device layer thicknesses and processing conditions it was possible to obtain a high power conversion efficiency of 14.2% (Jsc= 41 mA/cm2, Voc= 1.0 V, FF= 33%). This is currently the highest TiO2-Perovskite-P3HT device performance. Currently the highest reported efficiencies for TiO2-perovskite-P3HT devices are just over 6% and the world record efficiency for any type of Perovskite device is just over 18%. The results obtained here were from early stage processing variation studies. The next milestone will include a systematic study of varying processing conditions, and it can be expected that this would result in an even further increase in performance.
A variety of characterisation techniques were used in these studies. These include Transient absorption Spectroscopy (TAS) to investigate the TiO2-polymer interface with/without modifications. The recombination dynamics indicate the level of recombination of charge occurring at the device interface. This technique was used through collaboration with imperial College London (Prof. Jenny Nelson’s group). A variety of other characterisation techniques were used in the studies including current-voltage (J-V), Spectral Response (EQE), Ellipsometry, Dektak profilometer, etc. available at UNSW.

Plasmonic nanoparticles were included in the structure (and a protective over layer applied) to introduce light trapping in the device. These were carried out using the methods described in other studies for similar structures [3.4.2.24-3.4.2.26]. Gold nanoparticles (~5 nm) and TiO2 overlayers (amorphous ~2 nm or anatase ~6 nm) were coated over the nanoporous TiO2 layer. The techniques for applying nanoparticles and overlayers were sputter-coating and Atomic layer depositions (ALD). An increase in Jsc was observed for Perovskite devices. However the current was reduced in TiO2-dye-P3HT devices. It was concluded that optimising the thickness of the overlayer is important in this application. A very thick film would obstruct infiltration and would reduce effective Plasmon enhancement. However a very thin layer would result in charges recombining at the plasmonic NP. According to Ref[3.4.2.26], a thin film of ~1.1 nm Al2O3 would suffice to prevent charge recombination. The techniques for fabricating Au NP coated with thin film Al2O3 (ALD) has been completed. In the next milestone this technique will be investigated in optimised high efficiency devices. The overall aim of the project is to deliver a high efficiency (TiO2/P3HT multilayer hybrid) device. It can be expected that with further investigations in the next milestone the device performance can be increased even further.

Innovative UNSW Solar Cell technology: We are also working on the innovative technology “Organic-perovskite tandem solar cell”. The greatest improvements in efficiency and durability of such devices can be achieved through the proposed tandem device structure through the selection of suitable materials and optimization of device fabrication. Australia has a number of companies such as “Future Solar Technologies Pty Ltd” with an interest in establishing manufacturing of organic and tandem cells with initial applications of organic and tandem cells likely to be in consumer products. The Company has committed $1.5 million in funding to this project with UNSW during a three year period (2015 - 2017) during which it aims to develop and commercialise the cells. The intellectual property was made available through UNSW Innovations’ Easy Access IP scheme. Further details about this technology and the investor have been published in the Australian Financial Review on 17 March 2015:


3.4.2.11 Simulation Works
The CoE has purchased an upgrade of the Gaussian DFT program package to Gaussian09. W can model larger systems in the so-called ONIOM model which consists of up to three model shells of different accuracy. The highest accuracy is limited to the molecule of interest, while the lower accuracy regions are bigger and cover the electronic environment of the species under investigation. This can be neighbouring molecules for charge transfer as well as electrodes. An improved tool for calculating infrared- and Raman-spectra is included as well, providing an important link to experimental observations at the organic species. The present strengths include a dedicated ab-initio molecular simulation capability (Fig. 3.4.2.25) presently rated at 650 gigaflops but with upgrading to 1.6 teraflops planned for the near-term. To date, this facility has been used for ab-initio modelling of silicon quantum dots in a dielectric environment. The extended capability for excited state modelling should allow the screening of new candidate OPV materials for both performance and durability.
Figure 3.4.2.25: Dedicated Linux 64 bit cluster for ab-initio molecular simulations presently rated at 650 gigaflops.

Other strengths include past experience with a number of engineered vertical junction structures and with light-trapping, not yet fully exploited in OPV devices. The Centre has pioneered light-trapping in both wafer-based and silicon thin-film devices, as well as the use of plasmonics for light-trapping in thin, plane-parallel photovoltaic structures [3.4.2.27].

The Centre is also particularly interested in hybrid organic/inorganic systems as a way of improving both performance and stability. Some work in this area has already commenced as reported below. Hybrid solar cells are a mixer of nanostructures of both organic and inorganic materials. They combine the unique properties of inorganic semiconductor nanoparticles with properties of organic/polymeric materials. Inorganic semiconductor nanoparticles or quantum dots may have high absorption coefficients and particle size induced tunability of the optical band-gap. Band-gap tuning in inorganic nanoparticles with different nanoparticle sizes can be used for realization of device architectures, such as tandem solar cells in which the different bandgaps can be obtained by modifying only one chemical compound. Thus, the organic/inorganic hybrid concept for photovoltaic solar cells is getting interesting and attractive in recent years. The solubility of the n-type and p-type components is an important parameter of the construction of hybrid solar cells processed from solutions.

3.4.2.12 Ordered nanoparticle arrays for hybrid organic/inorganic solar cells

Experimental work on fabrication of highly ordered arrays of nanoparticles as absorber materials originally for hot carrier solar cells has been initiated as a potential means to realise ordered superlattice structures. In this work, the aim is to establish a fabrication system for depositing sequential monolayers of nanoparticles with uniform shells.

We have installed a Langmuir-Blodgett (LB) system for fabrication of highly ordered nanoparticle monolayers as shown in Fig. 3.4.2.26. The LB technique leads to the development of ordered monolayers at an air-water interface while exploiting the self-organization mechanism of colloidal dispersion. Compression of the monolayer is monitored via measurements of surface pressure and...
then controlled by a feedback loop. This unique technique allows transfer of this ordered monolayer onto a wide range of solid substrates such as glass or Si wafers. By controlling the interspacing between adjacent particles, i.e. the shell thickness, by varying the molecular weight of capping species, we can control the periodicity of the film - leading to new optical and electrical properties.

![Figure 3.4.2.26: Schematic of the LB apparatus used to fabricate a monolayer of encapsulated nanoparticles.](image)

Silicon (Si) nanoparticles are being used as core materials. In order to control the interspacing between the particles, the termination of Si nanoparticles is carried out using organosilanes of varying alkyl chain lengths, as shown in Fig. 3.4.2.27.

![Figure 3.4.2.27: Si nanoparticle encapsulated with organosilanes.](image)

Progress to date is reported elsewhere [3.4.2.28]. Once the assembly approach is mastered, it should be possible to build up device structures incorporating layers of quantum dots with the doping in each layer individually controlled.

**References**


3.4.2.5 [HTTP://OPTICS.ORG/NEWS/4/1/36, “HELIATEK ACHIEVES 12% ORGANIC SOLAR CELL EFFICIENCY”].


3.4.2.7 H.C. Hesse, J. Weickert, C. Hundschell, X. Feng, K. Müllen, B. Nickel, A.J. Mozer, L.


3.4.2.28 L. Treiber, C. Bumby, S. Huang, G. Conibeer, 23rd European Photovoltaic Solar Energy Conference, Valencia,
3.4.3 Earth-Abundant CZTS Photovoltaic Devices

University Staff
Dr Xiaojing Hao (group leader)
Prof. Martin Green

Research Fellows
Dr Hongtao Cui
Dr Fangyang Liu
Dr Wei Li
Ms Yidan Huang

Postgraduate Research Student
Xiaolei Liu
Ning Song
Jian Chen
Chang (Eric) Yan
Lei (Adrain) Shi
Xu Liu
Aobo Pu
Fangzhou Zhou
Kaiwen Sun
Jongsung Park
Ye Lin (Master by research)

Visiting Fellow
A/Prof Zhiping Zheng (Huazhong University of Science & Technology, China, till Dec 2012)
Dr Zhanxia Zhao (Shanghai University, China, till July 2013)

3.4.3.1 Strands Outline

All successfully commercialised non-concentrating photovoltaic technologies to date are based on silicon or the chalcogenides (semiconductors containing Group VI elements, specifically Te, Se and S). As indicated by Figure 3.4.3.1, the successful chalcogenide materials, CdTe and CuInSe₂, can be regarded as “synthetic silicon” where the balance between atoms in these materials provides the same average number of valence band electrons as in silicon.

![Figure 3.4.3.1: Synthetic silicon - Portion of the Periodic Table showing pathways to engineering semiconductors with 4 valence electrons/atom.]

Unfortunately Cd and Se are toxic “heavy metals” while Te and In are amongst the 12 most scare...
elements in the Earth's crust, factors that would seem to clearly limit the long-term potential of the established chalcogenide technologies. However, as indicated in Figure 3.4.3.1, by investigating more deeply into the Periodic Table, the compound Cu$_2$ZnSnS$_4$ is uncovered with the same number of valence band electrons on average but involving earth-abundant, non-toxic elements.

Although the potential of this material is relatively unexplored for photovoltaics, initial results have been promising with a group at IBM reporting 12.6% efficiency for small cells based on related materials (alloy of the above sulphide and the corresponding selenide). The appearance of the cells involved (Figure 3.4.3.2) is quite close to the appearance of cells made using CIGS technology (CuInSe$_2$ plus CuGaSe$_2$ alloy).

The Centre's work in this new strand of activity takes a different direction from most of the present international work in this area. The starting point is CZTS thin film solar cells through a viable high throughput manufacturing process. Efforts are to develop technology suitable for the desired process rather than persevering with solution growth processes that have given the best laboratory results to date. Materials selection would be guided by stable compositions formed in naturally occurring minerals such as kesterite and stannites. Another key area that is to be investigated in detail is epitaxial relationships to silicon to investigate the suitability for tandem cell stacks, including stacks involving silicon as the lowermost layer.

3.4.3.2 CZTS thin film solar cells

Summary:
In 2012, the CZTS solar cells research was focused on processing and optimising each constituent layers in parallel (shown in Figure 3.4.3.3).

In 2013, all constituent layers, including Mo back contact, CZTS absorber, CdS buffer, i-ZnO and ZnO:Al layers were engineered to meet their desired properties. The first integrated CZTS solar cells demonstrated an efficiency of 3.76%. With further optimisation on CZTS absorber, the efficiency of CZTS solar cells was improved to 4.5%. To improve the CZTS solar cell performance, the formation mechanism of CZTS made from sulfurising metal precursors was investigated. In addition, strategies for improving the defective back contact/absorber interface were developed.

In 2014, the efficiency of CZTS thin film solar cells on glass at UNSW has been driven to 6.7%. Various strategies for dealing with the problematic heterojunction and back contact interfaces have been developed, leading to improvement in all aspects of CZTS cell performance.
3.4.3.2.1 Back contact-Mo

The properties of low resistivity and good adhesion to soda-lime glass (SLG) substrate are basic requirements for back contact of CZTS solar cells. The strong adhesion of Mo thin films to SLG substrate is crucial for the subsequent deposition of CZTS thin films. The adhesion of Mo film to SLG substrate was improved with increasing pressure. This is mainly due to the transition from compressive to tensile stress in such Mo thin film and better adhesion is favored under tensile stress. However, higher pressure would result in higher resistivity (Figure 3.4.3.4). Therefore Mo films deposited at a certain Argon pressure cannot satisfy these two goals simultaneously. In addition to pressure, the power density applied to the Mo target and post-deposition heat treatment also affect the resistivity of Mo film (Figure 3.4.3.4). Higher power density gives a significantly lower resistivity.

A bilayer scheme was accordingly investigated and optimized, where the bottom layer was deposited at higher Argon pressure for strong adhesion to SLG and the top layer was deposited at lower Argon pressure for low resistivity. The double layer Mo film was deposited on SLG substrates at room temperature without intentional substrate heating. Argon pressure was varied during the deposition, with pressure of 10-20 mTorr at the beginning and 2mTorr for the rest of the deposition. For further improving the resistivity, one of the as-deposited Mo film was annealed at 550 °C for 5 min for a comparison. As shown in Figure 3.4.3.6, all Mo double-layer thin films exhibit preferred orientation of (111). It indicated that it is the original deposition conditions that largely determines the Mo film crystallinity though annealing can improve the crystallinity as well.

![Figure 3.4.3.4: The effect of pressure on Mo film resistivity.](image)

![Figure 3.4.3.5: The effect of pressure on surface roughness.](image)

![Figure 3.4.3.6: XRD spectra of Mo double layer on SLG.](image)

The lowest resistivity of 12.1 µΩcm was obtained after annealing the double layer with the pressure combination of 20 mTorr and 2 mTorr for bottom and top layers respectively, which might be due to the better crystallinity obtained under such a condition. Moreover, the best adhesion category of 4B was achieved on this Mo sample, which means less than 5 per cent of test area was removed. The surface morphology, also important for subsequent CZTS absorber growth was examined by using AFM. The surface roughness of Mo film increases with pressure applied in the Mo bottom layer.
deposition as shown in Figure 3.4.3.5. Based on the impacts of processing conditions on the properties of Mo in terms of resistivity, adhesion to the SLG and surface roughness, the Mo double layer was developed with the processing pressure combination of 20 and 2 mTorr for bottom and top Mo layers, respectively, to meet the requirement of the back contact.

### 3.4.3.2.2 CZTS absorber

In 2013, the fabrication of CZTS thin films was focused by the method of sulphurisation annealing of metal precursors. Key factors affecting CZTS absorber properties and corresponding device performances were investigated.

#### CZTS films and solar cells made from metal precursors

The effect of metal precursor stacking order on the properties of CZTS films

The structure of metal precursor is an important factor determining ultimate CZTS film quality. For instance, placing Cu and Zn in the adjacent layers is thought to be prone to large CZTS grain formation and a Cu top layer is thought to reduce Zn and Sn loss during the sulfurization [3.4.3.1, 3.4.3.2]. CZTS films made from the precursor structure of substrate/Zn/(Cu&Sn) was compared with those commonly-used precursor structures i.e. substrate/Zn/Sn/Cu and substrate/Zn/Cu/Sn/Cu.

CZTS thin films for this investigation were synthesised by sulfurising sputtered metal precursors in S atmosphere with a two-zone sulfurization furnace (OTF-1200X, MTI Corp) (Figure 3.4.3.7). Both soda-lime glass and Mo-coated soda-lime glass were used as substrates for the purpose of optical charaterisation and device-making, respectively. Cu (4N), Zn (4N) and Sn (4N) targets were used for the deposition of metal precursors by using a magnetron sputtering system (ATC-2200, AJA International, inc.). By controlling metal layer thickness, the chemical composition ratios of sulfurized metal precursors were adjusted to Cu/(Zn+Sn)=0.75 and Zn/Sn=1.2, desired ratios reported in most high-performance CZTS devices.

For as-deposited metal precursors sulfurized at 550°C for 30 minutes, SEM images in Figure 3.4.3.8 demonstrate significant difference in terms of grain size and overall structure. The CZTS film made from the precursor structure of substrate/Zn/Sn/Cu is mainly composed of small grains. In contrast, layer stratification were observed in the other two CZTS films made from precursors of substrate/Zn/(Cu&Sn) and substrate/Zn/Cu/Sn/Cu, where most big grains were found in the top layer of CZTS while small grains in the bottom layer. Large voids were observed in CZTS film made from the precursor of substrate/Zn/Cu/Sn/Cu. Absorbers prepared with precursor structures of substrate/Zn/Sn/Cu and substrate/Zn/(Cu&Sn) also have some voids in the bottom layer but much smaller. Therefore, the precursor Zn/(Cu&Sn) is the best among these three structures in terms of the average grain size and voids size.
Figure 3.4.3.7: Temperature profiles of the sulfurization process in sample zone and sulfur zone. The inserted figure is a schematic diagram for the OTF-1200X tube furnace. Sulfur is located at upstream zone and precursors are located at downstream zone.

Figure 3.4.3.8: Cross-section and surface SEM images for CZTS films by sulfurizing three stacking layer precursor structures at 550°C for 30 minutes (substrate/Zn/Cu/Sn/Cu (A1 & A2), substrate/Zn/(Cu&Sn) (B1 & B2), substrate/Zn/Sn/Cu (C1 & C2)).
CZTS solar cell performance made from substrate/ZnS/(Cu&Sn)
The precursor structure of Zn/(Cu&Sn) with optimised sulfurisation annealing conditions yielding the best CZTS film quality on soda lime glass was grown on the Mo coated soda-lime glass for device fabrication. XRD and Raman were applied to analyse the phases in the synthesized CZTS film. The primary CZTS phase was identified by XRD (Figure 3.4.3.10). It was also verified by the Raman spectrum showing CZTS Raman characteristic peaks at 251, 288, 338, 354, 372 cm⁻¹. SnS phases were not found in the XRD spectrum. It is difficult to identify the secondary phases of Cu₂SnS₃ and ZnS by TEM and Raman. Therefore, TEM was applied as a complementary tool to identify these two phases.

**Figure 3.4.3.9:** Cross-sectional SEM image of CZTS thin film prepared by sulfurizing the precursor of Zn/(Cu&Sn) at 560°C for one hour.

**Figure 3.4.3.10:** XRD patterns of CZTS absorber prepared by Zn/(Cu&Sn) metal precursor sulfurized at 560 °C for 1 hour and reference spectra with ICDD PDF numbers indicated. The inserted figure is the Raman spectrum of this sample. Dashed lines are added to each peak positions as guide lines.
Temperature effect
A higher sulfurization temperature and longer annealing duration could improve CZTS film quality by increasing the average grain size. The CZTS films made from substrate/Zn/(Cu&Sn) precursor were used for such investigation. With one hour sulfurization annealing at 560°C, the film quality made of substrate/Zn/(Cu&Sn) precursor is greatly improved as shown in Figure 3.4.3.9. The cross-sectional uniformity of CZTS film is much better than that sulfurized at 550°C for 30 minutes. It is notable that with higher sulfurization temperature and extended duration, no layer stratification was observed. In addition, the desired column grains were obtained and no obvious voids were present in the vicinity area of back contact.

As shown in the TEM EDS line scan of Figure 3.4.3.11(b), Zn peaks were seen at both surface and bottom regions of the absorber, indicating the presence of ZnS in these two regions. Besides, the thick MoS₂ layer (~200nm) was found at the interface between absorber layer and Mo back contact layer in the STEM image. Large voids are also present in the absorber in the STEM image.

The device performance was measured by light I-V, and EQE (Figure 3.4.3.12(a) and (a)), yielding an efficiency of 2.26%. The optical bandgap of the CZTS absorber estimated from the EQE spectrum is 1.438 eV as shown in the inserted figure in Figure 3.4.3.12(b). The cell performance is believed to be significantly affected by its defective film quality. Such as ZnS presence in both front and back absorber region might be a reason for the low Jsc and FF values since it is known detrimental to current conduction in the absorber. In addition, the thick MoS₂ interfacial layer between absorber and back contact is also known detrimental to cell performance as MoS₂ is a high resistivity material (829.54 Ωcm [3.4.3.3]). Both thick MoS₂ and voids would contribute to high series resistance in the device and thereby reduce FF and Jsc [3.4.3.4].

![Figure 3.4.3.11: STEM image of CZTS device (I) with the arrow marking the EDS line scan direction; the EDS line scan (II) from ZnO layer to Mo layer for elements of Cd, Cu, Zn, Sn, S and Mo.](image-url)
Figure 3.4.3.12. (a) light IV curve of fabricated CZTS device (Cell performance parameters are listed in the inserted table); (b) EQE spectra of the device. (Optical band gap plot using EQE data is inserted.)

Effect of chemical composition (Cu/Sn, Cu/(Zn+Sn)) of metal precursor (Zn/ (Cu & Sn)).
As for CIGS or CuInS₂ (CIS), higher copper content is believed to facilitate the growth of large grains [3.4.3.5, 3.4.3. 6]. In terms of CZTS, some also believed that copper rich compositions or Cu-S(e) phase can help generate large grains, which, however, would be highly dependent on the fabrication process. The effects of Cu content on the CZTS absorber properties and corresponding CZTS devices were therefore investigated.
The composition ratio of metallic precursor and corresponding sulfurized CZTS film measured by ICP are illustrated in Figure 3.4.3.13(a). As expected, upon sulfurisation annealing, the elemental ratio changed significantly. The precursor experienced a major loss of Sn. However, it is notable that the loss of tin is highly correlated with Cu content. Cu seems to capture Sn with the ratio of Cu/Sn constant at 2. As CZTS can be formed by direct reaction of binary compound (reaction (1)) and/or via ternary compounds (reaction 2), it is possible that Cu captures Sn via forming species of Cu$_2$ZnSnS$_4$ or Cu$_2$SnS$_3$ compound. The excess Sn might be lost through the volatile SnS. According to the ternary composition diagram (Figure 3.4.3.12(b)), the chemical composition of precursors move to nearly opposite direction of tin sulfide after sulfurization (red arrow in Figure 3.4.3.12(b)), clearly indicating the loss of tin during high temperature sulfurization process.

\[
\begin{align*}
\text{Cu}_2\text{S} + \text{SnS} + \text{ZnS} + \text{S}_2 &\rightarrow \text{Cu}_2\text{ZnSnS}_4 \quad (3.4.3.1) \\
\text{Cu}_2\text{SnS}_3 + \text{ZnS} + \text{S}_2 &\rightarrow \text{Cu}_2\text{ZnSnS}_4 \quad (3.4.3.2)
\end{align*}
\]

Compared to Sn loss, the Zn loss does not seem to be severe, which might be due to the reason that Zn was positioned in the bottom layer. The Zn/Sn ratio of sulfurized CZTS films is in the range of 1.8-1.3, and Cu/(Zn & Sn) ratio in the range of 0.72-0.85.

Figure 3.4.3.13: (a) Composition ratio of metallic precursors and sulphurised CZTS film determined by ICPMS; (b) corresponding ternary composition diagram. The black, red and green color represents A, B and C, the red arrow shows the composition changing trend after sulfurization.

Figure 3.4.3.14 demonstrates X-ray diffraction patterns of sulfurized CZTS films. All three samples can be readily indexed to kesterite Cu$_2$ZnSnS$_4$ (JCPDS no. 00-026-0575) with (112) preferred orientation. XRD peaks assigned to MoS$_2$ can also be found at 2\(\theta\) = 33.8°, indicating a MoS$_2$ layer was formed at the Mo/CZTS interface. No other impurities such as CuS, SnS$_2$, SnS were present within the detect limitation of XRD. The full width at half maximum (FWHM) value of the (112) plane of CZTS films with different compositions is displayed in the inset of Figure 3.4.3.14. Sample A (with low Cu-content and high Zn-content) shows sharper diffraction peaks, indicating either the grain size of sample A is larger, or its crystallinity is better. In addition, less crystalline defects (such as dislocations) presented in low Cu high Zn samples could also contribute to this change.
Raman scattering characterization was also carried out on the surface of CZTS samples shown in Figure 3.4.3.15. Raman together with XRD data, confirm that the formation of kesterite CZTS without impurity peaks, such as CuS/Cu$_{2-x}$S/Cu$_2$S. A shoulder peak at approximately 353 cm$^{-1}$ can be attributed to ZnS and/or Cu$_2$SnS$_3$. This might indicate that almost all of the copper has reacted with excess tin without yielding a Cu-S phase.

Figure 3.4.3.15: Raman spectra of sulphurised CZTS films with different composition.

Figure 3.4.3.16 (a-c) present the top view SEM images of CZTS samples with different compositions. All three samples display rough, loose as well as inhomogeneous surface morphology. It is notable that some pinholes with diameters ranging from 0.1 - 0.3 µm can be observed on the surfaces. These pinholes may serve as the escape pathways of Sn or SnS during sulfurization process resulting from the process of loss of tin or tin sulphide. Both large grains (size of 0.4 - 0.6 µm) with triangular shape and small grains with round shape (size of tens of nanometers) were present. No SnS$_2$ platelets, which has a hexagonal morphology and can be easily distinguished on the surface, were found on the surfaces of the films [3.4.3.7].

Figure 3.4.3.16 (a-c) present the top view SEM images of CZTS samples with different compositions. All three samples display rough, loose as well as inhomogeneous surface morphology. It is notable that some pinholes with diameters ranging from 0.1 - 0.3 µm can be observed on the surfaces. These pinholes may serve as the escape pathways of Sn or SnS during sulfurization process resulting from the process of loss of tin or tin sulphide. Both large grains (size of 0.4 - 0.6 µm) with triangular shape and small grains with round shape (size of tens of nanometers) were present. No SnS$_2$ platelets, which has a hexagonal morphology and can be easily distinguished on the surface, were found on the surfaces of the films [3.4.3.7].

The corresponding cross-sectional views of our CZTS device with different compositions are shown as Figure 3.4.3.16 (A-C). The thickness of the Mo back contact is approximately 1.1 - 1.2 µm with columnar grains. The darkening top parts of Mo and smaller particles within the upper part of Mo are due to the formation of MoS$_2$ layers with a thickness of 0.3 - 0.4 µm [3.4.3.8]. The thicknesses of CZTS layer are ranged between 0.9 and 1.1 µm and both large grains (hundreds nm) and small grains (tens of nm) coexist along the depth direction of CZTS absorber. It is notable that the average grain size in the top layer of CZTS is larger than that in the bottom. This might result from the growth sequence where grain in the top positions grow first and become larger grain as proposed by
Fairbrother et al. [3.4.3.9]. Similar bilayer CZTS structure with different grain sizes have also been reported elsewhere using metallic [3.4.3.11] and sulfide precursors [3.4.3.8].

The sample A (with high Zn content and low Cu content) demonstrates larger grains than that of sample B and C, consistent with the trend of FWHM values extracted from XRD data. This indicates that the sample with lowest Cu/(Sn & Zn) ratio has larger gains than samples with higher Cu/(Sn & Zn) ratio, contradicting with expected Cu-assisted crystal growth speculation in CIGS/CIS field.

The solar cell performances of CZTS devices with different absorber compositions are illustrated in Figure 3.4.3.17. As expected, sample A with high zinc content and larger grain size demonstrates the best conversion efficiency (2.59%) with all device performance indices (i.e. Voc, Jsc and Fill Factor) superior to the others. The FF of the best device was only 46.4%, which is quite low compared to high efficiency CZTS cells (with FF around 60%). According to the light J-V curve, the low FF of device A is due to shunting and high series resistance, which may be caused by pinholes observed in SEM images of CZTS surface and by thick MoS2 (0.3 - 0.4 μm), respectively. Other samples suffer a more severe shunting problem and high series resistance, leading to lower FF (merely 27-28%). According to dark J-V curves, sample A also shows better diode characteristic than those of sample B and C.

Figure 3.4.3.16: SEM images of top-viewed CZTS thin film with different composition (a,b,c) and cross sectional views of corresponding CZTS device (A,B,C).

Figure 3.4.3.17: a) light and b) dark J-V curves of CZTS devices with different composition.
Figure 3.4.3.18 demonstrates the External Quantum Efficiency (EQE) curves of the CZTS device with different composition. All EQE curves peaked at around 530 nm. The large decrease in the blue region is due to the absorption of i-ZnO/AZO (with band gap around 3.4 eV significantly absorbing light <380 nm) and CdS (with band gap around 2.4 eV significantly absorbing light <520 nm). In terms of wavelengths larger than 530 nm, the EQE value decays at two different slopes. Sample A demonstrates better characteristics.

![EQE curves of CZTS devices with different composition.](image)

Fromation mechanism of Cu₂ZnSnS₄ made from sputtered Zn/ (Cu&Sn) precursors

The detection of secondary phases such as ZnS and CTS, cannot be distinguished from CZTS by X-ray diffraction due to their characteristic Bragg peaks overlap with those of CZTS. Only a small portion of the secondary phase makes the characterisation even more challenging. Due to the limited penetration depth of the laser used for Raman spectroscopy, surface Raman spectroscopy cannot detect the phases buried close to the back contact while the depthresolved Raman measurements are needed for this purpose. This limits the study on the formation mechanism of CZTS absorber. To clarify the crystallisation process of CZTS, samples treated at various sulphurisation annealing stages were prepared as shown in Figure 3.4.3.19. Transmission electron microscopy (TEM) together with energy dispersive spectroscopy (EDS) is employed to characterize the existence and distribution of phases in samples at various sulphurisation annealing stages.

![Sulfurisation temperature profiles of the sulphur zone and sample zone.](image)
High-angle annular dark-field (HAADF) images were used to analyse the elements distribution in the metallic precursor after a specific sulphurisation annealing. After sulphurisation annealing at 250 °C for 30 mins (sample A), Cu has diffused to the bottom Zn layer as shown in the marked region “I” of Figure 3.4.3.20 (a) and the EDS line scan in Figure 3.4.3.20 (b). In the meantime, Zn has also diffused to the Cu and Sn layer as shown in the marked region “II” of Figure 3.4.3.20 (a) and the EDS line scan in Figure 3.4.3.20 (b). It was reported that binary Cu-Sn alloy has already formed in the metallic precursor during the sputtering process. As the annealing temperature increases, the alloy process will be rapidly accelerated. Because of the fast diffusivity of Cu through Sn, and the high reactivity of Zn, Cu reacts with Zn in the bottom region of the precursor and leaves Sn behind and thus Cu-Zn phases are formed in preference to Cu-Sn phases after sulphurisation annealing. On the other hand, Cu atoms can separate from the Cu-Sn alloy to react with Zn which is diffused from the bottom layer to form Cu-Zn alloy after annealing at 250 °C for 30 mins. Chou et al. reported that no ternary compound was found in the Cu-Zn-Sn system [3.4.3.11], indicating Cu, Zn and Sn can only be in the form of elemental phases or binary alloy like Cu₆Sn₅ and Cu₅Zn₈ which can be observed in X-ray diffraction (XRD) results (not shown here). Therefore, in Sn-rich region like region “III” of Figure 3.4.3.20 (a), almost no Zn can be found. In contrast, in the Zn rich region like region “II” of Figure 3.4.3.20, Sn concentration is very low while Cu is uniformly distributed in both of these two region “II” and “III”. Due to the fact that Sn and Zn have very limited mutual solubility, less than 0.5 wt% and that they do not form intermetallic compounds [3.4.3.12], no Sn-Zn alloy is found in Figure 3.4.3.20. It is notable that the surface region of the metallic stack contains only Zn and S two elements but no Cu and Sn can be observed from the EDS mapping and line scan in Figure 3.4.3.20 (a) and (b), respectively. The black contrast in the HAADF image in Figure 3.4.3.20 (a) also suggests that the lower atomic number in the top surface region because average atomic number of Zn and S is lower than that of the metallic alloys underneath. This results suggest that S has already been introduced into the metallic stack and reacted with Zn which segregates at the surface after sulphurisation annealing at 250 °C for 30 min. S does not react with Cu and Sn which are deposited at the top surface in the metallic stacking precursor but reacts with Zn which is used to be located at the bottom of the stack but now diffuses to the surface.

The calculated Gibbs free energy changes of Zn, Sn and Cu with S reactions in Table 3.4.3.1 are negative in the temperature range of 25 °C to 527 °C indicating all these reactions can happen during the sulphurisation annealing. The most likely reaction is that which has the smallest or most negative \( \Delta G \). \( \Delta G \) of the reaction for ZnS formation is the most negative so ZnS phase can be formed in preference to other metallic phases such as Cu₂₋ₓS and SnSₓ which is consistent with our observations in Figure 3.4.3.20.

### Table 3.4.3.1: Calculation for the Gibbs free energy change of the reactions between Cu, Zn, Sn and S at different annealing temperature

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Gibbs free energy change (( \Delta G )) kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25°C</td>
</tr>
<tr>
<td>Zn+1/8 Sₓ→ZnS</td>
<td>-206.3</td>
</tr>
<tr>
<td>Sn+1/4 Sₓ→SnS₂</td>
<td>-157.0</td>
</tr>
<tr>
<td>Sn+1/8 Sₓ→SnS (solid)</td>
<td>-112.4</td>
</tr>
<tr>
<td>2Cu+1/8 Sₓ→Cu₂S</td>
<td>-92.1</td>
</tr>
<tr>
<td>Cu+1/8 Sₓ→CuS</td>
<td>-54.8</td>
</tr>
</tbody>
</table>
As the sample zone temperature increases to 500 °C (sample B), it is found that ZnS and Cu$_2$S are segregated at the top surface. As shown in the HAADF image in Figure 3.4.3.21 (a), a large hump was formed on the film surface. Sn shows nearly no distribution inside the hump while S has been diffused into the whole thickness of the sample as shown in the EDS mapping of Figure 3.4.3.21 (a). Cu and Zn EDS mapping shows a completely different distribution for these two elements. On the left side of the hump, Cu concentration is almost zero while Zn concentration is the highest among all these elements. In contrast, the right side of the hump shows a completely opposite trend to the left of the hump. EDS line scans in Figure 3.4.3.21 (b) and (c), also proves that the left side of the hump is ZnS segregation while Cu$_2$S segregates at the right side. The Cu$_2$S phase can also be observed in corresponding XRD results (not shown here). The formation of secondary phases can be always found at low annealing temperature which is attributed to the high nucleation formation energy of CZTS compared to those of secondary phases. Therefore, nucleation of secondary phases occurs relatively...
easily compared to that of CZTS at low sulphurisation temperature. As the annealing temperature increases to the range of 350 °C to 400 °C, Cu₂Zn₈ has been reported to react with sulfur to form Cu₂₋ₓS and ZnS. In this case, it is always found that Cu and Zn can migrate to the surface of the film to facilitate the reaction with sulfur and form CuₓS and ZnS grains at the surface. It was also even reported that the entire Cu content of the film has migrated to the surface of the film to form Cu₂₋ₓS grains [3.4.3.13]. Due to the out-diffusion of Cu atoms to the film surface, there is a corresponding in-diffusion of vacancies to the back contact of the metallic stacks during sulphurisation annealing. Scragg also found that a large density of voids was located at the back contact region from SEM images [3.4.3.13]. In the HAADF image in Figure 3.4.3.21 (a), voids at the interface between CZTS precursor and Mo are also clearly observed. It is notable to find that elemental Sn is located at the back junction of the film after annealing at 500 °C. From the EDS mapping, some Sn spark spots can be observed. A more detailed elements distribution can be obtained by EDS line scan in Figure 3.4.3.21 (b) and (c) in which Sn peaks are found at the bottom of the film while all other elements intensities decrease to zero. All these prove that Sn is existed in form of pure element rather than in tin sulphides. The formation of elemental Sn during sulphurisation annealing at the temperature from 400 °C was also consistent with the XRD results. CZTS layer line scan results in Figure 3.4.3.21 (b) and (c) indicate that crystalline CZTS have already formed after sulphurisation annealing at 500 °C while no CTS can be observed.

Figure 3.4.3.21: (a) the HAADF and EDS mapping images from the sample B, (b) and (c) with corresponding EDS line scan taken along the arrow, L1 and L2 in HAADF image in (a), respectively.

When the annealing temperature increases to 575 °C (sample C), a layered structure is obvious as seen in Figure 3.4.3.22 (a) and (b). In the surface layer, the CZTS is the predominate phase while the bottom layer contains a high density of voids and smaller grains. The needle-like grain structure can also be observed in our film as shown in the Figure 3.4.3.22 (a). EDS line scans (red arrows labelled L1 and L2 in Figure 3.4.3.22 suggest that these needle-like grain structures are closely contacted ZnS and CTS secondary phases which have not been consumed to form CZTS phase. It is notable that in the sample sulfurized at 575 °C, no elemental Sn can be observed. This fact is completely different from the one at 500 °C in which no CTS is found in the whole film while a large quantity of elemental Sn is observed at the back contact region as shown in Figure 3.4.3.21. This suggests that at 575 °C the
reactions that consume Cu$_{2-x}$S and elemental Sn leading to CTS occur more rapidly. Schurr et al. suggested that the presence of a liquid phase (SnS$_2$) can greatly enhance a preferred crystal growth rate of CTS via the reaction between Cu$_{2-x}$S and SnS$_2$ when the sulphurisation annealing temperature is higher than 575 °C [3.4.3.14].

Figure 3.4.3.22: (a) the HAADF and EDS mapping images from the sample C, (b) with corresponding EDS line scan taken along the arrow in HAADF image in (a).

As the sulphurisation temperature keeps at 575 °C for 10 mins (sample D), Cu, Zn, Sn and S are uniformly distributed through the whole CZTS absorber as shown in Figure 3.4.3.23. The existence of Cu-rich secondary phases such as Cu$_{2-x}$S and CTS can be ruled out by EDS mapping and line scan in Figure 3.4.3.23 (a) and (b) while only ZnS phase is still left in the CZTS layer. Our samples are in the range of “Cu-poor, Zn-rich” so the existence of ZnS phase is expected. CTS has been vanished indicating that chemical reaction between CTS and ZnS can be completed in a short anneal at 575 °C. As similar results are reported by Chalapathy et al. that the CZTS phase is completed in about 7 min of ramping to 580 °C in S atmosphere [3.4.3.4]. The MoS$_x$ is always found at the back contact [3.4.3.29]. In our sample, an around 200 nm thick MoS$_x$ layer is also observed at the interface between Mo and CZTS layer. In the EDS line scan, a lower Mo-K signal intensity is found at the interface than in the Mo layer. Due to the Mo sulphurisation to MoS$_x$ at the interface, a decreasing Mo concentration at the Mo surface is expected which results in the lower Mo-K signal intensity.
HAADF images for the sample A-D are shown in Figure 3.4.3.24. The film thickness and morphology undergo a great change during sulphurisation process. At 250 °C for 30 min, sample A is only slightly sulfurized on the film surface so the film thickness is only about 650 nm. As sulphurisation annealing temperature increases to 500 °C, a large hump which is uniformly distributed on the film surface can be observed in the Figure 3.4.3.24 (b). The maximum film thickness at the hump region reaches up to 3.7 µm due to the secondary phase segregation while in other regions the film thickness is only about 1.4 µm. The hump is uniformly distributed on the whole film surface. As the annealing temperature increases further to 575 °C, a large density of voids is formed at the back contact region. The whole film thickness gets to around 1.6 µm but the thickness of the upper part without too many voids is still around 1.3 µm. With extending the duration time at 575 °C to 10 min, film thickness remains almost unchanged. Therefore, the variation of film thickness mainly takes place when the temperature increases from 250 to 500 °C. During this period, metallic layers are sulfurized to metallic sulphides. Theoretical calculation suggests the film thickness of the sulfurized CZTS film will be 2.3 times thicker than the metallic precursor by taking the material density, material loss and CZTS chemical composition into consideration. Experimentally, it is always found that the film thickness is doubled or tripled after the sulfurization. The film morphology changing is mainly due to the secondary phase segregation at the film surface. As the annealing temperature increases further to 575 °C, these secondary phases are consumed by forming crystalline CZTS and the film becoming relatively smoother. No voids can be seen in the sample A. The black contrast in Figure 3.4.3.24 (a) results from the elements (like Zn) with lower atomic number rather than voids. It indicates that the void should not be existed before sulphurisation annealing. As the annealing temperature increases to 500 °C, voids starts to appear at the bottom layer of the sample. These voids are believed to be related to the Cu and Zn out-diffusion and segregation at
the film surface. As the annealing temperature increases further to 575 °C, much more voids are formed at the back contact region than that at 500 °C. In this stage, the void formation mainly results from the Sn loss through a path of SnS at such high temperature. After all the elemental Sn is consumed and reacted to CTS phase. No further void formation can be observed as the annealing duration increases to 10 min at 575 °C. The formation of MoSx at the back contact may facilitate an electrical quasi-ohmic contact and improve the adhesion of CZTS to Mo back contact, leading to high series resistance and accordingly deteriorates the solar cell performance. A 200 thick MoSx can only be observed in sample D. However, all the EDS scans in Samples A-C indicates MoSx thickness is below the detection limit for TEM EDS line scan. This suggests that large amount of MoS2 is formed after the metallic layer is fully sulfurized and CZTS grains are almost crystallised. Extending the duration time at 575 °C to 10 min, the MoSx thickness increases from undetectable thickness to 200 nm. Although a longer duration time can improve CZTS crystallinity, a short dwell period of 3 min at 557 °C is sufficient to induce crystallization of the CZTS phase and results in a dramatic increase in grain size.

Figure 3.4.3.24: Cross-sectional HAADF images (A-D) of sulfurized sample A, B, C, and D, respectively.

Different from using the metal precursor in previous years, in 2014, the CZST absorber was synthesized by rapid thermal sulfurizing the mixed metal & metal sulphide precursors. In this way, the efficiency of CZTS solar cells was improved to 6.7% (w/o ARC), which is comparable to the current certified record of 8.5% (with ARC). Details of this work will be presented in annual report in 2015.
CZTS/Mo back contact interface engineering

The formation of MoS(e)₂ at the back contact/CZTS(e) interface during CZTS(e) thin film growth is inevitable via reactions between Mo and chalcogen at high chalcogen partial pressure or CZTS(e) in the absence of chalcogen excess, which may facilitate an electrical quasi-ohmic contact and improve the adhesion of CZTS(e) to Mo back contact, but leads to high series resistance and accordingly deteriorates the device efficiency if not thin enough, similar to the case of CIGSe solar cells [3.4.3.15]. It is advantageous to inhibit the formation of MoS(e)₂ by introducing an intermediate layer into CZTS(e) absorber/Mo back contact interface.

We employ titanium diboride TiB₂, which is a refractory intermetallic compound with excellent chemical stability and electrical conductivity, as intermediate layer to block the sulfurization of Mo during Cu₂ZnSnS₄ absorber preparation and eliminate (or greatly reduce) the formation of MoS₂.

Cross-sectional SEM images of the fabricated CZTS solar cells without and with 30 nm TiB₂ as intermediate layer are displayed in Figure 3.4.3.26(a) and (b), respectively and their corresponding TEM cross sectional images are displayed in Figure 3.4.3.26 (c) and (d). As shown in Figure 3.4.3.26, the formation of a MoS₂ interfacial layer of 400 nm for device without TiB₂ layer is evident between CZTS absorber layer and Mo substrate, which is inhibited significantly when inserting 30 nm TiB₂ as intermediate layer. The inhibition of MoS₂ formation using TiB₂ can be identified again from the composition profiles by TEM EDS line scan spanning from CZTS absorber into Mo as shown in the insets of TEM images. Besides, the Cu out-diffusion from CZTS into MoS₂ and even Mo can be observed from the EDS composition profile (inset of Figure 3.4.3.26 (c)), which has been noted by others [3.4.3.16, 3.4.3.17], and believed to be solely from the TEM specimen preparation by FIB and not an inherent part of the synthesis process. This out-diffusion of Cu also can be suppressed greatly by introducing TiB₂ layer as shown in the inset of 3.4.3.26 (d), implying good blocking capability of TiB₂ layer. Moreover, it should be noted that the presence of voids at the absorber bottom region for both samples can be observed from TEM cross section images. The size and roughness of the voids reduce which reveals the improvement of interface morphology by using 30 nm TiB₂ intermediate layer.

Figure 3.4.3.25: Progress chart of energy conversion efficiency of CZTS solar cells.
To check whether TiB₂ prevents the formation of MoS₂ completely, Raman tests were employed to examine the back contact region after mechanical removal of the absorber. As is clear in Figure 3.4.3.27(a), without TiB₂ layer, the strong Raman peaks at 407 cm⁻¹, 381 cm⁻¹ and 285 cm⁻¹ demonstrate very thick MoS₂ covering on Mo substrate, while these peaks become much weaker for sample with 30 nm TiB₂ layer. These results are indicative that TiB₂ as the intermediate layer between CZTS and Mo blocks the sulfurization of Mo and inhibits MoS₂ formation effectively, but doesn't eliminate the formation of MoS₂ completely. It is important to remark that the presence of MoS₂ suggests the intermixing of MoS₂ and TiB₂ leading to a mixed MoS₂/TiB₂ back contact. This can avoid the formation of hole barrier that enhances recombination velocity near the back contact and the rise in contact resistance, and remains the advantages of MoS₂ such as high work function and quasi-ohmic contact with CZTS.

With regard to CZTS absorber quality, in both cases, the grown CZTS thin films show large-grain structure with some grains extending from the bottom to the top of the films from SEM and TEM morphology observation. In order to examine this further, we characterized the CZTS absorbers obtained on Mo substrate without and with 10-70 nm TiB₂ layer as intermediate layer by XRD and Raman, as shown in Figure 3.4.3.27 (b) and (c). XRD patterns and Raman spectra confirm that the crystallographic structure of all films to be in good agreement with that of tetragonal kesterite CZTS (JCPDS No. 026-0575). No obvious Raman or XRD peaks resulting from minor second phases can be observed for all samples. This also indicates that the presence of such a thin
TiB$_2$ layer does not appear to result in the formation of secondary phases in CZTS absorber. However, we found that the both XRD (112) and Raman (336 cm$^{-1}$) main peaks are broadened slightly with the introduction of TiB$_2$ layer and the increase in TiB$_2$ thickness. This variation shows that average grain size of CZTS absorbers decreases indicating more grain boundaries and worse crystallinity when grown on TiB$_2$ modified Mo substrate.

![Figure 3.4.3.27:](image)

Figure 3.4.3.27: (a) Raman spectra taken from the back contact region of samples with and without 30 nm TiB$_2$ intermediate layer after mechanical removal of the CZTS absorber layers; X-ray diffraction patterns (b) and Raman spectra (c) of the CZTS thin films on Mo back contacts with 0-70 nm TiB$_2$ intermediate layers.

Figure 3.4.3.28 illustrates the J-V characteristics of the CZTS devices with and without TiB$_2$ layers between CZTS and Mo substrate. As indicated, the device efficiency raises from 3.06% to 4.40% when inserting a 30nm TiB$_2$ intermediate layer compared to the controlled device without TiB$_2$ due to the significant boost in J$\text{sc}$ as well as some increase in FF. This improvement in J$\text{sc}$ and FF can be reasonably attributed to the substantial reduction in MoS$_2$ thickness and voids size at back contact region, and accordingly the decrease in the series resistance (from 22.0 $\Omega$ cm$^2$ to 10.3 $\Omega$ cm$^2$) as 30 nm TiB$_2$ is introduced into CZTS/Mo interface in combination with the SEM and TEM analysis in Figure 3.4.3.26. However, the Voc shows a conspicuous drop for devices with TiB$_2$ intermediate layer, which could be related to the decay in crystallinity of CZTS absorber by the smaller grain size and more grain boundaries when grown on TiB$_2$ coated Mo substrate. As the thickness of TiB$_2$ reaches 70 nm, the conversion efficiency begins to decrease through the falling down of J$\text{sc}$ and FF, which also can be associated with the further degradation of CZTS absorber crystal quality combining with Raman and XRD analysis. Therefore, these results allow us to conclude that the introducing of a
thin TiB_2 layer between CZTS absorber and Mo back contact can inhibit the formation of MoS_2 interfacial layer and diminish the interface voids significantly and consequently reduce the series resistance and boost the device efficiency greatly by large improvement in J_sc and FF. However, on the other hand, it would degrade the CZTS absorber crystallinity and thereby deteriorate the device performance from all aspects (V_oc, J_sc, FF and EFF) especially in V_oc.

![Figure 3.4.3.28](image)

Figure 3.4.3.28: J–V characteristics of the CZTS devices under AM 1.5G illumination. The efficiency EFF, open-circuit voltage V_oc, short circuit current density J_sc, fill factor FF, and series resistance Rs are given in the figure.

In addition to TiB_2 intermediate layer between Mo and CZTS absorber, the intermediate layer such as ZnO, Ag were also investigated with details in [Li W., Liu X., Cui H., Huang S., Hao X.J., “The role of Ag in (Ag,Cu)ZnSnS_4 thin film for solar cell application”, Journal of Alloy and Compounds, (in press, Acepted 22nd Nov 2014)] [Liu X., Cui H., Li W., Song N., Lui F., Conibeer G., Hao X.J., “Improving Cu_2ZnSnS_4 (CZTS) solar cell performance by an ultrathin ZnO intermediate layer between CZTS absorber and Mo back contact”, Phys. Status Solidi RRL, 1-5 (2014), DOI 10.1002/pssr.201409052.]. While these intermediate layer has either negative impact in V_oc or FF, an innovative intermediate layer improving cell performance without degradation in all aspects (V_oc, FF and J_sc) was discovered. The details of this approach will be enclosed in 2015 Annual report.

### 4.4.3.2.3 Cd buffer layer

The primary function of a buffer layer in a heterojunction is to form a junction with the absorber layer while admitting a maximum amount of light to the junction region and absorber layer. As thus, this layer should have (1) large energy band gap for minimal absorption losses; (2) a suitable conduction band line-up to the absorber and to i-ZnO. Based on the understanding of record CIGS cells, a moderate spike is preferred for conduction band offset for reducing interface cross-recombination; (3) a very low defect density at the absorber/buffer interface by less lattice mismatch at the junction for consideration for epitaxial or highly oriented layers; (4) desired doping density sufficiently exceeding that of the absorber to confine the space charge region at absorber; (5) Position of the Fermi level at the absorber/buffer interface close to the absorber conduction band, i.e., achieve type inversion of the
A very thin CdS (50-80nm) film is an indispensable layer for the highest efficiency CIGS solar cells and currently adopted in most of CZTS devices. Not only CdS serves as a hetero-junction partner (n-type), but also as a “buffer” layer, namely, facilitating lattice matching, band alignment, protecting absorbing layer from damaging by sputtered ZnO etc. For High efficiency CIGS and/or CZTSSe solar cells, CdS buffer layer by chemical bath deposition (CBD) method has been employed to deposit device owing to great advantages of CBD over other deposition methods. CBD process is a “soft” method, avoiding the direct ion damage to CZTS absorber. In addition, this wet chemical process helps “clean” the surface of the absorber, and specifically, removes the excess sodium and some oxide on the surface.

With the completed CBD setup, Cadmium sulfate (CdSO₄), thiourea (H₂NCSNH₂) and ammonium hydroxide (NH₄OH) were used to synthesis CdS by CBD method.

Both XRD (Figure 3.4.3.29) and Raman (Figure 3.4.3.30) confirmed the crystalline phase of CdS. As shown in Figure 3.4.3.29, the synthesized CdS thin film by CBD possess has the cubic rather than hexagonal structure, d-spacing of the (111) plane is 3.36Å, which is well matched with CIGS (112) plane (around 3.3 Å), but has larger mismatch with CZTS the main spacing (112) plane measured to be 3.13 Å.

The CBD synthesized CdS is more like Cd (S,O) with O homogeneously distributed within the depth of the CdS film (Figure 3.4.3.31). This is likely because the O is from Cdₓ(OH)ᵧ in the CBD of CdS synthesis process serving as an importance nuclei for deposition of well-adhered CdS film. The problem of CdS is its lower badgap around 2.4 eV estimated tauc plot shown in Figure 3.4.3.32. A significant drop of the transmission at wavelength range of 500-530nm is due to the absorption by CdS (shown in Figure 3.4.3.32).
Absorption of CdS will result in less absorption in the underlying absorber. Such problem can be resolved by reducing the thickness of CdS. Along with the decreasing thickness, the absorption of incident light at "blue" region is reduced (shown in Figure 3.4.3.34).

Another solution is by replacing CdS with an alternative high bandgap buffer. One critical criterion is the optimal conduction band alignment to meet the requirement of ideal heterojunction. Our measured conduction band offset between synthesized CdS and CZTS is an unfavorable cliff around 0.2-0.3 eV, resulting in the detrimental interface recombination. Based on the estimation of conduction-band alignment between CZTS absorber and various buffer options carried out at Australian Synchotron [Yan C., Liu F., Song N., Ng B. K., Stride J. A., Tadich A, Hao X.J., “Band alignments of different buffer layers (CdS, Zn(O,S), and In2S3) on Cu2ZnSnS4”, Applied Physics Letters, 104, 173901 (2014)]. Based on this result, a promising hybrid buffer material were presented. With the band alignment improved from cliff-like to spike-like by this hybrid layer, the open circuit voltage was increased from around 650mV to 714 mV. This Voc improvement was verified to be reproducible. In addition to the improvement in Voc. Details of this approach will be disclosed in 2015 Annual report.

### 3.4.3.2.4 Al:ZnO (AZO) window layer

Among transparent conducting oxides, AZO is the most promising material for window layers in thin film solar cells and modules because of its wide band gap, high conductivity, relatively low cost and the non-toxicity of the material [3.4.3.18]. Many techniques have been employed to fabricate AZO
films. However, magnetron sputtering is the most promising, permitting deposition at low temperature, and giving better adhesion on the substrate and higher film density than other methods. For its application in CZTS solar cells, AZO needs to be also highly transparent in UV range and near IR range as well. The latter requires the AZO has high mobility to remain the low resistivity since in the near IR range free carrier absorption dominants. In order to prepare AZO thin films with low resistivity and high transparency for its application in CZTS thin film solar cells, the influences of the thickness and substrate temperature on the structural, electrical, and optical properties of AZO films were investigated.

AZO films deposited in Ar atmosphere

The AZO films were deposited on quartz substrates by sputtering a 2 wt.% Al₂O₃ doped ZnO target. In order to minimize the plasma bombardment damage on the substrates, a lower RF power was applied on the target. As the film is thicker than 140 nm, TEM (Figure 3.4.3.38) and AFM (Figure 3.4.3.39) images indicated that the growth mode changed from vertical to lateral. A lateral growth mode is beneficial for forming high quality films. The growth mode transition maybe due to the decreasing stress within the grains as the film thickness increases. Bulk resistivity, carrier concentration and Hall mobility changed accordingly, as displayed in Figure 3.4.3.35.

**Figure 3.4.3.35:** Bulk resistivity, carrier concentration and Hall mobility of AZO films as a function of film thickness.

**Figure 3.4.3.36:** Optical transmission of AZO films as a function of film thickness.

**Figure 3.4.3.37:** Square of the absorption coefficient as a function of photon energy for AZO thin films with different thicknesses.
Figure 3.4.3.38: TEM image of AZO film with thickness of 551 nm.

Figure 3.4.3.39: AFM images for films with different thickness: (a) 67nm (b) 335nm (c) 551nm.

The average transmission is higher than 85% for all AZO layers in the wavelength range of 390 to 1100 nm, as shown in Figure 3.4.3.36. The obvious drop in transmission of the IR region as film thickness increases is mainly due to the increment of free carrier absorption. Such transmission drop can be reduced by decreasing the free carrier concentration while increasing the mobility without sacrificing the desired resistivity. Figure 3.4.3.37 shows that the Eg of AZO film increases from 3.4 to 3.55 eV with its thickness increasing from 143 to 551 nm, which can be explained by the Burstein-Moss shift.

The deposition temperature of AZO is critical that needs to be high enough to yield good crystallinity and low resistivity of AZO while has no detrimental effect on the underlying CZTS absorber and thereby formed heterojunction. AZO films were prepared under different substrate temperatures, from room temperature (RT) to 450 °C. To ensure high transmission and low resistivity, the film thickness of around 330 nm was chosen. Other deposition parameters were retained the same as previously detailed. The minimum resistivity was obtained from the sample prepared at 250 °C, as shown in Figure 3.4.3.40. The electrical properties of the film deposited at RT were beyond the detection limit and therefore not shown here. The electrical properties of the film are improved as the substrate temperature increases from RT to 450 °C. This may be explained by increased grain size and thus reduced grain boundaries with an increase in the substrate temperature. However, the electrical qualities deteriorate at temperature above 250 °C. This can be expected since the grain boundary barrier was known to increase with the substrate temperature above 200 °C.

Figure 3.4.3.41 shows the optical transmission of AZO films prepared under various substrate temperatures. The average transmission was higher than 85% for all AZO layers in the wavelength range of 390 to 1100 nm. The lowest transmittance in the IR region is obtained from the sample prepared at 250 °C which was attributed to the highest free carrier concentration. Correspondingly, as
we can see in Figure 3.4.3.42, this sample had the largest $E_g$ of 3.5 eV as a result of the Burstein-Moss shift. Therefore, 250 °C is close to the optimum substrate temperature that allowing the synthesis of high quality AZO films and in the meanwhile will not decompose the underneath CZTS absorber. However, the mobility needs to be improved to reduce the free carrier concentration to allow for retaining the desired low resistivity.

**Figure 3.4.3.40:** Electrical properties of AZO films as a function of substrate temperature.

AZO films deposited in H$_2$ & Ar atmosphere
The AZO films were deposited on quartz substrates by sputtering a similar 2 wt.% Al$_2$O$_3$ doped ZnO target. The deposition processes were conducted in an atmosphere of Ar:H$_2$=95:1. The substrate temperature was retained at 200 °C. H$_2$ added to the sputtering ambient could reduce absorbed O$^-$ on ZnO grain boundaries by reacting with O$^-$ to form complexes. This can return carriers to conduction band and thus increase the measured Hall mobility. H$_2$ addition also enables environment to form V$_0$ and Zn$_i$. In ZnO, only H$^+$ is stable, and hence hydrogen exclusively acts as a donor. Such deposited AZO films were compared with that of NREL’s used in their high efficiency CIGS solar cells. As shown in Table 3.4.3.2, both of our films have higher mobility, lower carrier concentration and lower resistivity than that of NREL’s, which will maintain the desired resistivity while reduce the IR absorption.

**Figure 3.4.3.41:** Transmission of AZO films as a function of substrate temperature.

**Figure 3.4.3.42:** Optical band-gap of AZO films as a function of substrate temperature.
<table>
<thead>
<tr>
<th>Thickness (nm)</th>
<th>Resistivity (Ωcm)</th>
<th>Carrier concentration (cm⁻³)</th>
<th>Mobility (cm²/Vs)</th>
<th>Average Transmission (390nm-1100nm)</th>
<th>Bandgap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UNSW 283</td>
<td>2.7×10⁻⁴</td>
<td>4.4×10¹⁰</td>
<td>57.9</td>
<td>86.9</td>
<td>3.75</td>
</tr>
<tr>
<td>UNSW 123</td>
<td>5.7×10⁻⁴</td>
<td>2.6×10²⁰</td>
<td>43</td>
<td>87.9</td>
<td>3.72</td>
</tr>
<tr>
<td>NREL 120</td>
<td>8.5×10⁻⁴</td>
<td>5.6×10²⁰</td>
<td>13</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### 3.4.3.3 CZTS/Si multijunction solar cells

The highest efficiency solar cells achieved so far is by using single crystal III-V semiconductor homojunctions grown on Ge substrates to form monolithic three-junction cells. All three junctions must be approximately lattice-matched to minimize crystal imperfections, which will reduce minority-carrier recombination times and hence cell efficiencies. The lattice matching requirement limits the choice of bandgaps and thus the efficiencies, although efficiencies over 41% have been achieved under high light concentrations. In addition, their high cost has limited the applications of these cells to space and to high concentration photovoltaic systems. The high cost of high concentration PV system itself has been a substantial drawback. In contrast, Si is an optimum choice as the bottom cell for tandem application. For a single cell, Si record cell (25% at UNSW) has already achieved 86% of the silicon limit (29%). Until now silicon wafer based cell still accounts for about 90% of the solar cell market and will continue to dominate the PV market in the future. Any concept, allowing significant boost to higher efficiency and lower cost, and fully making advantage of and being compatible with commercialized Si wafer cell technology, would be a natural “add-on” to Si wafer based PV. The concept of a tandem cell with Si as bottom cell offers the best opportunity to boost the efficiency beyond 30% or even 40%. This suggests the use of absorber system which is lattice matched with Si and also flexible in tuning to the desired bandgap combination for tandem cells.

**CIGS** has been shown to have a large range of bandgap tunability. However, a lattice matched substrate suitable for their growth acting as bottom cell is absent. On the other hand, even though CIGS based chalcopyrite devices has been reported as the highest efficiency (20.3%) in thin film solar cell area, efficiencies are still lower as compared to single crystalline solar cells based on Si (25% at UNSW) or GaAs (29% under unconcentrated light). The question arises how far the polycrystalline nature of these materials limits their efficiencies. Single crystalline materials, obtained by single crystal or epitaxial growth would bear the possibility to avoid the disadvantageous influence of grain boundaries and interfaces in this compound. CZTS, as the most promising substituting material for CIGS, is suitable for epitaxial growth on Si due to very low lattice mismatch and also feasible for the tandem cell structure due to its large tunable bandgap range, spanning a wider range in energy beyond 2.25 eV which is above the accessible range for the highest efficiency III-V top junction materials. Therefore this will allow the exploration of both CZTS family/Si based tandem cells by taking advantage of single crystalline CZTS and mature Si wafer cell technology.

#### 3.4.3.3.1 CZTS on Si substrate

**CZTS on Si with different orientation**

Hetero-epitaxial growth is a highly desirable approach for achieving high quality single-crystalline or preferred-orientation materials. One-stage fabrication is necessary for such epitaxial growth. Si and ZnS/Si were investigated as alternative substrates to engineer the crystalline properties of CZTS. Orientated CZTS film was obtained by using these substrates. This allows for alternative paths for forming high quality crystalline CZTS absorber with desired orientation.
About 400 nm CZTS thin films were deposited on different orientated Si wafers by sputtering of a single CZTS target. The orientation of Si wafer used for substrates are (100), (100)\(^4^\)°, (111), (111)\(^4^\)° and (110). It was found in Figure 3.4.3.43, that the XRD patterns of the thin films show the preferred orientations of the (112), (220) depending on the substrate orientation. Here we use the intensity ratio of \(I_{220}\)/\(I_{112}\) to relatively compare the variation of preferred orientation upon various substrates. As shown in Table 3.4.3.3, the maximal ratio of \(I_{220}/I_{112}\) of CZTS thin films is obtained on Si (110) substrate while that of the minimal is on Si (100) substrates, indicating CZTS grown on Si (100) yields preferred (112) orientation while that on Si(110) yields (220) preferred orientation. This proves the concept that CZTS with desired orientation could be achieved by surface engineering of the Si substrate and thus the increased CZTS solar cell performance resulting from the high quality of CZTS absorber with desired crystallographic orientation. The mechanism of the effect needs to be further studied.

**Table 3.4.3.3**: \(I_{220}/I_{112}\) of XRD peaks of CZTS films on Si substrates with different orientations.

<table>
<thead>
<tr>
<th>Substrate orientation</th>
<th>(I_{220}/I_{112})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(100)</td>
<td>0.082</td>
</tr>
<tr>
<td>(100)(^4^)°</td>
<td>0.115</td>
</tr>
<tr>
<td>(111)</td>
<td>0.223</td>
</tr>
<tr>
<td>(111)(^4^)°</td>
<td>0.286</td>
</tr>
<tr>
<td>(110)</td>
<td>0.298</td>
</tr>
</tbody>
</table>

Figure 3.4.3.44 presents Raman scattering spectra of CZTS thin films. The trend of intensity of CZTS peaks upon substrate orientations agres well with that of XRD, indicating crystalline of CZTS thin films is affected by the orientation of the Si substrates.

Figure 3.4.3.45 shows the SEM micrographs of CZTS films. All CZTS films are columnar structured but slightly different in crystal size and shape, suggesting that the morphology of CZTS thin films is also affected by the orientations of the Si substrates.
Figure 3.4.3.44: Raman spectra of CZTS films on Si substrates with different orientations.
Figure 3.4.3.45: SEM images of CZTS films on Si substrates with different orientations. (a) CZTS on Si (100) cross section, (b) CZTS on Si (100) surface, (c) CZTS on Si (100)4° cross section, (d) CZTS on Si (100)4° surface (e) CZTS on Si (111) cross section, (f) CZTS on Si (111) surface, (g) CZTS on Si (111) 4° cross section, (h) CZTS on Si (111) 4° surface, (i) CZTS on Si (110) cross section, (j) CZTS on Si (110) surface.
Figure 3.4.3.46: Concentration depth profile of CZTS film on Si (100).

Figure 3.4.3.46 shows the concentration depth profile of CZTS film on Si (100) substrate by XPS. From the surface to the interface of CZTS and Si, the relative concentrations of each element are almost constant. It is notable that an obvious oxygen hump is presented at the Si/CZTS interface which might be due to SiO$_2$ formed on the surface of the Si wafer before CZTS was deposited on it. This is likely because of long duration pumping down required for achieving the desired base pressure due to the lack of load lock in current sputter system. This might also be due to the reaction between Si wafer and sputtered species, which needs further investigation.

CZTS on ZnS-coated Si substrates

A thin ZnS layer was deposited on HF-dipped Si wafer by thermo evaporation and thereafter the ZnS-coated wafer was used as a substrate for CZTS deposition. The same deposition parameters used in the deposition of CZTS on Si wafer were applied to the deposition of CZTS on ZnS-coated Si. Figure 3.4.3.47 shows the TEM image of CZTS on ZnS-coated Si. Both ZnS and CZTS are polycrystal and in columnar structure.

Sulfurisation annealing was applied with an aim of improving the CZTS film crystallinity. 530 °C was found a favourable temperature for sulfurization annealing of CZTS on ZnS-coated Si. To improve the film quality, we have extended the sulfurization annealing duration from 5 min to 0.5 hour. Figure 3.4.3.48 shows that after 5 mins sulfurization, the intensity of (112) increased and the ratio of I$_{220}$/I$_{112}$ changed from 0.717 to 0.244, indicating the improved crystallinity with the preferred orientation of (112). In addition, there is no significant change in the surface roughness as shown in the background of Raman spectra (Figure 3.4.3.49). With the annealing time extended to 0.5 hour, I$_{220}$/I$_{112}$ continues to decrease to 0.092, indicating the further growth of CZTS crystal along the
orientation of (112). The growth of CZTS crystal can also be evidenced by the significant increase in the scattering of incoming laser beam indicating the much rougher surface resulted from bigger CZTS crystal size.

**Figure 3.4.3.48**: XRD patterns of CZTS films on Si (100) sulfurized at 530 °C within 5min and 0.5h.

**Figure 3.4.3.49**: Raman spectra of CZTS films on Si (100) sulfurized at 530 °C within 5min and 0.5h.

**Epi-CZTS on sapphire substrate**

The theoretical highest achievable conversion efficiency for CZTS exceeds 30% [3.4.3.18]. However, to date, the highest efficiency of the CZTS solar cell is only 8.4% reported by Shin, B., et al. [3.4.3.19], which is considerably less than other chalcogenide based solar cells (Cu(InGa)Se 2:20.4%). To fully explore the potential of CZTS for single-junction solar cells as well as its combination with Si wafer cells for high efficiency tandem solar cells, a better understanding of the fundamental properties of the CZTS absorber itself by obtaining high-quality single crystalline material is essential. However, it is well acknowledged that growth of high quality single crystals is particularly difficult for quaternary compounds. Therefore, epitaxial growth might be an alternative route to achieve crystalline CZTS films.

As aforementioned of problem of Si wafer oxidisation prior to the sputtering process, sapphire substrate, inert to the air atmosphere, was adopted for explore the capability of the epitaxial growth of CZTS film by RF magnetron sputtering from a single CZTS target. As discussed as follows, we demonstrated the successful epi-CZTS thin film on sapphire (0001) substrates by RF magnetron sputtering.

The sputtered CZTS thin film is mirror-like from appearance. The surface morphology and microstructure were characterized by atomic force microscopy (AFM). The film displayed granular surface structure with a root-mean-square roughness of 5.44 nm, which is typical for thin films grown
by sputter epitaxy technology, suggesting a three-dimensional island-like growth mechanism. Figure 3.4.3.50 (a) shows a typical XRD 0-2θ pattern of the sputtered film. Along with the diffraction peaks of sapphire (0003), (0006), (00012), only (112), (224), (336) peaks of the kesterite structure of the CZTS film are observed (JCPDS No. 026-0575), which indicates that the film is highly oriented in (112) direction parallel to sapphire (0001). Complementary Raman spectroscopy measurements were performed to rule out the existence of secondary phases. Figure 3.4.3.50 (b) shows a typical Raman spectrum with no sign of secondary phases within the detection limit: all the peaks near 257, 288, 338 and 370 cm\(^{-1}\) can be attributed to CZTS phase.

![Figure 3.4.3.50: (a) XRD pattern (b) Raman spectrum of sputtered CZTS film on sapphire (0001).](image)

To obtain the in-plane ordering as well as determine the epitaxial relationship between as-prepared CZTS and sapphire substrate, XRD Phi scans were further performed with Empyrean diffractometer with Cu Kα (λ=1.5406 Å) radiation. Curves in Figure 3.4.3.51 show the Phi-scan spectrum recorded at CZTS \{204\}/\{220\} (Chi=34.72°, \(2θ=47.327^°\)), along with that for sapphire \{02\(\bar{2}\)4\} (Chi=57.11°, \(2θ=52.527^°\)). Sharp distinct reflexes represent the well-defined azimuthal alignment of the CZTS lattice planes. Similar to CuInS\(_2\) on sapphire (0001) [3.4.3.20], six peaks instead of three, are observed, which was also reported in CuInS\(_2\) epilayer on sapphire (0001) substrates by RF reactive sputtering and CuInS\(_2\) epilayer on Si (111) substrates by molecular beam epitaxy (MBE) [3.4.3.21]. Both 60 degree and 180 degree rotations would account for the outcome of six peaks. The rotations might be caused by the existence of anti-phase domain, which needs to be further investigated. From the Phi-scan measurements, an in-plane orientation relationship of CZTS[20\(\bar{1}\)] || sapphire (01\(\bar{1}\)0) can be concluded.

![Figure 3.4.3.51: In-plane Phi scan of CZTS film recorded at \{204\}/\{220\} and sapphire substrate recorded at \{02\(\bar{2}\)4\}.](image)
Sapphire has a hexagonal structure, while CZTS crystallizes tetragonal. The structure distinction seems less likely to result in the epitaxial growth between these two materials. Figure 3.4.3.52 depicts the projections of the CZTS and sapphire unit cells on the (112) and (0001) planes, respectively. In Figure 3.4.3.52 (a), the top graph stands for CZTS unit cell in which S atoms were blocked by other cations in this projection, while the bottom one stands for the surface network of CZTS layer. A hexagon can be observed in the (0001) -projected sapphire unit cell, if considering Al atoms only. In contrast, a similar concentric hexagon exists in the CZTS (112) projection. The similarity of the hexagonal feature of both unit cells in the depicted projections reveals the possibility for heteroepitaxy. The side length of the hexagon in the sapphire {0001} plane is 0.47587 nm, and 0.38368 nm in the CZTS {112} plane, corresponding to a mismatch of approximately 19.4%. However the mismatch reduces to 3.2% if one considers a group of five sapphire and six CZTS hexagons. The thermal expansion coefficient of CZTS is similar to that of CuInS$_2$ ($\alpha_c=9.6 \times 10^{-6}$ K$^{-1}$), as well as comparable with that of sapphire ($\alpha_c=4.75 \times 10^{-6}$ K$^{-1}$). The similarity in plane hexagonal symmetry, well matched lattice spacing, as well as comparable thermal expansion coefficient in the growth direction would enable the epitaxial growth of CZTS on sapphire (0001) substrates.

In addition to XRD, TEM was used to obtain a deeper insight into the internal microstructure. Figure 3.4.3.53 shows a HRTEM cross-sectional image of CZTS-sapphire interface region. Similar to CuInS$_2$ epilayer grown on sapphire by reactive sputtering, an interfacial layer with a thickness of a few angstroms formed between the sputtered CZTS film and the sapphire substrate. However, in general, the CZTS layer is well aligned with the substrate and has a highly ordered structure in accordance with the XRD results.
Among the hetero-epitaxial work, epi-CZTS on ZnS was selected as the cover of Physical Status Solidi Rapid Research Letters (see Figure 4.4.3.54).

A 1.8% efficient bifacial CZTS solar cell on ITO coated glass was achieved for 4-terminal tandem cells (see Figure 4.4.3.55).

Figure 4.4.3.53. Cross-sectional HRTEM image recorded at the interface region.

Figure 4.4.3.54. Epi-CZTS work on ZnS wafer was selected as a cover of Physical Status Solidi Rapid Research Letters.

Figure 4.4.3.55. Working bifacial CZTS solar cells on ITO glass.
References


3.4.3.7 J.G. Bolke, Investigation of surface phase formation during Sn-rich growth of Cu$_2$ZnSnS$_4$ polycrystalline thin films for solar cells, The University of Utah, 2012, pp. 1-49.


3.4.3.11 Chou C-y and Chen S-w 2006 Phase equilibria of the Sn-Zn-Cu ternary system Acta Materialia 54, 2393-2500.


3.4.3.15 X. Zhu, Z. Zhou, Y. Wang, L. Zhang, A. Li, and F. Huang, Solar Energy Materials and Solar Cells 101(0), 57 (2012).


3.5 Third Generation Strand - Advanced Concepts

**University Staff:**
Prof. Gavin Conibear (group leader)
Dr Richard Corkish
Prof. Martin Green

**Senior Lecturers:**
Dr Santosh Shrestha
Dr Ivan Perez-Wurfl

**Senior Research Fellows:**
Dr Shujuan Huang
Dr Dirk König

**Research Fellows:**
Dr Xiaojing “Jeana” Hao (ARENA Fellow)
Dr Supriya Pillai (ARENA Fellow)

**Postdoctoral Fellows:**
Dr Robert Patterson (ARENA Fellow)
Dr Binesh Puthen-Veettil (ARENA Fellow)
Dr Yu Feng
Dr Xiaoming Wen
Dr Craig Johnson (ARENA Fellow)
Dr Siva Karaturi (until April 2014)
Dr Yuanxun Liao (from Nov 2014)
Dr Pengfei Zhang (from Nov 2014)

**Professional Officers:**
Dr Tom Puzzer (part time)
Dr Patrick Campbell (shared with Thin Film)
Mark Griffin (shared with Thin Film)

**Higher Degree Students:**
Haixiang Zhang (until Sept 14)
Tian Zhang
Pengfei Zhang (until Sept 14)
Sanghun Woo
Yao Yao (until Sept 14)
Neeti Gupta
Chien-Jen “Terry” Yang
Ibraheem Al Mansouri (until Dec 14)
Yuanxun “Steven” Liao (until Sept 14)
Suntrana Smyth (until Sept 14)
Lingfeng Wu
Xuguang Jia
Ziyun Lin
Hongze Xia
Xi Dai
Shu Lin
Abstract

Silicon nanostructure tandem cells have seen an increase in understanding of the materials and of the growth conditions required for good material. This has now allowed much greater repeatability of results. The devices have seen $V_{oc}$ over 500mV and currents increased significantly by anti-reflection and light trapping approaches. Device integrated vertically have been developed further with pseudo conductive substrates fabricated from either silicon rich silicon carbide or molybdenum.

Hot carrier cell work has seen further development of modelling of phonon energies. Deposition and characterisation of several promising hot carrier absorber materials including hafnium nitride and Si nanoparticles. Carrier cooling rates have been measured as quite slow in these materials and long lifetimes measured for both HfN and Si nanoparticles. Nanoparticle arrays of high 2D crystalinity have been developed to 3D stacks. Very long hot carrier lifetimes have been measured in these materials indicative of phonon bottleneck effects restricting cooling. Several materials combinations have now been demonstrated as resonant tunnelling energy selective contacts with a big improvement, more than 5 fold, increase in quality factor of energy selection. A new strand has been developed of investigating optical extraction of energy from hot carriers with modelling of enhanced external luminescence and reduced radiative lifetime, experimental work on this approach is commencing.

Erbium doped phosphors for up-conversion are made in-house. Improvements in the mesoporous structure have increased efficiency of up-conversion. Sensitisation of Er using PbS quantum dots has shown increased sensitivity to shorter wavelengths.

Photoelectrochemical cells using both a photo-anode and a photo-cathode continue to be developed. A combined hematite silicon carbide device has shown spontaneous water splitting under illumination.

Third generation approaches are developing well and integrating with each other and with other projects. Nanoparticles are proving increasingly important because of their versatility of properties.

3.5.1 Third Generation Photovoltaics

The "Third Generation" photovoltaic approach is to achieve high efficiency whilst still using "thin film" second generation deposition methods. The concept is to do this with only a small increase in areal costs and to use abundant and non-toxic materials and hence reduce the cost per Watt peak [3.5.1]. Thus these "third generation" technologies will be compatible with large scale implementation of photovoltaics. The aim is to decrease costs to well below US$0.50/W, towards US$0.20/W or better, by dramatically increasing efficiencies but maintaining the economic and
environmental cost advantages of thin film deposition techniques (see Fig. 4.1.3 showing the three PV generations) [3.5.1, 3.5.2]. To achieve such efficiency improvements such devices aim to circumvent the Shockley-Queisser limit for single band gap devices that limits efficiencies to the “Present limit” of either 31% or 41% (depending on concentration ratio). This requires multiple energy threshold devices such as the tandem or multi-colour solar cell. The Third Generation Strand is investigating several approaches to achieve such multiple energy threshold device [3.5.1, 3.5.3].

The two most important power loss mechanisms in single-band gap cells are the inability to absorb photons with energy less than the band gap (1 in Fig. 3.5.1), and thermalisation of photon energy exceeding the band gap, (2 in Fig. 3.5.1). These two mechanisms alone amount to the loss of about half of the incident solar energy in solar cell conversion to electricity. Multiple energy threshold approaches can utilise some of this lost energy. Such approaches do not in fact disprove the validity of the Shockley-Queisser limit, rather they avoid it by the exploitation of more than one energy level for which the limit does not apply. The limit which does apply is the thermodynamic limit shown in Fig. 3.1.3, of 68.2% or 86.8% (again depending on concentration).

Figure 3.5.1: Loss processes in a standard solar cell: (1) non-absorption of below band gap photons; (2) lattice thermalisation loss; (3) and (4) junction and contact voltage losses; (5) recombination loss.

In the Third Generation Strand, we aim to introduce multiple energy levels by fabricating a tandem cell based on silicon and its oxides, nitrides and carbides using reduced dimension silicon nanostructures to engineer the band gap of an upper cell material. We are aiming to collect photo-generated carriers before they thermalise in the “Hot Carrier” solar cell. Also we are investigating absorption of two below bandgap photons to produce an electron-hole pair in the cell by up-conversion in a layer behind the Si cell using erbium doped host materials. In order to optimise the requisite properties, all these structures are likely to be thin hence maximising absorption of light in thin structures through light trapping is very important. Hence we are also investigating localised surface plasmon enhanced coupling of light into these Third Generation devices.
3.5.2 Si nanostructure solar cells
Researchers:
Ivan Perez-Wurfl, Binesh Puthen-Veettil, Lingfeng Wu, Xuguang Jia, Ziyun Lin, Tian Zhang, Terry Yang, Keita Nomoto, Gavin Conibeer

3.5.2.1 The “all-Si” Tandem cell

We are developing a material based on Si (or other group IV) quantum dot (QD) or quantum well (QW) nanostructures, from which we can engineer a wider band gap material to be used in tandem photovoltaic cell element(s) positioned above a thin film bulk Si cell, see Fig. 3.5.2.

Previously we have demonstrated the ability to fabricate materials which exhibit a blue shift in the effective band gap as the QD or QW size is reduced, using photoluminescence [3.5.4] and absorption [3.5.5] data [3.5.6]. A thin film deposition of a self-organised QD nanostructure is achieved through a sputtered multi-layer of alternating Si rich material and stoichiometric dielectric [3.5.4]. On annealing the excess Si precipitates into small nanocrystals which are limited in size by the layer thickness, thus giving reasonable size uniformity, as first demonstrated by Zacharias [3.5.7]. Demonstration of doping of these layers with both phosphorus and boron to create a rectifying p-n junction has resulted in devices with a photovoltaic open circuit voltage of 490mV [3.5.6, 3.5.7, 3.5.8].

Figure 3.5.2: A tandem photovoltaic cell using quantum confined QDs or QWs to engineer the band gap of the top cell and potentially also the lower cells. Short wavelength light is absorbed in the top cell and longer wavelengths in lower cells, thus boosting the overall voltage generated and hence efficiency. Formation of Si (or Ge or Sn) QDs through layered thin film deposition of Si rich material which crystallises into uniform sized QDs on annealing.

A cell based entirely of Si, or other group IV elements, and their dielectric compounds with other abundant elements (i.e. silicon oxide, nitride or carbide) fabricated with thin film techniques, is advantageous in terms of potential for large scale manufacturability and in long term availability of its constituents. Such thin film implementation implies low temperature deposition without melt processing, it hence also involves imperfect crystallisation with high defect densities. Hence devices must be thin to limit recombination due to their short diffusion lengths, which in turn means they must have high absorption coefficients.

For photovoltaic applications, nanocrystal materials may allow the fabrication of higher band gap solar cells that can be used as tandem cell elements on top of normal Si cells [3.5.11, 3.5.12]. For an AM1.5 solar spectrum the optimal band gap of the top cell required to maximize conversion efficiency is ~1.7 to 1.8eV for a 2-cell tandem with a Si bottom cell [3.5.13]. To date, considerable work has been done on the growth and characterization of Si nanocrystals embedded in oxide [3.5.7, 3.5.14] and nitride [3.5.15, 3.5.16] dielectric matrices. However, little has been reported on the experimental properties of Si nanocrystals embedded in SiC matrix [3.5.17]. These are of particular
interest for application in photovoltaic devices because of an expected significant increase in carrier transport due to a decrease in the barrier height between adjacent nanocrystals [3.5.18]. As a result, sufficient carrier mobility can be obtained to satisfy device fabrication requirements.

3.5.2.2 Modelling of absorption and electrical properties of materials and devices

Optical models have been developed previously. [Jia] Device models have also been developed and applied to existing cells [Perez-Wurl]. Further modelling on absorption and measurement and modelling of photoluminescence for an overall picture of photogeneration in these materials.

The main focus of work in this period has been to characterise silicon quantum dot materials more thoroughly to better understand the parameters required to fabricate better performing devices. We have focused on developing these key building blocks independently with the intention of putting them together in a device that will perform with improved properties. A significant amount of effort has gone into developing a better understanding of the material by means of developing models and characterisation techniques. The results of these efforts are now being assessed by the scientific community either as conference presentations, scientific paper submitted to technical journals or both. The details of these publications are listed in the section below on publications.

We have identified a key aspect to ensure an improved efficiency of these devices, namely, a contact layer compatible with high temperature processing. As such, we have made use of external facilities to investigate two possible solutions: Molybdenum and Aluminium Zinc Oxide. Both approaches have shown potential as the desired contact but will need to be tested on the actual device structure to confirm compatibility.

Our focus on modelling and characterisation has resulted in a strong framework to assess the material quality required to be deposited. With the models developed we are now capable of using photoluminescence (PL) as a characterisation tool well beyond its initial limited applicability. PL was originally used to identify a peak in the emission that was loosely linked to the size of the Si Quantum Dots (Si QD). Our current model allows us now to identify average Si QD size and its variation. This feedback will become a key factor when depositing Si QD material. PL measurements take only a few seconds so that our current model will allow us to optimise the material within a few weeks. PL has also been used to demonstrate the ability of reducing defects in the material with the use of Boron. Using a combination of steady state, transient PL and Electron paramagnetic Resonance measurements we have confirmed Boron can be used to mitigate the effect of defects. Ellipsometry is another characterisation technique that will be essential to calibrate and monitor thickness and composition of our films. An ellipsometry measurement also takes a few seconds to perform but it is only useful if a reliable optical model is available. We have developed a model that allows us to use this technique with complete confidence. We have also developed unique electrical models to identify the electronic quality of the Si QD material. Specifically, capacitance-voltage measurements and temperature dependent I-V properties can be used to determine doping, trap density and effective bandgap. The feedback to the fabrication using these techniques is much slower than PL and ellipsometry as they require the fabrication of devices. However, these electrical characterisation techniques along with the specific models we have developed, will allow us to optimise the devices in a much more effective manner.

In summary, we have put in place a set of characterisation tools and models to allow us to optimise the material in a short time once we get access to key equipment in our labs. We have also demonstrated two possible solutions to address the key issue of contacts compatible with high temperature processing.

3.5.2.3 Heterojunctions devices

In this work the aim is to develop two different structures for vertical structured Si quantum dots (QDs) solar cells to avoid previously found current crowding effect in mesa-structures. The working mechanisms are demonstrated in Figure 3.5.3 a vertical structure is expected to eliminate the lateral carrier transport since all current would flow perpendicular to the junction. Additionally, a vertical
structure will be necessary in the future to stack single junction Si QDs solar cells in series to form full tandem structure. In this work, two approaches are currently under investigation: Approach 1, using Molybdenum (Mo) as back contact interlayer; and Approach 2, membrane cells through rear vias method. Schematic diagrams for these two approaches are illustrated in Figure 3.5.3.

Figure 3.5.3: Mechanisms of current flows in (left) the mesa-structured and (right) the proposed vertical structure Si QDs solar cells. The effect of current crowding due to high lateral resistance to the back contact in mesa-structure is overcome in the vertical structure (not to scale).

For the first approach, Si QDs solar cell is patterned and sputtered on Si or fused silica substrates that have a pre-sputtered metal interlayer as back contact. Mo is selected for this contact layer due to its high melting point, good electrical conductivity, and high optical reflectivity. As the Mo interlayer will be annealed under 1100°C along with the Si QDs bilayers to assist Si nanocrystal formations, the key task is to guarantee the thermal stability of the interface between the Mo interlayer and the Si QDs bilayers. The silicon nanostructures are first deposited and then annealed. After annealing, the formation of Si nanocrystals was confirmed using both Raman and PL spectroscopy. From the Raman spectra in Figure 3.5.4 (left), sharp Raman shifts at 521.5 cm⁻¹ were identified from all n-i-p mesas with different device sizes. The 1.5 cm⁻¹ shift of this peak compared to the reference Si peak at 520 cm⁻¹ was within the resolution of the Raman station (1.7 cm⁻¹), which indicated the presence of Si QDs in n-i-p mesas. PL measurement was conducted using a violet-blue laser with 405 nm wavelength. Normalized PL spectra of these two devices were present in Figure 3.5.4 (right) and a peak at around 1.37 eV was found. The domain of the peak position in this work is consistent with previous results, which also verified the formation of Si QDs in the vertical devices.

Figure 3.5.4: (left) Raman spectra of n-i-p devices with varied sizes; (right) normalized PL of n-i-p devices with 5000 um² and 2500 um² sizes respectively
IV characterizations were determined using DarkStar IV measurement station under both dark and 1-Sun illuminated conditions. Measurement connection and IV curves of device with 2500 um² size are shown in Figure 4. The IV characteristics demonstrated rectifying feature and light response, indicating the existence of diode within the device. From the 1-Sun illuminated IV curve, \( V_{oc} = 40 \text{ mV} \) and \( J_{sc} = 2.7 \times 10^{-4} \text{ mA/cm}^2 \) were extracted respectively. It was noted that the device had a shunting issue, which limited its overall performance.

**Figure 3.5.5:** (left) IV measurement connection, and (right) dark and 1-Sun illuminated IV curves of 2500 um² device. The inset shows the zoomed in IV curves of the same sample in voltage range of (-0.1, +0.1) V.

For the second approach, a membrane of Si QDs cell is fabricated on a SiO₂ window deposited on Si wafer. The SiO₂ layer, which will be removed after annealing in order to allow metal evaporation from the back, serves as a mechanical support for the sputtered Si QDs bilayers; it also acts as a buffer layer that blocks the responses from the Si wafer substrates. As this structure allows post-metallization, there is no need to pre-sputter and anneal any back contact metals that have to withstand high temperature process, making the whole structure more sustainable.

**Figure 3.5.6:** Schematic diagram of proposed vertical structures using (left) Approach 1: using Mo as back contact interlayer; and (right) Approach 2: membrane cells through rear window method.

By the end of this project, it is expected that working single junction Si QDs solar cells with vertical structures can be fabricated using both of the proposed schemes. Characterizations including Si crystallinity, interface properties, current-voltage characteristics will be conducted. Improvements in current output will be quantified and compared with the previous mesa-structured devices. It is also expected to see the possibilities of making real tandem Si QDs solar cells by stacking different single junction cells in series based on these vertical structures.

### 3.5.2.5 Tandem Si QD cells

The first tandem devices have been demonstrated with a series connection of two solar cells:

- a large bandgap (1.8 to 2eV) SRO pin diode on top of a pn junction solar cell on a silicon substrate and
- a medium bandgap device (1.4 to 1.6 eV) on top of a thin film polycrystalline pn solar cell.
These devices have at least a 30% larger efficiency than that of a single junction Si QD device.

The tandem structure demonstrated is a Si-QD solar cell mechanically stacked on a silicon thin film solar cell on glass. The reason for choosing this device configuration is due to the bandgap of the Si-QD cell. According to its PL emission, the bandgap of the Si-QD solar cell is around 1.4 eV. A silicon thin film solar cell was then required as the bottom cell to and a working tandem device was successfully fabricated. The open circuit voltage was improved in the tandem cell compared to the top Si-QD by 56.5%. The short circuit current of the tandem cell was somewhat unexpectedly improved as well by 66.4%. The improvement of the efficiency of the tandem structure compared to the top Si-QD cell was demonstrated to be 172%. A diagram of the mechanically stacked solar cell is shown in Figure 3.5.7. Notice that the need for mechanical stacking is unavoidable in the case of the thin silicon on glass solar cell because the base and emitter contacts are on the same side of the cell just as in our QD solar cells.

**Figure 3.5.7:** Schematic diagram of the mechanically stacked Si-QD solar cell on a thin film Si solar cell. Top cell absorbs short wavelength photons, bottom cell absorbs mid range photons and partially absorbs long wavelength photons. Some of the reflected photons make it back to the top cell and improve the short circuit current compared to that of the Si-QD cell on its own.
Pictures of the actual device on its test fixture are shown in Figure 3.5.8.

**Figure 3.5.8:** (A) View of the Top cell Si QD cell (B) View of the rear showing the bottom thin film Si on glass cell.

The connection of the tandem solar cell is shown in Figure 3.5.8. Figure 3.5.8(A) shows the connection of the top cell while Figure 3.5.8(B) shows the connection of the bottom cell. They were connected in series using probes and wires as shown in the pictures. The area of bottom cell exposed to light was limited with a mask (white in picture A) to ensure it was the same size as the area of the top cell.

The device tested is an interdigitated solar cell with two large pads for ease of testing. The I-V characteristics of the tandem structure are shown in Figure 3.5.9.

**Figure 3.5.9:** I-V characteristics of the tandem structure compared to the Si-QD solar cell on its own. A working tandem structure is demonstrated here (illuminated I-V Tandem) to satisfy Milestone 5A.

The device performs as expected in terms of voltage; the open circuit voltage of the tandem structure is close to the sum of the open circuit voltage of each one of the cells individually tested. The short circuit current of the quantum dot cell, on the other hand, is actually improved by 66%. This is not an
expected result as the Si-QD solar cell, ideally sets the limit of the short circuit current. However, when the current of the individual devices in a tandem structure is not matched, the device with the higher current boosts the current of the device with lower current. The improved short circuit current in this case is due to the higher current available from the bottom cell. When the tandem structure operates under an external short circuit condition, some of the excess photocurrent from the bottom cell is injected into the top cell through the top cell shunt. The top cell is then actually operating in a reverse bias condition and the bottom cell is forward biased with the exact opposite voltage compared to the Si-QD cell. The current of the tandem device is then the short circuit current of the top cell plus the excess current injected from the bottom cell. The overall result is an improvement of the short circuit current and ultimately a higher improvement in the performance.

The improvements demonstrated are however not sufficient to make this device competitive yet with other similar tandem structures such as the Micromorph cell, also based purely on Silicon. The three key aspects to improve the technology are common to all other technologies, even those of very mature high efficiency technologies such as HIT or IBC cells. These key aspects are: improving fill factor, increasing the short circuit current of the top cell and improving the open circuit voltage of the top and bottom cells. These aspects are analysed in more detail to predict the potential benefits of improving the present limiting conditions.

3.5.2.6 Tandem Si QD cells

There are two activities in associated projects to report in this field:

The use of Si rich silicon carbide grown by sputtering for photoelectrochemical photocathodes. The application of colloidal Si QDs to a range of applications.

Si rich SiC:
Sputtered Si rich SiC is deposited in a similar way to SRO. This results in a material with modified bandgap between that of SiC and Si. It is predominantly cubic reproducing the 4c-SiC structure rather than the hexagonal forms. The material is usually doped p-type using Al or Sb doping but can be grown as n-type without any intentional doping.

The main application is as the p-type photocathode in a PEC cell.

Water splitting with evolution of hydrogen is achieved with a bias voltage of about 2.1V. This is seen to reduce to about 1.8V on illumination with white light.

One experiment carried out with a SiRSiC photo-cathode and a Fe₂O₃ (hematite) photo-anode achieved spontaneous water splitting under illumination when measured with a three terminal potentiostat.

Problems with parasitic reactions, usually oxidation of cathode and dissolution of anode are being further investigated.

Colloidal Si QDs:
Colloidal QDs of highly monodisperse particle size where the size can be either 5 or 10nm, are obtained from the University of Minnesota. These have been grown by a time of flight vapour CVD method and do give high size uniformity. Typically the NPs are capped with chlorine to prevent oxidation although they can be capped with SiO₂.

These colloidal NPs are investigated for hot carrier properties and for multiple exciton generation. Long lifetimes of a few ns have been observed using transient absorption. They have also been used in comparison of absorption measurements with photoluminescence to investigate the reasons for the difference between these measurements. The monodispersion of size removes one of the possible reasons for a difference (i.e. variable particle size).

3.5.3 Hot Carrier cells
Researchers:
Shujuan Huang, Santosh Shreshtha, Robert Patterson, Binesh Puthen Veettil, Xiaoming Wen, Yu Feng, Pengfei Zhang, Hongze Xia, Neeti Gupta, Yuanxun Liao, Suntrana Smyth, Xi Dai, Shulin Pei
Hot carrier solar cells offer the possibility of very high efficiencies (limiting efficiency above 65% for unconcentrated illumination) but with a structure that could be conceptually simple compared to other very high efficiency PV devices – such as multi-junction monolithic tandem cells. For this reason, the approach lends itself to ‘thin film’ deposition techniques, with their attendant low costs in materials and energy usage and facility to use abundant, non-toxic elements.

An ideal Hot Carrier cell would absorb a wide range of photon energies and extract a large fraction of the energy to give very high efficiencies by extracting ‘hot’ carriers before they thermalise to the band edges. Hence an important property of a hot carrier cell is to slow the rate of carrier cooling to allow hot carriers to be collected whilst they are still at elevated energies (“hot”), and thus allowing higher voltages to be achieved from the cell and hence higher efficiency. A Hot Carrier cell must also only allow extraction of carriers from the device through contacts which accept only a very narrow range of energies (energy selective contacts or ESCs). This is necessary in order to prevent cold carriers in the contact from cooling the hot carriers, i.e. the increase in entropy on carrier extraction is minimized [3.5.19]. The limiting efficiency for the hot carrier cell is over 65% at 1 sun and 85% at maximum concentration – very close to the limits for an infinite number of energy levels [3.5.1, 3.5.20, 3.5.21]. Fig. 3.5.10 is a schematic band diagram of a Hot Carrier cell illustrating these two requirements.

**Figure 3.5.10:** Band diagram of the Hot Carrier cell. The device has four stringent requirements: a) To absorb a wide range of photon energies; b) to slow the rate of photogenerated carrier cooling in the absorber; c) To extract these ‘hot carriers’ over a narrow range of energies, such that excess carrier energy is not lost to the cold contacts; d) to allow efficient renormalisation of carrier energy via carrier-carrier scattering.

Full devices will either have selective contacts on an efficient absorber to extract carriers at high voltage (see Fig. 3.5.10, or have an absorber with slowed carrier cooling operate in open circuit emitting a wide range of photon energies through an optical filter onto a standard solar cell. This second optical only approach has the advantage that only optical properties need be optimized not electrical transport and is very promising at least for proof of concept devices and quite possibly for final high efficiency devices.

### 3.5.3.1 Modeling of phonon dispersions in MQW

InN/InGaAsN multiple quantum-well superlattices (MQW-SL) with wurtzite crystal structure are studied as the absorber of the hot carrier solar cell. Such a structure will exploit both the significant hot-phonon-bottleneck effects of the component materials and the known slowed carrier cooling in...
MQWs. The former is due to the large contrast of the atomic masses, and hence a large band-gap between high-lying and low-lying phonon modes. The phonon band-gap effectively stops Klemens decay, i.e. one high-lying phonon decaying into two low-lying phonons, and produce hot population on the polar modes, feeding energy back to electrons. InN and In\textsubscript{x}Ga\textsubscript{1-x}N have very similar lattice structures, with almost the same lattice constant. This benefits the solar energy conversion, in terms of both the carrier transport and the reduction of recombination sites. The 1-dimensional superlattice structure ensures a continuous electronic energy spectrum and hence a broad-band absorption. The absorption is further enhanced by the small electronic band-gap of InN.

The calculation of the rate of polar interaction between hot electrons (here emission by holes is not of concern) and polar phonons are based on the Frohlich-type Hamiltonian and the 1-st order perturbation theory. A hot reservoir of electrons at 1000K is assumed, with heat transferred to the cold reservoir of lattice modes at 300K. The energy relaxation times referring to the polar phonon emission are illustrated in Figure 3.5.11, for all the MQW-SL configurations, i.e. for different well and barrier thicknesses and different barrier materials. 18\times 18 combinations of the thicknesses are sampled for representing all the possible structures from 2nm to 9nm. The number of combinations comes from the fact that a complete well/barrier layer should include an integer number of unit cells. Figure 3.5.11 is generated by interpolating the relaxation time data of the sampling combinations.

![Figure 3.5.11: Energy relaxation times of the hot electron system (1000K), in the reservoir of phonons (300K), with superlattice structures of different well/barrier thicknesses and In\textsubscript{x}Ga\textsubscript{1-x}N compositions (Left: x=0 Right: x=0.2)](image)

The energy relaxation times of high-lying longitude optical phonons are demonstrated in Figure 3.5.12, for different combinations of well and barrier thicknesses. For Indium mole fraction x=0 (left figure), the contrast of relaxation times are larger than that for the case for x=0.2 (right figure); this is reasonable for as the higher Indium content in the barrier layer would make the structure closer to bulk InN. Both figures show the same trend with different barrier/well thicknesses: the relaxation time increases with thicker well layers and thinner barrier layers, in spite of some irregular local variations. The regular variation mainly results from the change of numbers of InN-like modes and InGaN-like modes. Here a hot reservoir of high-lying modes at 1000K is assumed, with heat transferred to the cold reservoir of low-lying lattice modes at 300K. The non-equilibrium between the two systems is physical due to their significant frequency separation.
Figure 3.5.12: Energy relaxation times of the high-lying LO phonon system (1000K), in the reservoir of 1000K high-lying phonons and 300K low-lying phonons, with superlattice structures of different well/barrier thicknesses and In$_x$Ga$_{1-x}$N compositions (Left: x=0 Right: x=0.2)

To explain the variation, we need to first examine the phonon dispersions of the MQW-SL. Taking x=0 as an example, the left figure in Figure 3.5.13 shows the dispersions of InN/GaN SL structure, with 6 layers of nitrogen atoms inside each layer (the same for both the InN layer and the GaN layer). From the number of atomic layers involved we could expect the same number of high-lying optical modes which are InN-like and GaN-like respectively. The GaN-like optical modes (blue color: solid line for LO, dash line for TO) have much higher frequencies than the InN-like optical modes (green color), for the bond force constants of GaN is larger than for InN and the atomic mass of Ga is smaller than In. There are also four branches (orange colour: two of LO and two of TO) corresponding to the interfacial modes (IF), with frequencies between GaN-like modes and InN-like modes. From the right figure of Figure 3.5.13, the vibrations can be seen to be almost completely confined in the respective layers, for InN-like and GaN-like optical modes. For IF most of the vibrational energy is within the 1st and 2nd nitrogen atoms from the interface, and hence has little overlap with InN-like or GaN-like modes.

Figure 3.5.13: The left figure indicates the phonon decay paths and the sample dispersion for a SL structure with 3 layers of unit cells inside each layer (barrier or well). The right figure shows the phonon modulation function of a representative mode from each category of modes, computed from the eigenfunctions of the lattice dynamic equation. The transverse modes have similar modulation functions and hence only that part of the longitude modes is shown.
Considering all three-phonon processes, only the Ridley channel and the Shrivistava-Barmann channel (decaying into a high-lying optical phonon and a low-lying optical phonon) are allowed due to the energy conservation law. As in wurtzite-structured SL, the difference between the acoustic branches and the low-lying optical branches becomes almost indistinguishable with both having partial optical-like character. These low-lying branches can be separated into two categories: GaN-confined modes (red lines) and GaN-InN mixed modes (grey lines). In fact the InN-like low-lying modes sit within the allowed frequency band of GaN, hence vibrations in GaN layers are excited too. Therefore no InN-confined modes exist in the low-lying branches. Among all allowed three-phonon processes, GaN-like optical modes can decay into both types of low-lying modes (See the solid arrow and the dashed arrow in Fig3.5.13, while InN-like optical modes can only decay into the mixed modes as they only overlap with the mixed modes. Besides, the energy gap between GaN-like LO modes and GaN-like TO modes is relatively large; hence the resulting low-lying phonons have relatively high energies, compared to the decayed low-lying phonons from the InN-like modes. Since the low-lying branches with high energies are generally flatter, leading to a larger joint density of states of transition, the decay rates of GaN-like LO modes could be enhanced further. Due to the two reasons explained above the GaN-like LO modes decay faster than the InN-like LO modes. Therefore with a thicker well layer (or a thinner barrier layer), the energy relaxation time of the high-lying LO phonon system becomes longer, for it introduces more InN-like modes (or fewer InGaN-like modes).

According to Figure 3.5.12 the relaxation time of high-lying phonons could go up to 300ps, which is significantly longer than the bulk value of around 1ps. And according to 3.5.12 the relaxation time of hot electrons (if phonons are completely thermalized) can go up to more than 1ps, this is also much longer than the bulk value. Combining these two, an optimized MQW-SL structure should involve a thin barrier layer and a thick well layer. The contrast in phonon energies between the well and the barrier also needs to be large, indicating a small Indium content in the barrier. In addition, such a structures could potentially prevent hot phonons diffusing out, which makes it even more attractive than bulk materials.

3.5.3.2 Hot Carrier absorber using bulk materials

Hafnium nitride and zirconium nitride have been shown, both theoretically and experimentally, to have a large optical phonon (OP) - acoustic phonon (AP) bandgap [3.5.20]. This gap is big enough to prevent Klemens’ decay- the main route of carrier cooling. Aundance of Hf and Zr is also relatively high. Hence these materials are expected to show slow carrier cooling rate suitable for the hot carrier solar cell.

Thin films of Hf and Zr nitride have been deposited by DC and RF sputtering, respectively using Hf and Zr targets, respectively, in nitrogen atmosphere. Process parameters such as growth temperature and gas flow were varied to optimise the film quality. An XPS depth profile of a ZrN film deposited at 200 °C with 5% nitrogen partial pressure is shown in Figure 3.5.14. The XPS analysis was performed by an ESCALAB 250Xi spectrometer using a monochromatic Al Kα 1486.68 eV X-ray source. Besides Zr and N, the film contains some oxygen. The high level of oxygen at the surface can be attributed to the oxidation of the Zr which is highly reactive to oxygen. The oxygen content decreases with the film depth to less than 5% for etch time longer than 350s. The oxygen content in the bulk of the film is likely to be due to the residual oxygen in the growth chamber. A part from right at the surface, the Zr and N content in the film are reasonably uniform. Results for HfN films also show that Hf and N content of the films are uniform through the film. Oxygen contamination in HfN films is insignificant. XPS result indicates that both ZrN and HfN films are typically metal-rich.
Figure 3.5.14: Results of XPS measurement on a typical ZrN$_x$ film grown at at 200 °C with N$_2$/Ar+N$_2$=0.05. Compositional depth profiling of Zr, N and O are shown.

Slow carrier cooling properties of selected HfN and ZrN films were investigated by ultrafast transient absorption (TA) spectroscopy. Samples grown on quartz substrates were used to detect the transmitted signals. Crystal quality of the films grown on quartz substrates was inferior to those grown on silicon substrates which are expected to decrease carrier lifetimes by introducing additional phonon modes in the phonon gap allowing decay processes to occur. The fs pump-probe experiments were performed using 400 nm excitation pump source with 100 fs duration and 1 kHz repetition rate. White light continuum was used as the probe beam and detected by a polychromator CCD.

Figure 3.5.15: Result of ultrafast transient absorption spectroscopy on a HfN film showing (a) change in optical density (OD) as a function of wavelength at different time delays. (b) Time evolution of change in OD as a function of delay time.
In Figure 3.5.15(a) TA spectra of a HfN film at various time delays are shown. The changes in optical density $\Delta OD$ before and after the pump are plotted as a function of probe wavelength. An excited state absorption peak around 440 nm and a bleaching peak 730 nm can be observed. In Figure 3.5.15(b) time evolution of $\Delta OD$ at 485 nm is plotted as a function of time delays. Immediately after the pump a rapid change in OD is observed which may be due to electron-electron scattering. Then it slowly decreases with delay time. The red curve is the single exponential fit which gives decay time constant of about 2 ns. For zirconium nitride films the decay constant is about 0.5 ns, see Figure 3.5.16.

![Figure 3.5.15(a)](image1)

![Figure 3.5.15(b)](image2)

**Figure 3.5.16:** Result of ultrafast transient absorption spectroscopy on a ZrN film showing (a) change in optical density (OD) as a function of wavelength at different time delays. (b) Time evolution of change in OD as a function of delay time.

Work is in progress to investigate if the observed slow cooling rates are related to hot carriers. Considering the hot carrier lifetime of 3 ns, hot carrier solar cell can theoretically achieve efficiency over 55% under 1000x concentration. However, in reality the efficiency may be a lot lower due to nonidealities such as contact losses and incomplete light absorption.
3.5.3.3 Nanostructures for hot carrier absorbers

A series of semiconductor nanoparticles (NPs) of different sizes, including Si, PbS and Ag$_2$S, have been employed to fabricate mono/multi-layer structures via Langmuir Blodgett (LB) and Langmuir Schaefer (LS) deposition. Corresponding physical and optical characterisation can confirm the formation of mono/multi layers. The multilayer structures, if arranged properly, can be seen as a super-lattice structure. According to our former theoretical model [3.5.20] they may successfully function as a hot carrier absorber by providing a “phonon bottleneck”. Through photoluminescence (PL) measurements, especially time-resolved photoluminescence measurement (TRPL), hot-carrier features have been detected in LB multilayers of Si NPs.

**LB and LS deposition of NPs**

A typical LB system usually consists of a trough, a pair of barriers, a surface pressure sensor (Wilhelmy Plate and a microbalance system), a dipping unit and a solid substrate where the NPs will be transferred. Both mono and multiplayer of closed pack arrays of Si NP have been demonstrated using LB. Besides Si NPs, we have also successfully synthesised uniform PbS nanoparticles. Close-packed arrays of these NPs are also achieved by LB deposition at a suitable surface pressure as shown in Figure 3.5.17.

![Figure 3.5.17: TEM image of LB monolayer of PbS NPs showing good local periodicity.](image)

To confirm the formation of LB multilayers, AFM measurements were carried out on LB multilayers. Figure 3.5.18 (a) shows a 2-layer LB film. From the cross section profile, a film of ~12 nm thickness is detected, which shows that it consists of two layers of 6.2nm NPs. To further investigate multilayer growth, a set of 6.2nm Si NPs films with 3, 5 and 15 LB layers deposited onto quartz substrate were characterized Raman spectroscopy. Figure 3.5.18 (b) shows that the first order Raman peak at ~518 cm$^{-1}$ from 6.2nm Si NPs is much stronger in thicker films, evidencing multilayer deposition.
Figure 3.5.18: Confirmation of multi LB layers. (a), AFM image of 2-layer 6.2 Si NPs LB film, the cross section view clearly shows a thickness of 2 monolayers; (b), Raman scattering spectroscopy from LB films formed by different number of layers of 6.2 Si NPs.

Characterisation of hot carrier properties

Carrier dynamic of Si NPs were investigated for different sizes (2.2nm, 3.8nm and 6.2nm). For this steady-state (ss) and time-resolved (TR) PL measurements on LB and drop cast films of Si NPs were used. ss-PL for both the LB and drop cast films, as expected, showed blue shift of the emission peak positions with decrease of sizes of Si NPs is observed expected. To investigate the hot carrier behaviour within the Si NPs LB films, 2-D TRPL mapping was acquired, as shown in Figure 3.5.19 (a). In this map, a high energy area ranging from 570 nm to 610 nm appears within 20 ns. Figure 3.5.19(b) shows that this PL peak vanishes within 50 ns. Considering the carriers energy states as a Fermi-Dirac distribution, a Planck-like distribution is applied to the high energy tails of the PL peak. In Figure 3.5.19(c) the data is re-drawn in log scale and exponential fitting is applied to the data from 2.27 eV. An example of the fit is shown in the inset of Figure 3.5.19 (d). Temperature calculated from the fitting is shown in Figure 3.5.19(d). It indicates an average temperature ~550 K for LB films and ~450K for drop casting films. This demonstrates that ordered, highly packed LB films have high carrier temperature, and are hence more promising as a hot carrier absorber material.
3.5.3.4 Energy Selective Contacts

**ESCs based on crystallized Ge well and amorphous Al$_2$O$_3$ barrier**

Resonant tunnelling diodes (RTD) based on amorphous Al$_2$O$_3$ barriers and crystallized Ge (well) is a promising structures to show room temperature tunnelling due to a high band-offset between Al$_2$O$_3$/Ge. Moreover, crystallization of ultrathin Ge films by thermal annealing is easier than Si sandwiched in oxide layers.

Crystallisation of Ge/Al$_2$O$_3$ multilayer samples grown by RF sputtering at room temperature was investigated with conventional thermal annealing (TA) and rapid thermal annealing (RTA). Annealing was conducted in N$_2$ atmosphere. These samples are multilayer structures of alternating Ge and Al$_2$O$_3$ thin layers as shown in Table 3.5.1.

Previous experimental results and theoretical analysis for ultrathin Ge films of thickness less than 10nm separated by oxides have shown that crystallization temperatures (T$_c$) is higher for thinner Ge layer, i.e. T$_c$ is 800 °C for 7.2nm film whereas it is 950 °C for 1.9nm film. In this work however, TA at 700 °C for 30min resulted in oxidation of Ge films. TA at 600 °C for 1hr and 2hrs have also oxidised all samples, except for the sample with 7.2 nm Ge film. Crystallisation did not occur with annealing at 500°C.

Table 3.5.1: Ge/Al$_2$O$_3$ samples used for annealing studies.

<table>
<thead>
<tr>
<th>No.</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge thickness (nm)</td>
<td>1.9</td>
<td>3.6</td>
<td>7.2</td>
</tr>
<tr>
<td>Al$_2$O$_3$ thickness (nm)</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>No. of Ge layers</td>
<td>5</td>
<td>4</td>
<td>2</td>
</tr>
</tbody>
</table>
With RTA, Ge layer in Samples B and C achieved optimum crystallisation at 900 °C. No further improvement in crystal quality was observed with annealing at higher temperature. A partial oxidation of Ge layer in Sample A was observed up to 800 °C annealing. The film was fully oxidised annealing above 900 °C. In order to avoid the oxidation of thin Ge layers, a 0.5nm Al intermediate layers are added to each Al$_2$O$_3$/Ge interface as shown in Figure 3.5.20 (a). Raman spectra show that the 1.9nm Ge film dies not suffer from oxidation and show similar behaviour as B and C, see Figure 3.5.20 (b).

**Figure 3.5.20:** (a) 0.5nm Al intermediate layer inserted at each Al$_2$O$_3$/Ge interface. (b) Normalized Raman spectra show the temperature (600~1000 °C) dependence of the sample of (a) annealed by RTA for 10s.

I-V properties of DBRTD structures (Al$_2$O$_3$/Ge/Al$_2$O$_3$) as shown in Figure 3.5.21 (a) were investigated. The devices were grown on highly doped n-type Si (100) wafer. Top Al contacts were deposited as shown in Figure 3.5.21(b) and the back metal contacts were made by sputtered gold. The 90K I-V scan (Figure 3.5.22) demonstrates resonant tunnelling at 0.84V. The scan shows very good PVCR of 12.2 and QF of 330/V.

**Figure 3.5.21:** (a) DBRTD of 0.5nm Al$_2$O$_3$ / 4nm Ge / 0.5nm Al$_2$O$_3$. (b) Top Al contact by photolithography and etch-back.
ESCs using colloidal-based Silicon Quantum Dots

In principle, quantum dot (QDs) should show better resonant tunnelling due to 3D confinement. We have demonstrated resonant tunnelling through SiO$_2$/Si QD/SiO$_2$ deposited by physical deposition. However, the quality of resonant was compromised by non-uniformity QD sizes in the structure. Langmuir–Blodgett (L-B) method allows deposition of monodisperse QD nanoparticles. In this work this technique has been used to make Energy Selective Contacts (ESCs) using double barrier resonant tunnelling structures (RTDs). The RTD structure investigated is shown in Figure 3.5.23. Samples were grown on highly doped Si substrates. The first Al$_2$O$_3$ layer was deposited by thermal Atomic Layer Deposition at 200 °C; then a layer of Si QD is deposited on the Al$_2$O$_3$ layer by L-B method. Next, the samples were placed in ALD and sintered at 200 °C for half an hour to dehydrogenate or desorb the surfactant of Si QDs. Finally, the second Al$_2$O$_3$ layer is deposited by ALD at 200 °C. The size of the Si QD was 3.8 nm and Al$_2$O$_3$ barrier layers were 0.5 nm thick. The Si QDs studied here were synthesized by a gas-phase non-thermal plasma-assisted approach developed by Kortshagen et al. and surface-functionalized in the liquid phase. These Si QDs are roughly spherical in shape and relatively uniform with the Gaussian size distribution of standard deviation about 0.18 $d$, where $d$ is mean size. Pt contacts on top the Al$_2$O$_3$ layer were made by e-beam deposition under SEM monitoring. Back contacts at the bottom of highly doped Si substrates were made of sputtered gold.

Figure 3.5.23: Schematic illustration of the Energy selective contact DBRT structure.

I-V measurement is done with the Lakeshore PS-100 probe station which has current resolution of 1pA and voltage resolution 1mV. The probe tip diameter is about 3.5µm. As shown in Fig 3.5.24, the first forward scan reveals four peaks, A, B, C, D; while the following backward scan only show two peaks, A and C which is reproducible until the fourth scan. This suggests that the reproducible peaks A and C are the resonant peaks, while B and D may have been due to carriers trapped by defects or impurity bands. The I-V curves show many noisy peaks. work is in progress to improve the quality of the samples.
3.5.4 Up-conversion

Researchers:
Sanghun Woo, Craig Johnson, Supriya Pillai, Shujuan Huang, Qiyuan Wu, William Tian, Richard Corkish, Gavin Conibeer

Collaboration with:
Peter Reece (Physics, UNSW), John Stride (Chemistry, UNSW)

Up-conversion in novel silicon-based materials

Up-conversion (UC) in erbium-doped phosphor compounds (particularly NaYF₄:Er) has been shown to be a promising means of enhancing the sub-band-gap spectral response of conventional Si solar cells without modification of the electrical properties of the cell [3.5.22]. In this scheme, a layer containing the phosphor is applied to the rear of a high-efficiency bifacial cell. After absorbing two long-wavelength (~1500nm) photons - which are transmitted by the cell - the excited Er ions can relax by emitting a photon with an energy greater than the Si band gap, thereby increasing the current that can be extracted from the cell.

Synthesis of Er doped NaYF₄ phosphors for UC

Fabrication of in-house phosphors allows control over the growth process and the ability to control Er doping levels and the possibility to include co-dopants.

NaY₁₋ₓF₄ₓ:Erₙ nanocrystals were synthesized by thermal decomposition of metal trifluoroacetate (TFA) precursors [3.5.23, 3.5.24]. After the reaction at 80°C for two hours, oleic acid (OA) and 1-octadecene (ODE) were added to the reaction and slowly heated for 1 hour at 280°C. At this stage, NaYF₄:Er NCs formed in the alpha phase. To convert NCs from alpha to the beta phase, the
temperature was slowly increased to 320°C for 3 hours. The resulting solution was treated to remove unreacted precursors, excess OA and 1-ODE. NaYF₄:Er NC films were fabricated by spin casting followed by nucleophilic ligand exchange. NC films were coated on the glass by multiple spin castings.

Figure 3.5.25(A) shows HRTEM images of hexagonal beta phase NaYF₄:Er NCs. The dominant and most distinguishable lattice (100) of the hexagonal beta phase NaYF₄ NCs had a fringe distance of 0.54 nm. The histogram in Fig. 3.5.25 (B) indicates that particles had sizes ranging from 25 to 35 nm with a narrow size distribution peaking around 30 nm.

Figure 3.5.25: Electron microscope data for NaYF₄: 10% Er. (A) low and high resolution TEM. Both scale bars correspond to 50nm. (B) Histogram of diameters of Er dope NCs

The absorption spectrum of UC NCs is shown in Figure 3.5.26 and corresponds to all energy levels up to 3.1 eV of NaYF₄:Er NCs. Figure 3.5.26 (B) shows five red-shifted peaks compared to the absorbance which were resulted from radiative relaxations from ⁴H₁₁/₂, ⁴S₃/₂, ⁴F₉/₂, ⁴I₉/₂ and ⁴I₁₁/₂. As shown by UC luminescence images in insets of Figure 3.5.26 (B) increased Er concentrations in UC NCs accelerated multi-phonon relaxation processes between ⁴S₃/₂ and ⁴F₉/₂, which emphasizes the importance of optimization between slowing non-radiative decay rates and increasing absorption sites in NCs.

Figure 3.5.26: The SEM images of spin cast films before and after the soaking process in a MPA solution are shown in Fig. 3.5.25 (A) and (B) respectively. Without the post soaking process, NCs were coated separately from neighbouring crystals, and packed closely. By treating with a 3-MPA solution, NCs were agglomerated and linked to each other resulting in a bulk-like feature. The cross-linked NC film made with 3-MPA brings about easy handling, light trapping in NC layers, and a reduced film thickness.
Figure 3.5.27: (A) SEM images of morphology of upconverting layer (A) before and (B) after soaking in a MPA solution. (C) Up-conversion spectroscopy showing the intensities of emitted photons in terms of laser power densities and Er doping concentration. (D) Film thickness dependent upconversion under three different excitation powers.

Figure 3.5.27 (C) shows the total intensity of upconverted photons from energy levels above \(4I_{11/2}\), which are all able to contribute to the photoconversion process in c-Si solar cells, depending on the excitation power between 30 \(\mu\)W and 215 mW and the Er concentration between 2 and 100% substituting Y sites of the NaYF\(_4\) host structure. 15% Er doped UC layers always gave the best upconversion regardless of the excitation power. This means that increasing Er doping concentration did not affect the number of photons that could meet with each trivalent Er ion.

Using the brightest UC NCs with a 15% doping concentration of Er, the film thickness was optimized under various excitation fluxes, as illustrated in Figure 3.5.27 (D). From the excitation coefficient information, the UC films had to be thicker than 20 \(\mu\)m, so that all photons within energies of \(4I_{11/2}\) could be absorbed by the UC phosphor. However, the required film thicknesses to perform the saturated emission were only about 2.5 \(\mu\)m under a 1 mW laser, 3 \(\mu\)m under a 5 mW laser and 5 \(\mu\)m under a 10 mW laser. This is because upper UC NC layers re-absorbed upconverted photons emitted from the lower layers. Also, the stable bulk-like layers may have a higher absorption coefficient than simply packed NCs, resulting in relatively thinner thicknesses required for the saturated UC efficiency.

**Sensitisation of Er phosphors to a wider wavelength range**

Er has an absorption window at the \(I_{13/2}\) level from 1480nm to 1580nm. This narrow range means that it is inefficient at absorbing below Si band gap photons. Sensitizing to the 1100-1500nm range would significantly enhance the absorption and hence have a dramatic effect on the up-conversion efficiency, because of its non-linear dependence.

PbS nanoparticles have a wide absorption range below 1100nm. They can also be tuned in size to emit at 1500nm, with absorbed photons being downshifted to 1500nm at some quantum efficiency less than 100%.

Such PbS NCs have been synthesized based on the procedure developed by Cademartiri et al. [3.5.25] by decomposition of PbCl\(_2\) with sulphur solution. PbS QDs and Er-doped NaYF\(_4\) NC films were fabricated by the simple spin casting method followed by nucleophilic cross-linking of NCs.

The sizes, the size distribution and the fringe distance of resulting UC NCs were determined using HRTEM and glancing incident x-ray diffraction (GI XRD) was carried out to investigate the crystalline structures of PbS QDs.
Figure 3.5.28: Absorbance and emission data from UV-V is spectroscopy. (a) for PbS quantum dots showing the desired slight mismatch between absorbance and emission such that re-absorption is unlikely. (b) Absorbance for Er doped NCs and emission from PbS QDs, showing the good match between PbS emission to pump Er absorption at the.

Figure 3.5.28 shows absorbance and emission data for PbS QDs and Er doped NaYF₄ NCs. The range of absorbance for PbS QDs is close to ideal for absorbance of light below the Si bandgap but stopping short of the emission. This emission, tuned to 1500nm, is ideal for pumping the I₃/2 level at 1520nm in Er, without being re-absorbed by the PbS. Thus the sensitization of Er to a significantly wider wavelength range should be very valuable in increasing the flux of photons which can be absorbed and up-converted by the Er doped phosphor.

Conclusion
Up-conversion in Er doped phosphors shows very promising results. Fabrication of NaYF₄ NCs allows greater control over doping levels and geometries for efficient up-conversion. Progress towards sensitisation of Er to a wider wavelength range using down shifting PbS quantum dots tuned to emit at 1500nm has been made. Combination of all these elements in an up-conversion structure is expected to boost UC efficiencies for Si cells.

3.5.5 Photoelectrochemical water splitting
Researchers:
Haixiang Zhang, Siva Karuturi, Shujuan Huang, Qiyuan Wu, William Tian, Gavin Conibeer
Collaboration with:
Yun Hao Ng, Rose Amal (Chem Eng, UNSW)
Judy Hart (Materials, UNSW)

The concept of the Photoelectrolysis (PE) cell is to split water directly into hydrogen and oxygen using only solar illumination. Such a technology has great potential for direct storage of solar energy in a high energy fuel (H₂). There are very few materials which generate a high enough voltage to exceed the redox potential of water of 1.23V (or 1.4V to also exceed the unavoidable over-potential). Lower band gap materials can be used, such as GaAs, with high current efficiency, but they have two problems. Firstly such narrow band-gap semiconductors are often unstable in water and are eventually dissolved by competing electrochemical decomposition. Secondly in order to achieve adequate voltage, the cell must be boosted by an external bias, either electrical or chemical, but both requiring an external energy source. A tandem device can be used for the electrode but this is either prohibitively expensive or has the problem of complex and hence expensive fabrication, including the requirement of an interband tunnel junction at the cell interface. Titanium dioxide is also often used, this is cheap to deposit and is stable in water, but has a high band gap about 3.0eV and hence has small absorption and also only produces 0.7V, insufficient to electrolyse water on its own.
Dual photo-electrode cell:
Most PE devices such as described above employ a single photo-electrode. For these cells a Pt counter electrode is invariably used. The current project investigates the required properties and feasibility of a tandem cell which uses two photo-electrodes. [3.5.26] An important aspect is to aim for a device, which uses thin film materials, in such a way as to avoid the high costs normally associated with tandem devices. The two photo-electrode approach allows this because no p-n or tunnel junctions are required. An important aspect is to aim for a device, which uses thin film materials, in such a way as to avoid the high costs normally associated with tandem devices. The two photo-electrode approach allows this because no p-n or tunnel junctions are required.

Figure 3.5.29: Illustration of the device deposited on both sides of a glass substrate.

Figure 3.5.30: Band diagram of the tandem device. [3.5.26].

The physical concept of the device is illustrated in Figure 3.5.29 and involves deposition of an n-type titania photo-anode [3.5.27] and a p-type semiconductor photo-cathode on either side of a glass substrate. Before the semiconductor deposition the glass substrate is coated with a conductive layer of ITO, zinc oxide or other TCO on both sides. This may require p- and n-type TCO for ohmic contact to the p-type photo-cathode and n-type photo-anode respectively (e.g. p- and n-type ZnO). The junction between these metallic layers will then effectively act as the inter-band tunnelling contact between the two half cells, but in a way which is much easier to fabricate than in a monolithic device.

Figure 3.5.30 is the band diagram of the device – albeit with fairly idealized band structure – in practice band line-ups will differ. Sunlight incident on the cell illuminates the titania side and photons >3.2eV generate electron hole pairs. Energetic holes migrate to the n-type titania surface and take part in the anode half reaction:
\[ \text{OH}^- + 2h^+ + H^+ = \frac{1}{2}O_2 \uparrow + 2H^+ \] the oxygen being evolved.

Photons < 3.2eV but greater than the band-gap of the p-type photo-cathode are transmitted through the titania and absorbed in the p-type layer. [This band-gap, \( E_g(p\text{-type}) \), will be \( > 1.1 \text{eV} \) to \( < 3.2 \text{eV} \) depending on material.] This absorption also generates electron-hole pairs, with the electrons migrating to the p-type semiconductor surface and taking part in the cathode half reaction:

\[ 2H^+ + 2e^- = H_2 \uparrow \] with hydrogen evolved.

The opposite type charge carriers (electrons in titania, holes in p-type photo-cathode) migrate to the interface ITO layer where they cross over to the other cell and also to the other band thus becoming unenergised – thus completing the circuit. The photovoltage from each half-cell is equal to the split in quasi-Fermi levels in each material under illumination (less any resistive loss in the semiconductor electrode). The photovoltage typically achieved from titania photo-anodes is 0.7V [3.5.28]. The addition of the two photovoltages thus depends on these specific Fermi level alignment but it must also overcome other voltage drops due to resistive losses at the TCO contacts, in the electrolyte and in the two very thin Helmholtz layers caused by dipole alignment at the two electrolyte semiconductor interfaces. These latter can be up to a third to a half of the split in quasi-Fermi levels in each case [3.5.29]. The split in quasi-Fermi levels, and hence the effective photovoltage, depends on the recombination in the semiconductor (and hence its quality) and the illumination level and spectrum, as well as the current in the cell. The Fermi level position with respect to the redox potentials is determined by the doping level – higher doping will tend to improve the alignment – and \( pH \) of the electrolyte - a lower \( pH \) will tend to drive the redox potential to more negative energies relative to the vacuum level, thus favouring the \( \text{H}^\text{+}/\text{H}_2 \) half reaction.

### 3.5.6 Concluding remarks for the Third Generation section

Work has proceeded significantly in the areas of Third Generation research, with improved fabrication and characterisation of materials and complexity of modelling which together give an overall better understanding and optimisation of devices.

The work on Si nanostructure tandem cells is now more repeatable with greater understanding of conductive substrate materials and improved heterojunctions approaches. The first tandem cell devices on crystalline silicon and thin film silicon cells have been fabricated with promising efficiencies demonstrated.

Hot Carrier cells have seen further development in modelling and some important slowed carrier cooling results for potential absorber materials, both for bulk HfN and for QD nanostructures. Contacts with improved energy selection in both the \( \text{Al}_2\text{O}_3/\text{Ge/Al}_2\text{O}_3 \) system and with QDs as resonant centres have been demonstrated.

Up-conversion is now able to use phosphors fabricated in house and sensitisation using PbS nanoparticles looks promising. The new area of photo-electrolysis is promising for direct solar water splitting to store solar energy.

On going development of these projects is expected with several more areas coming on-line in the near future.

### References:


3.5.8 X.J. Hao, I. Perez-Wurfl, G. Conibeer, M.A. Green, 19th PVSEC, Korea, Nov 2009.
3.5.7 New Third Generation Projects

3.5.7.1 Introduction
Several new projects in the Third Generation strand have been initiated in 2014 and will continue in 2015. Summaries of these projects are as follows.

3.5.7.2 Direct photo-electrolysis of water for cost-effective hydrogen production with enhanced photocathode and photoanode efficiency

Staff
S. Huang, J. Hart, R. Patterson, S. Shrestha, G. Conibeer

Summary
For large-scale use of intermittent renewable energy sources to be feasible, an efficient means of storing the energy must be found. Photocatalytic materials are semiconductors that can directly convert solar energy to hydrogen by absorbing sunlight and transferring the energy to water molecules, which decompose to form hydrogen and oxygen. The hydrogen produced allows solar energy to be stored, while also providing a non-polluting transport fuel. The development of efficient photocatalytic materials for water splitting is thus crucial for a clean energy future. There are significant difficulties in achieving overall photocatalysis using a single semiconducting material and solar-to-hydrogen efficiencies remain low despite many years of research. An attractive alternative is to use a two-step process with two different semiconductors in a photoelectrochemical cell - one semiconductor at the anode catalyses water oxidation, while a second semiconductor at the cathode catalyses hydrogen reduction. However, current efficiencies for this two-step process are low, and the materials used are often expensive. The aim of this project is to develop cost-effective and highly-efficient photoelectrochemical cells for water splitting, by using novel electrode designs to optimise efficiencies, thus making hydrogen production commercially viable.

3.5.7.3 Enhanced Si solar cell efficiency by optically coupling of high energy carriers.

Staff
Y. Feng, Jianfeng Yang, G. Conibeer, S. Huang, Santosh Shrestha

Summary
Efficiency of single junction solar cells is constrained by Shockley and Queisser (S-Q) limit. This limits efficiency of silicon solar cells to 29% under 1-sun concentration. In this project, we propose to significantly improve efficiency by controlling the spectrum of the light incident on a solar cell. We will design a converter that will absorb most of the solar spectrum and convert them into a particular energy band (near monochromatic) with minimum energy loss. The converted light will be incident on high efficiency silicon solar cells. Our theoretical modeling has demonstrated that this approach can boost efficiency of silicon solar cells up to 67% which is significantly higher than the S-Q limit.

3.5.7.4 Heterogeneous array of nanoparticles: a new approach to realise the high-efficiency hot carrier cell

Staff
Y. Feng, S. Huang, G. Conibeer, S. Shrestha, Xiaoming Wen

Summary
The hot carrier solar cell, as a novel photovoltaic approach of surpassing the efficiency limit for single-junction cells, has not been realized. The main problem is the toughness of maintaining a hot distribution of photo-generated carriers, due to their ultra-fast rates of energy dissipation via the lattice.
In this project, we aim to realize the high efficiency hot carrier cell, by using a yet unexplored approach. Different types of nanoparticles will be individually synthesized and then deposited together. The large mismatch of their acoustic impedances significantly reduces the lattice thermal conductivity. This keeps the lattice energy localised, resulting in a hot distribution of photo-generated carriers. On the other hand, the electrical conductivity is not impaired, as the nanoparticles are physically closed packed and chemically linked. The electronic mismatch (band gap & electron affinity) can be minimised due to their tunable diameters. A part from the reduced rates of carrier cooling, the proposed structure has other advantages. If optimised, this structure can easily dissociate photo-generated excitons, for the component nanoparticles function as either "acceptor" or "donor", similar to that in organic cells. More important, carrier extraction via discrete energy levels in nanodots can have a minimised entropy generation, further improving the efficiency.

3.5.7.5 Enhanced up-conversion in rare earths for silicon solar cells

Staff
G. Conibeer, C. Johnson, Supriya Pillai, S. Woo

Summary
Up-conversion (UC) for Si cells offers the possibility to boost efficiencies by one or two percent, very important in a production line. Materials for UC need to be optimised. Erbium based UC offers best possibility for below band gap UC, but suffers from problems with efficiency. The project uses four discrete approaches to boost Er UC in a combined device. Boosting the inherent efficiency of Er; sensitising Er to a wider wavelength range; plasmonic coupling of light into Er; and photonic light trapping of light for Er UC. The combined device will incorporate all of these mechanisms for overall increase in efficiency of UC.

Research Project
Technical Approach:
Strand 1: Sensitisation to wider wavelength range:
Use of a secondary absorber with tuned emission is proposed. This has been demonstrated by Hummelen using dye sensitisation (Hummelen 2013). And also attempted by Woo et al using PbS nanoparticles tuned in size to emit at 1500nm. (Woo 2013), Emission and absorption spectra for 10nm PbS QDs. (Woo 2013), PbS nanoparticles can have broadband absorption from 1000nm to 1600nm. With a uniform particle size tuned to 8nm they can be made to luminesce at 1500nm. Ideally the absorption and emission spectra would be separate, but as shown below in fact they overlap. This means that many of the emitted photons will be reabsorbed in PbS before they can be absorbed in neighbouring Er layer.

Strand 2: Modification of absorption in erbium:
The transitions required for absorption and emission in Er for up-conversion are strictly forbidden. The levels are broadened somewhat in a phosphor system such that these selection rules are not absolute, but they still result in very weak processes. Dionne et al 2013, have shown that these transition strengths can be modified by changing the crystal field of the Er phosphor under high hydrostatic pressures in a diamond anvil, such that the emission is reduced. This occurs because of modification of the crystal field of the Er which modifies the transition selection rules. We propose to use either uniaxial or biaxial strain (rather than hydrostatic) to modify the Er crystal field anisotropically. This can result in a greater breaking of the selection rules and hence greater transition probability.

Such biaxial strain can be achieved by compressing a thin layer of NaYF4:Er nanoparticles between two transparent sheets. Uniaxial strain by growth of long filaments of nanoparticles on a plane substrate an then again compressing between two plates. Other methods will include growth on mismatched substrates perhaps with large differential thermal expansion such that strain is induced (either uni- or biaxial) on cooling.
Photoluminescence will be used to assess the results of these strain experiment. Illuminating at 1520nm and measuring upconversion emission and quantum yield at 810nm and 980nm.

Strand 3: Photonic structures to enhance up-conversion:
The use of a long pass filter to prevent reabsorption in PbS has already been mentioned. Distributed Bragg reflectors using SiNx/SiNy multilayers with large refractive index contrast. Such DBR photonic structures will also be used to enhance coupling into Er at 1520nm through the use of the slowed light modes on the edge of the stop band of a DBR notch filter. This has been demonstrated by some of the current authors (Johnson 2012) in porous Si DBR structures. Experiments to optimise this effect will be carried out.

Strand 4: Fabrication of complete up-conversion devices:
Combinations of Er phosphor, bifacial Si cell, PbS downshifting nanoparticles and photonic DBR structures will be investigated, both in far-field and near-field configurations. These will be characterised using photoluminescence and I-V measurement of the Si cell under various single colour, two colour or broadband illumination conditions.
3.6 Silicon Photonics and Device Characterisation

3.6.1 Photoluminescence based characterisation of silicon

University Staff
A/Prof. Thorsten Trupke

Project technicians and Scientists
Allen Yee

Postgraduate Students and Postdocs
Yael Augarten
Mattias Juhl
Bernhard Mitchell

External and internal Collaborators
Catherine Chan, Malcolm Abbott, UNSW
Robert A. Bardos, Visiting Fellow, UNSW
J. Weber, BT Imaging Pty Ltd
Ron Sinton, Sinton Consulting
Daniel Macdonald, Hang Sio, Daniel Walter, ANU
Ziv Hameiri, SERIS
Johannes Greulich, Fraunhofer ISE, Germany

3.6.1.1 Background

In photoluminescence (PL) imaging an intense light source is used to illuminate large area samples such as silicon bricks, wafers or complete solar cells homogeneously with typically one-sun equivalent illumination intensity. A CCD camera captures a high resolution picture of the luminescent light that the sample emits. This technology, which was first demonstrated on silicon wafers and solar cells by our group in 2005 [3.6.1.1] is now widely used in research laboratories worldwide and is increasingly adopted also in industrial manufacturing, for example for quality inspection of as-cut wafers for outgoing (wafer manufacturers) or incoming (cell manufacturers) quality control.

Main benefits of PL imaging, apart from its contactless and non-destructive nature include typically very high spatial resolution and short measurement times. Megapixel luminescence images can be captured within seconds or even fractions of a second, allowing very fast and detailed studies of specific material and device properties. Over the last few years PL imaging has seen the development of a range of specific applications that are applicable across the PV value chain. Examples include series resistance imaging [3.6.1.2] and diffusion length imaging [3.6.1.3] on fully processed cells, which were both first demonstrated at UNSW. The PL group at UNSW continues to further develop PL imaging and find new applications and analysis methodologies. This year the research by our group continued on the application of the photoluminescence intensity ratio method for measurements of the bulk lifetime on silicon bricks (Section 3.6.1.2) with emphasis on quantification of limitations of that method and experimental and analytical methods to mitigate the impact of these limitations. In addition some emphasis was on lifetime measurements from full spectrum analysis, which complements the above two filter method and verifies the underlying theoretical modeling.

In another project the impact of lateral doping variations within a wafer on minority carrier lifetimes via quasi steady state photoconductance measurements (QSSPC) and quasi steady state photoluminescence measurements (QSSPL) was investigated (Section 3.6.1.3) and it was shown that QSSPL has some advantages over the more widely used QSSPC technique for specific samples. The ability to obtain bulk doping concentration from a comparison of QSSPL and QSSPC data was
demonstrated by our group earlier. Extending that work, it was shown in a collaborative project lead by Dr. Ziv Hameiri from SERIS that the above simultaneously measured experimental QSSPL and QSSPC data can also be used for measuring the mobility sum in both conventional and partially compensated silicon wafers (Section 3.6.1.4).

Light spreading within the camera CCD chip can affect the quantitative analysis of PL imaging experiments. These effects and analytical and experimental methods to mitigate them were investigated in a collaborative project lead by the Australian National University (ANU) (Section 3.6.1.5).

UNSW spin-off company BT Imaging Pty Ltd continues the successful commercialisation of the UNSW developed and patented PL imaging technology. Since 2007 BT Imaging have not only significantly extended the associated patent portfolio but also made significant progress with the further improvement of the hardware and associated image analysis software, with specific emphasis on the development of fast systems that enable as-cut wafer inspection on the fly at line speed in solar cell production. Line scanning PL imaging with throughput of 3,600 wafers per hour are now being adopted in the PV industry for incoming and outgoing quality control purposes (section 3.6.1.6).

3.6.1.2 PL imaging on Si bricks

Photoluminescence imaging is an ideal tool for fast characterisation of silicon bricks, giving instant information about the position of low lifetime regions that are commonly observed near the bottom and top of a brick and also exposing areas of high structural defect (dislocation) density. This information can be used for example as process feedback during the production of silicon wafers or as a cutting guide for the removal and recycling of low lifetime regions, the processing of which would result in under-performing cells.

Our previous work has shown that spectral photoluminescence imaging on side facets of silicon bricks can provide quantitative bulk lifetime and doping images if applied on silicon bricks or thick silicon wafers [3.6.1.4]. A photoluminescence intensity ratio (PLIR) is measured in that technique using two different spectral filters in front of the camera. This so called two-filter method relies on the impact that the bulk lifetime has on the emission spectrum. In order to confirm the underlying theoretical analysis we performed full spectrum PL measurements on silicon bricks and compared the emission spectrum to the predicted spectrum, the latter based on literature data for the optical properties of c-Si. Using the bulk lifetime in that modelling as a fit parameter allows quantitative interpretation of the PL spectrum in terms of bulk lifetime [3.6.1.5].

Figure 3.6.1.1: Photoluminescence spectra measured on different locations of a silicon brick. Symbols represent the experimental data, lines the theoretical fits to the data, with \( t_{bulk} \) a fit parameter used to obtain the best fit with the data. The bulk lifetime extracted for each point is given in the figure legend.

![Photoluminescence spectra](image)

Some examples for PL spectra measured on the side facets of both multicrystalline and monocrystalline silicon bricks are shown in Fig. 3.6.1.1. These spectra were measured in regions of the bricks, which are qualitatively known to have substantial differences in bulk lifetime, e.g. from the centre region and from the impurity rich bottom region of a brick. The spectra are normalised at long wavelengths. The spectrum becomes narrower with increasing bulk lifetime, an effect that is due to a
higher proportion of photon reabsorption at short wavelength for photons emitted deeper inside the brick.

### 3.6.1.3 Artefacts in QSS PC and QSS PL lifetime measurements

Quasi steady state Photoluminescence was established by our group as an alternative technique to the more established Quasi steady state Photoconductance for measurements of the excess minority carrier lifetime in silicon wafers. Previous work by other groups had shown that when interpreting photoconductance based lifetime measurements, it is important to account for various experimental artefacts that can cause a severe over-estimation of the carrier lifetime, such as minority carrier trapping or the depletion region modulation (DRM) effect. Our work on QSSPL showed that Photoluminescence based measurements are either not at all or only insignificantly affected by these effects, a major advantage, particularly under low to intermediate injection conditions.

![Figure 3.6.1.2: QSS-PC (closed symbols) and QSS-PL (open symbols) of various test structures, demonstrating a new artefact in QSS-PC based lifetime measurements that is not related to minority carrier trapping or DRM effects. The QSS-PL measurement on the same sample is unaffected by this effect. Data from [3.6.1.6].](image)

Additional artefacts, unrelated to the above trapping and DRM effects, were discovered on silicon samples with alternating localized areas of p-type and n-type doping [3.6.1.6]. The green curve in Fig. 6.6.1.2 (circles) represent QSSPC (Closed symbols) and QSSPL (open symbols) lifetime measurements on a p-type silicon wafer after phosphorous emitter diffusion and after additional p-type doped lines were processed into the emitter. Dramatic artefacts in the QSSPC effective lifetime measurements are observed across the entire injection level range (green full circles). In contrast the QSSPL measurements (green open circles) are unaffected by this effect. The other curves (blue triangles and red diamonds) represent other test structures, which were used to rule out minority carrier trapping or DRM effect as the underlying cause for the strong artefacts in this sample.

The cause of these artefacts was investigated and found to be due to a reduction in the wafer’s dark conductance, which is partially recovered upon illumination. All above mentioned artefacts in QSSPC are related to an increase in the measured sample conductance under illumination, which is misinterpreted in terms of an apparent excess minority carrier concentration. In QSSPC lifetime measurements the excess conductance upon illumination is measured as the difference between the conductance with extra illumination and the dark conductance. In a diffused wafer the dark conductance is determined by both the base resistivity and by the conductance of the emitter. The presence of doped lines of opposite polarity intersecting the emitter causes a barrier for eddy currents to flow laterally within the emitter, which causes an apparent reduction in dark conductance. Upon illumination the lateral eddy current flow across these doping structures is enabled, in a similar fashion as the conductance of a phototransistor is increased by illumination. This increase in conductance is unrelated to a photoconductance due to excess minority carriers and results in the overestimation of the measured lifetime shown in Fig. 3.6.1.2 (full circles). A number of detailed experiments were performed to confirm the above interpretation [3.6.1.6].

In the presence of such locally varying doping patterns, as they are commonly used for example in the processing of high efficiency interdigitated back contact solar cells, QSSPL is thus the preferred
measurement technique for minority carrier lifetime measurements across the entire injection level range from low to high injection conditions.

3.6.1.4 Measuring the mobility sum

The carrier mobility is an important electrical parameter, which significantly influences the performance of crystalline silicon solar cells, as it impacts parameters such as the diffusion length and the series resistance (the latter via lateral carrier transport to the contacts). Accurate data for carrier mobility are also required for other purposes, such as photoconductance-based effective lifetime measurements.

![Figure 3.6.1.3: Mobility sum measured on a partially compensated Si wafer using the comparison of QSS-PC and QSS-PL data, respectively. The solid line represents theoretical data according to a widely used and accepted model. Data from [3.6.1.7].](image)

Models of carrier mobility in monocrystalline Si are well established and include the effects of doping density injection level, and temperature on the mobility. However, the effects of compensating dopants and grain boundaries have been less widely studied and there is yet to emerge a coherent model that accounts for these effects. More generally, there is a lack of experimental data regarding the impact of injection level on carrier mobility. Some information can be found in the literature; however, so far, this data has been mainly obtained from high-resistivity Si wafers. A wide variety of methods were employed in the past to measure the mobility. Previous methods required electrical contacts and a relatively complicated device structure for such measurements.

In this work, a contactless method to measure the carrier mobility sum $\mu_{\text{sum}} = (\mu_e + \mu_h)$ where $\mu_e$ and $\mu_h$ are the electron and hole mobility, respectively, based on a comparison between photoluminescence and photoconductance measurements was presented [3.6.1.7]. The basic idea of this project, led by Dr. Ziv Hameiri from SERIS, is to compare the excess minority carrier concentration $\Delta n$ that is separately extracted from simultaneous QSSPC and QSSPL measurements. In an ideal case, i.e. with the correct modelling parameters and in the absence of experimental artefacts, the two measurements should provide identical excess minority carrier concentration.

The conversion of the PC signal into $\Delta n$ usually requires data for the mobility sum. In this study the mobility sum was used as a fit parameter that is varied to get the best fit between excess minority carrier concentrations from QSSPC and from QSSPL, respectively. This approach was demonstrated for conventional crystalline silicon, and good agreement with established theoretical models for the mobility sum could be demonstrated. The approach was then demonstrated also for partially compensated silicon wafers to demonstrate the capability of this method to get experimental data for the mobility sum in this type of material. As an example Fig. 6.3.1.3 shows the mobility sum experimentally determined as described above, compared to the mobility sum according to the so-called Klaassen model. Ignoring some measurement noise at low minority carrier concentrations, good agreement between the model and the experimental data is observed. Systematic application of
this method to a wide range of compensation ratios will allow the theoretical models to be tested and refined.

3.6.1.5 Image deconvolution

Commercial and R&D photoluminescence imaging systems typically employ silicon CCD imaging sensors. Silicon is a weak absorber of the near-infrared band-to-band emission of silicon. Consequently lateral smearing of the luminescence signal within the sensor can occur if photons are not absorbed in the camera pixel where they initially enter the CCD. Left uncorrected, this effect can reduce image contrast, introduce artificial signal gradients and limit the minimum feature size for which accurate quantitative measurements can be derived. Empirical quantification of the smearing effect defined in terms of the point-spread function (PSF) for the imaging apparatus allows for post-processing deconvolution, which improves image accuracy and contrast. A quantitative analysis of these effects and demonstration of partial correction of the image smearing effects was the subject of a collaborative project lead by Daniel Walter from the Australian National University [3.6.1.8]. Quantitative assessment of the impact of photon-spread indicates that the extent of the signal smear is sufficient to warrant the application of deconvolution, particularly in the absence of short-pass filtering. Short-pass filtering provides partial reduction of lateral photon-smear with the advantage of reduced experimental and analytical complexity.

![Figure 3.6.1.4: Comparison of 2 dimensional cross section of PSF with and without short-pass filtering, the full CCD field of view (right) and region of CCD centred at the point-source (left). Data from [3.6.1.8].](image)

The above point spread functions (PSF), shown in Fig. 3.6.1.4 indicate the probability for a photon that strikes the CCD array in a specific camera pixel to be erroneously detected in another pixel, as a function of the distance between the two pixels. This PSF was measured experimentally and used for deconvolution on a range of test samples. A significant reduction in image smearing and improvement in PL intensity contrast, particularly for small scale features, could be demonstrated.
3.6.1.6 Commercialisation of PL imaging by BT Imaging

UNSW spin-off company BT Imaging continued the successful commercialisation of its proprietary PL imaging technology. The iLS-W2 (Fig. 3.6.1.5) is a line scanning PL system, which achieves 3,600 wafer per hour throughput at line speeds of up to 300mm/s. Importantly measurements are carried out “on the fly”, i.e. without the need to stop the wafer, which facilitates integration into existing wafer and cell lines.

One key application for this system, which has seen increasing adoption by both cell- and wafer manufacturers in 2013, is as-cut wafer inspection for quality control purposes. The system is capable of measuring various types of wafers, including conventional multi crystalline-, cast mono-, mono crystalline- and importantly also the new types of high performance multi crystalline silicon wafers, which appear to become a very competitive alternative to conventional wafers, primarily as a result of reduced dislocation density throughout the ingot. Systematic analysis of these high performance multi crystalline wafers with inline PL imaging does indeed confirm an overall lower dislocation density, which results in up to 0.5% absolute efficiency gain on average, but also shows that there still exist significant variation in dislocation density within batches from one manufacturer and between manufacturers as shown in Fig. 3.6.1.6. Cell makers can use the iLS-W2 for incoming wafer inspection, whereas wafer suppliers use PL for systematic process improvements and to qualify and sort their product into different quality grades. The iLS-W2 is available in various automation configurations.

The flagship BT Imaging laboratory tool, the LIS-R1 was replaced by a technically improved LIS-R2 in 2012. The R2 incorporates improved optics, enabling further improvements in image quality even beyond the industry leading standard of the R1 and substantial reduction in measurement time for wafers and bricks.
Figure 3.6.1.6: PL images taken using a BT Imaging iLS-W2 on a high performance multi wafer with low dislocation density (left), a high performance multi wafer with high dislocation density (center) and a conventional multicrystalline wafer with high dislocation density (right). The blue colour overlay represents the locations of dislocations identified by BT Imaging’s proprietary image processing algorithms.

3.6.1.7 Summary

An exceptional variety of material and solar cell parameters can already be measured on silicon bricks, silicon wafers and silicon solar cells with high lateral spatial resolution and short measurement time using luminescence imaging techniques. The range of applications continues to grow, with new applications for PL imaging being developed at UNSW, and increasingly also in other research institutes and by R&D groups in PV companies. BT Imaging continues to adapt their products by implementing these state of the art developments. PL imaging, introduced at UNSW only a few years ago, has been rapidly adopted as a standard characterisation method, with PL tools now in use at virtually all leading research institutes worldwide and also by leading wafer and solar cell manufacturers. A range of opportunities for in-line quality control, process monitoring and process control have been demonstrated and are enabled by the high resolution and speed of PL imaging. The adoption of these techniques continues and will contribute to the further cost reduction in silicon solar cell manufacturing and to the widespread adoption of PV as a cost competitive energy source.

References

3.6.2 Other Optical Characterisation Techniques

University Staff
Dr Henner Kampwerth (Group Leader)
Prof Martin A Green
Dr Yang Yang

Postgraduate Students
Kai Wang (PhD student)
Xiaoqi Xu (PhD student)
Taufiq Abdullah (PhD student)

External Collaborators
Dr Bill McLean, UNSW
A/Prof Daniel Macdonald, ANU
Dr Martin Schubert, FHG-ISE, Germany

3.6.2.1 Background

The photovoltaic industry is constantly trying to decrease the cost-per-watt ratio of solar cells. This is achieved either by (a) lowering the manufacturing costs, which involves the use of new manufacturing techniques and lower-quality materials without lowering the established cell efficiency or (b) using higher-efficiency cell designs without increasing the cost. Both approaches require the development of new, more accurate and easier-to-interpret measurement techniques. Lower-quality materials with their higher levels of impurities and defects need to be better understood. Also, higher-efficiency cell designs with their stricter process tolerances need to be monitored more precisely.

With its leading role in research and development for industry and academia, our Centre is particularly interested in measurement techniques that can produce accurate and meaningful data. The improvement of measurement techniques has a direct impact on research activities and the optimisation of procedures used in manufacturing. The time and number of experiments needed to understand a certain phenomenon can be greatly reduced. Correct interpretation of these results is also a central concern.

This research group focuses primarily on the significant improvement of existing techniques but also on the development of completely new measurement concepts that would be of value for multiple research projects. Since mid-2012, our research has focused especially on increasing the applicability of advanced time-resolved photoluminescence spectroscopy (section 3.6.2.2). We also accompany this experimental work by theoretical concepts to make use of experimental data (section 3.6.2.3). A different and very new project was initiated by Prof Green to more precisely measure the room temperature energies of excitons (section 3.6.2.4). Work has continued toward developing algorithms for the extraction of local diode characteristics from photoluminescence images (section 3.6.2.5), an activity connected to the work of A/Prof. Trupke’s group (section 3.6.1). The third research activity in this group is focused on the optical reflection characteristics of solar cell back reflectors. Dr Yang developed the experimental setup in this group, and it is now being used for research in the High Efficiency Cells group under Dr Anita Ho-Baillie.

3.6.2.2 Fast Time-Resolved Photoluminescence Spectroscopy Measurement Setup

The minority carrier lifetime is a key parameter in determining the performance of a solar cell. The detailed study of this parameter and its dependence on various types of defects are the focus of an international research project under the lead of Dr Kampwerth and supported by ASI/ARENA [3.6.2.1]. Project partners are Dr Macdonald (ANU, Canberra) and Dr Schubert and Dr Schön (Fraunhofer ISE Freiburg, Germany).
Highly contaminated or defect-rich silicon, which is often found in thin film solar cells or in grain boundaries of multicrystalline silicon, has very short minority carrier lifetimes of often less than 1 µs. Measurement of this parameter with commonly-used techniques (such as quasi-steady-state photoluminescence decay or standard photoconductance decay techniques) is impossible as they are limited to larger lifetimes and probing areas. An additional difficulty is that short lifetimes, thin test-samples or small areas create only very weak luminescence and photoconductance signals. This is often beyond the speed and sensitivity of typically-used analogue detectors and electronics.

In this project, we at UNSW are building a unique and state-of-the-art system for very detailed minority carrier lifetime measurements. It will close the vital gap between the ultrafast optically-gated PL spectrometer—which measures lifetimes in the fs to ps range—used by the Third Generation group (section 3.5), and the more commonly-used optical lifetime techniques used in photovoltaics which work in the range of &micro;s to ms.

The system is designed to measure:

- (photo-) luminescence with 600-ps time resolution. This allows the measurement of a minimal minority carrier lifetime of 1 ns. The longest lifetime to be measured will be beyond 1 µs. (Overcoming technical barriers to exceed 1 µs are the focus of current work.)
- with a very high usable light sensitivity of 10 fA equivalent, or 1x10^4 photons/s and a wide dynamic range. This is equivalent to highly amplified cooled analogue detectors.
- with detectors sensitive in a wavelength range between 500 nm and 1,600 nm with sub-nm spectral resolution.
- with an illumination wavelength range variable between 500 nm and 2,200 nm with several-nm spectral resolution.
- on small spots on the test sample of less than 40 µm in diameter.
- while the test sample is heated or cooled between 105 K and 370 K (-168°C and +97°C).

This system combines several characteristics that are usually distributed over multiple individual systems. For example, common spectroscopes measure the luminescence spectrum without any time resolution and time resolved setups often do not feature optical spectral resolution, measuring at one or a few wavelengths. By combining both features it becomes possible to obtain luminescence spectra within the first 1 ns after excitation. In this time scale charge carriers will not have moved and spatial scans will be blur-free.

The functionality of the system, which is depicted with its components in Fig. 3.6.2.1, can be explained as follows: a very short laser pulse illuminates the test sample and generates minority carriers. These carriers recombine after a statistical lifetime, a material parameter of utmost importance to photovoltaic device operation. A certain percentage of these charge carriers will decay via a radiative recombination process that creates photons. These photons are then measured with an extremely sensitive and fast detector. Spectral filters for the excitation and detection beams allow the further investigation of energy levels, concentrations and lifetimes of various contaminants and defects in detail. To investigate very small and often difficult-to-measure sections such as grain boundaries, laser doped areas or Si-metal contact regions, a confocal microscope is used to pump and probe the sample on very small spots. Attenuators are used to change the excitation light intensity on the sample and to avoid overexposure of the detectors. For practical reasons, a camera with its own illumination source can be temporarily used to find spots of interest on the test sample before the actual measurement. Two optical fibres mechanically separate the main sections of excitation light conditioning, probing and analysis. This allows not only a plug-and-play interface with other setups, but also limits re-alignment and optimisation procedures to the section that is modified.
Figure 3.6.2.1: The basic components of the time resolved PL spectroscopy setup. It is separated into three major operational blocks of the conditioning of the excitation beam (upper part of figure), probing of the test sample (lower right hand side) and the analysis of the probe beam (lower left hand side). Top: A custom-built OPO laser generates pulses of variable frequency and a very broad spectral range. Its outputs are mixed, then its intensity is attenuated and spectrally filtered. After it is coupled into a fibre, it enters the confocal microscope. Bottom right: A confocal microscope focuses the excitation beam onto the test sample, which is controlled in its temperature and x,y,z position. For spot finding on the sample, a camera with its own illumination source can be used temporarily. The response signal from the sample is then fed into another fibre. Bottom left: The probe beam is first spectrally filtered via a monochromator, intensity attenuated and then fed into one of two fast APD detectors via fibre. Not shown are the timing, counting, switching and other assisting electronics.

3.6.2.3 Fast Time-Resolved Photoluminescence Spectroscopy Measurement Theory

Luminescence decay measurements with high time resolution provide more details than what has been commonly used for lifetime measurements. To make use of all details of the measurement signal, we have begun to develop more sophisticated mathematical models. These will then be used for iterative curve fitting to measured data to extract material parameters.

PhD candidate Kai Wang is focusing on the equations for time- and spectrally-resolved luminescence. Since last year’s annual report, significant advances have been made. Together with input of Dr Bill McLean, we have found an accurate and practical mathematical model [3.6.2.2] that can simulate...
time-resolved photoluminescence (PL) response from silicon wafers, as shown in Figure 3.6.2.1. The model is compatible with illumination sources, such as fast repetitive excitation pulses, which are often used in TCSPC acquisition techniques. Due to the complexity, a computer program was written to enable other researchers to use this mathematical model for practical work. A future benefit of this mathematical simulation model is that in iterative simulation, experimental measured data can be fitted to extract electric material parameters.

Figure 3.6.2.2: A silicon wafer is illuminated by monochromatic light with absorption coefficient $\alpha_1$ and PL is measured at a wavelength with absorption coefficient $\alpha_2$. Wafer thickness is assumed to be $W$ (along depth direction) and external front ($R_f$), internal front ($R_{in}$) and rear ($R_{bn}$) reflection have been taken into consideration.

Three recombination properties—bulk lifetime ($\tau_b$) and front and rear surface recombination velocities ($S_0$ and $S_W$, respectively)—have been taken into consideration, thus requiring the determination of depth- and time-dependent excess minority carrier density. Time-resolved PL can then be obtained by taking the reabsorption effect into consideration.

Eqs. 3.6.2.1 to 3.6.2.2 are the essential equations used to determine carrier density $n(z, t)$, where $D$ is the carrier diffusivity and $g(z)$ stands for the depth-dependent generation rate.

$$\frac{\partial n(z,t)}{\partial t} = D \frac{\partial^2 n(z,t)}{\partial z^2} - \frac{n(z,t)}{\tau_b} + g(z)$$  \hspace{1cm} (3.6.2.1)

$$D \frac{\partial n(z,t)}{\partial z} \bigg|_{z=0} = S_0 n(0,t)$$  \hspace{1cm} (3.6.2.2)

$$D \frac{\partial n(z,t)}{\partial z} \bigg|_{z=W} = -S_W n(W,t)$$  \hspace{1cm} (3.6.2.3)

By applying fast repetitive excitation pulses, carrier density will build up when the excitation is on and decay when it is off (as shown in Figure 3.6.2.3). Compared with the traditional solution, which uses infinite series summation, our method employs finite element analysis (FEA) to make the solution more practical. This algorithm has been implemented in a MATLAB program called TPL1D (Transient PL in 1D), which can be downloaded for academic use from the websites of UNSW SPREE and PV Lighthouse [3.6.2.3].

- 273 -
Figure 3.6.2.3: A depth- and time-dependent minority carrier density distribution in a p-type semiconductor under repetitive excitation pulses.

The user interface of TPL1D is shown in Figure 3.6.2.4, where users may specify the parameters of silicon wafer as well as the excitation conditions. Two plots can be obtained, including time-dependent PL intensity and depth- and time-dependent carrier density. The program is designed for simulating PL response from silicon wafers under the excitation of repetitive pulses yet it can also be used for simulating PL response including steady state and simple light-on and light-off conditions (see definition in [3.6.2.4]). Silicon bricks may also be simulated by simply setting the sample thickness to several centimetres. The validity of the FEA algorithm has been confirmed by comparison with PC1D [3.6.2.5].

A lifetime separation algorithm, similar to that in Ref. [3.6.2.6], has also been proposed. A deviation function between the simulated data and experimental data is defined as in Eq. 3.6.2.4 and by minimising the deviation function, lifetime separation can be achieved.

\[ \text{DEV} (\tau_b, S_D, S_W) = \sqrt{\frac{1}{N} \sum_{i=1}^{N} \left( \frac{\text{PL}(\tau_b, S_D, S_W) - \text{PL}_\text{exp}(\tau_i)}{\text{PL}_\text{exp}(\tau_i)} \right)^2} \]  

(3.6.2.4)

3.6.2.4 Exciton Binding Energy of Si

This project was initiated by Prof Martin Green. Its aim is to generate improved data for the electrical properties of the bandgap of silicon, especially the precise binding energy of excitons. The results are needed to calculate more accurate efficiency limits of Si solar cells, but are also needed for work on future Third Generation concepts. As this measurement requires an unusual optical measurement setup, the project fits naturally into our group’s portfolio. Ms Xu focuses her 4th year research on this experiment.

The exciton, a quasi-particle that consists of a negatively charged electron from the conduction band and a positively charged hole from the valance band, is bound by electrostatic Coulomb force. A simplified model for excitons is very similar to a hydrogen atom composed of an electron and a proton. The effective mass and permittivity of a Si exciton are both weaker than those of a hydrogen atom, resulting in relatively small excitonic binding energy. An exciton lowers by its own binding energy the photon absorption energy threshold at the silicon absorption edge. [3.6.2.9] The commonly accepted low-temperature excitonic binding energy for Si of 14.7±0.4 meV [3.6.2.10] has recently been revised by Prof. Green to an improved value of 15.01±0.06 meV [3.6.2.7]. While the excitonic effect is known to decrease with increasing temperature and even further with material impurities and defects [3.6.2.9], Aagnostopoulos et al. [3.6.2.11] calculated that an excitonic effect can still be seen at room temperature (25°C).
Due to the role of excitons in assisting optical absorption even at room temperature, the bandgap obtained from optical measurements usually includes the excitonic binding energy and does not provide the correct energy of the bandgap itself [3.6.2.7]. Thus a critical investigation of the exciton binding energy is necessary to correlate the optical absorption threshold and the bandgap. According to three-particle theory (electrons, holes and excitons) developed by Corkish et al. [3.6.2.8], excitons may also contribute to device current and thus improve solar cell output in some scenarios. Although electronically neutral, excitons may reduce the darksaturation current by up to 30% and simultaneously improve light-generated current by up to 40% when the exciton diffusion length exceeds that of the minority carriers [3.6.2.8].

Previous publications [3.6.2.10–12] successfully used wavelength derivative spectroscopy to measure excitonic effects. This spectroscopy technique provides significantly higher sensitivity than traditional wavelength modulation [3.6.2.13]. The derivative technique was previously realised with vibrating mirrors or vibrating slits in combination with a monochromator to create the required wavelength modulation [3.6.2.10]. In our experiment we use an analogue steering mirror at an open exit port of a monochromator and refocus on a slit, as shown in Figure 3.6.2.5. We expect to be able to measure the room temperature excitonic effect which could previously only be calculated [3.6.2.11], with results to be published soon.

![Figure 3.6.2.5: Closed-loop steering mirror modulation setup. The open exit port of a monochromator emits a spatially separated spectrum of wavelengths. An oscillating steering mirror reflects this light onto a slit, which lets only one wavelength through. The oscillation of the mirror in combination with the slit creates a modulation of the centre wavelength. The light is then simultaneously detected by the sample, a Si solar cell, and a reference, a germanium detector. Both signals are connected to lock-in amplifiers. The normalised derivative of the sample response is then calculated.](image)

3.6.2.5 Local I-V Characteristics from PL Images

In recent years, several publications have focused on the extraction of spatially resolved maps of electrical parameters from photoluminescence (PL) images, since Trupke et al. [3.6.2.14] demonstrated the feasibility of this idea in 2006. These maps show a local electrical parameter for
each point of the solar cell. Most of these parameters correspond to a relatively simple equivalent circuit, the one-diode model with series resistance.

PhD candidate Chao Shen successfully extended these theories in partially collaboration with Dr. Breitenstein to the more commonly used two-diode equation and derived several valuable parameter maps from this [3.6.2.15]. Even though the newly developed technique requires a longer measurement time than other PL imaging techniques, it offers the advantages of producing maps of the following local parameters (denoted with index \(xy\), referring to spatial coordinates):

- series resistance \(R_{S,xy}\)
- dark saturation current density \(J_{01,xy}\) (diode 1)
- dark saturation current density \(J_{02,xy}\) (diode 2)
- net generated / sunk current density \(J_{xy}(V_{\text{term}})\) (at arbitrary terminal voltages \(V_{\text{term}}\))
- voltage \(V_{xy}(V_{\text{term}})\) (at arbitrary terminal voltages \(V_{\text{term}}\))
- power density \(P_{xy}(V_{\text{term}})\) (at arbitrary terminal voltages \(V_{\text{term}}\))
- efficiency \(\eta_{xy}\)

The maps of parameters \(J_{02,xy}\), \(J_{xy}(V_{\text{term}})\), \(P_{xy}(V_{\text{term}})\), \(\eta_{xy}\) are new to PL-based imaging techniques and promise to be a useful addition. The different parameter maps are demonstrated on a single multicrystalline Si solar cell in Figures 3.6.2.6 to 3.6.2.10. The series resistance \(R_{S,xy}\) highlights all ohmic resistance problems in Figure 3.6.2.6. In this image a typical pattern of a conveyer belt is visible. It belongs to a belt furnace that was used during co-firing. It is likely that the belt was at a lower than targeted temperature, causing an insufficient formation of a low metal-Si contact. Also visible are interruptions of the metal grid, such as broken fingers or even cracks. The advantage of an image displaying electrical parameters becomes here obvious as the impact of a crack becomes visible, which might be otherwise not detectable via normal optical inspection due to its small size.

The images of the dark saturation current \(J_{01,xy}\) and \(J_{02,xy}\) of the first and second diode of a two diode equivalent model indicate recombination activity in the often associated bulk and junction areas, see Figure 3.6.2.7. A serial number is visible in the \(J_{02,xy}\) map, indicating damage to the junction and a reduction of cell performance; see Figure 3.6.2.9.

Figure 3.6.2.8 shows maps of the local voltage and effective current density at one-sun equivalent illumination and maximum operating voltage at the cell terminals. The cracks in the metal grid mostly impact the voltage in this particular cell. Only the highest series resistance area from the belt furnace step and the damaged junction had a noticeable impact on the current. Figure 3.6.2.9 shows the local values of the fill factor \(FF\) and the efficiency \(\eta_{xy}\). Thanks to the quantitative values in the maps, underperforming areas can be easily identified and their overall impact estimated. Figure 3.6.2.10 is a comparison between the efficiency calculated by this PL method and the power loss calculated via CELLO [3.6.2.16].

Our current research is focused on improving these algorithms. For example, the homogeneous series resistance patterns in Figure 3.6.2.6 are also visible in the dark saturation current density maps \(J_{01,xy}\) and \(J_{02,xy}\). This is likely due to an insufficient separation of these parameters in the calculation.
**Figure 3.6.2.6**: The local effective series resistance $R_{S,xy}$ shows a pattern belonging to the conveyer belt of a belt-furnace. The impact of broken fingers and cracks are also visible.

**Figure 3.6.2.7** left: the dark saturation current density of the first diode in a two diode model $J_{01,xy}$ and right: that of the second diode $J_{02,xy}$. This image also shows a serial number, which has obviously damaged the junction.
Figure 3.6.2.8 left: The voltage map at one-sun illumination with the terminals biased at the maximum power point. The crack, section A, the pattern of the belt furnace, section B and C, and the serial number, section D, all reduced the local voltage. Right: The current density map under the same operation conditions is more homogeneous. Only the most severe belt furnace marks and the serial number, section B and D, reduced the current.

Figure 3.6.2.9 left: The fill factor \( FF \) and right: the efficiency \( \eta_{xy} \) are good maps that summarise the performance of a cell. Areas that underperform are clearly visible, and the magnitude of the parameter is presented quantitatively.
Figure 3.6.2.10 bottom: A comparison between the efficiency calculated from PL images and power loss via CELLO method. (Please note that one colour scheme was inverted for compatibility reasons.) The agreement is a good preliminary result.

3.6.2.5 Summary

The results of the ongoing and new research activities in this growing group have been excellent. New concepts for photoluminescence imaging algorithms created notable advances in quantitative PL imaging of solar cells. The new project for fast and microscopic photoluminescence spectroscopy has also seen useful results in the theoretical work. The project to measure room temperature exciton binding energy is also an exciting project which will soon give results. Future measurement capabilities, together with advances in related data processing will create an additional world leading competence in our centre.

References

3.6.2.1 ASI / ARENA 1-GER010 Time- and spectrally- resolved Photoluminescence for Silicon Solar Cell Characterisation, 2012-2015
3.6.2.9 M. Green, Silicon Solar Cell - Advance Principles and Practice, University of New South Wales, 1995.
4. PUBLICATIONS

4.1 BOOKS


4.2 BOOK CHAPTERS


4.3 PATENTS


4.4 PAPERS IN REFEREED SCIENTIFIC AND TECHNICAL JOURNALS


4.5 CONFERENCE PAPERS AND OTHER PRESENTATIONS


Hameiri, Z., Ma, F. and McIntosh, K.R., “Investigation of low injection effects using the local ideality factor obtained from effective lifetime measurements”, 40th IEEE Photovoltaic Specialists Conference, Denver, June 2014.


Soufiani, A.M., “From low-temperature to high-temperature phase exciton binding energy and band gap evaluation of CH$_3$NH$_3$PbI$_3$ and CH$_3$NH$_3$PbI$_3-x$Cl$_x$ perovskites”, 2014 Asia-Pacific Solar Research Conference, Sydney, December 2014


4.6 REPORTS


4.7 RESEARCH TRAINING TOOL