## Contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Directors’ Report</td>
<td>2</td>
</tr>
<tr>
<td>2. Highlights</td>
<td>4</td>
</tr>
<tr>
<td>3. Staff List</td>
<td>12</td>
</tr>
<tr>
<td>4. Research</td>
<td></td>
</tr>
<tr>
<td>4.1. Introduction To Research</td>
<td>17</td>
</tr>
<tr>
<td>4.2. Facilities And Infrastructure</td>
<td>20</td>
</tr>
<tr>
<td>4.3. First Generation Wafer Based Projects</td>
<td>27</td>
</tr>
<tr>
<td>4.4. Second Generation: Silicon And Organic Thin-Films</td>
<td>48</td>
</tr>
<tr>
<td>4.5. Third Generation Strand – Advanced Concepts</td>
<td>75</td>
</tr>
<tr>
<td>4.6. Photonics: Photoluminescence Based Characterisation Of Silicon</td>
<td>112</td>
</tr>
<tr>
<td>5. Education</td>
<td>116</td>
</tr>
<tr>
<td>6. Organisational Structure</td>
<td>132</td>
</tr>
<tr>
<td>7. Financial Summary</td>
<td>134</td>
</tr>
<tr>
<td>8. Publications</td>
<td>136</td>
</tr>
</tbody>
</table>
The Australian Research Council (ARC) Photovoltaics Centre of Excellence commenced at the University of New South Wales (UNSW) on 13th June, 2003 with funding until 31st December 2010. The Centre’s mission is to advance silicon photovoltaic research on three separate fronts, as well as to apply these advances to the related field of silicon photonics. The educational activities of the former Key Centre for Photovoltaic Engineering are also integrated into the Centre.

Over the period of funding, 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. As evidence for growing maturity, the electricity generating capacity of new photovoltaic product manufactured in 2006 exceeded new nuclear power capacity for the first time, with the gap widening in 2007 and further in 2008 and 2009. Reducing prices, partly traceable to past Centre initiatives, means the technology is approaching “retail grid parity”, 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.

Most present photovoltaic sales are of “first-generation” solar cells made from silicon wafers, similar to the wafers used in microelectronics. The Centre’s world-leadership with these “first-generation” devices, with international records for the highest-performing silicon cells in most major categories (including the outright highest-performing cells and modules) was extended in 2008 with the demonstration of the first 25% efficient silicon solar cell. In 2009, a first-generation Centre cell of this type was key to establishing a new world record of 43% for the conversion of sunlight to electricity by any means. First-generation Centre research addresses the dual challenges of reducing cost and further improving efficiency. The rapid growth of the photovoltaic industry is generating widespread interest in ongoing innovations of the Centre’s first generation technology with several distinct technologies now in large-scale production and additional licences signed during 2009. A notable achievement during 2009 was the introduction of high-efficiency Pluto technology, co-developed with Suntech Power, the world’s largest silicon cell manufacturer, onto the market in large volumes.

Silicon is quite brittle so silicon wafers have to be reasonably thick, a fraction 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, over 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 saving 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, appearing on the market in 2006. Several megawatt fields of CSG Solar panels are now operating in Europe. During 2009, with support from an Australian Research Council Linkage Grant, collaborative work commenced with CSG Solar Pty Ltd aimed at further reducing the costs of this approach. The project is 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, rather than using brute-force processing in furnaces, as at present.

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. Over the last decade, Ashraf has been conducting research on organic light-emitting diodes. A team consisting of Ashraf, Martin Green, with an interest in organic solar cells since the 1970s, Gavin Conibeer who started his professional career as a polymer scientist, and Dirk König, the Centre’s ab-initio material simulation specialist, has been formed to spear-head the Centre’s effort in this area. This work, since a new area not foreshadowed in the ARC-funded Centre program, is supported by an ARC Discovery Grant.

The “second generation” thin-films have a large 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 targeting 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 concentrating on “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. Cells based on “hot” carriers are also of great interest since they offer the potential for very high efficiency from simple device structures. Although their implementation poses daunting challenges, considerable progress on addressing these was made during 2009.

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, established itself as the premium equipment supplier internationally using this approach during 2009.

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 sixth cohort of students from the Bachelor of Engineering (Photovoltaics and Renewable Energy) program graduated during the year. 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 fourth group of students have now graduated from the Centre’s second undergraduate program, leading to a Bachelor of Engineering (Renewable Energy).

We thank all those who contributed to the Centre’s success during 2009, particularly the Australian Research Council for its on-going support. The present continues to be a most 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 impending 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.
2. Highlights
RECORD 43% SUNLIGHT CONVERSION EFFICIENCY

After setting a new record of 25% last year for an individual silicon solar cell, the Centre provided the key contribution to a multi-cell combination that set a new outright record of 43% efficiency for converting sunlight into electricity by any means, irrespective of complexity or cost.

Because sunlight is made up of many colours of different energy, from the high energy ultraviolet to the low energy infrared, a combination of solar cells of different materials can convert sunlight more efficiently than any single cell. The Centre’s silicon cells are particularly efficient at converting red and near infrared wavelengths, showing conversion of these particular colours with efficiency up to 46%.

To produce the 43% sunlight conversion result, the Centre’s silicon cell was assigned its own specific colour band to convert. The four other cells involved in the new result were likewise assigned their own optimal colour bands ranging from the ultraviolet to the far infrared. These other four cells had been fabricated earlier by two separate US-based groups at the National Renewable Energy Laboratory and Emcore Corporation. These cells were also part of a combination that set the previously confirmed best result of 42.7%. The UNSW cell was fabricated by Drs Aihua Wang and Jianhua Zhao who have since left UNSW to set up Sunergy in China.

The 43% efficiency is the highest reported for any solar to electricity conversion process. It is not directly comparable to the Centre’s earlier 25% silicon cell result because it involves an expensive combination of five cells and the sunlight was focussed to produce a much higher intensity than standard sunlight for these measurements. The Centre is exploring the application of these results to photovoltaic “power towers”, where sunlight is reflected by a large field of mirror heliostats to a central receiver. The extra efficiency and reduction of waste heat may more than pay for the extra receiver complexity, in this case.

PLUTO MODULE SETS NEW WORLD RECORD

Dr Zhengrong Shi (left), CEO and Chairman of Suntech Power and former Centre researcher, with Professor Martin Green and Pluto module.

During 2009, early production modules from the Suntech Power using “Pluto” cell technology exceeded all previous international records for multi-crystalline silicon module conversion efficiency. Pluto technology is a joint development between the Centre and Suntech Power, a Centre partner. In August, a commercial Suntech module surpassed the previous record of 15.5% aperture area efficiency set by a small Sandia National Laboratory hand-crafted research module 15 years ago. Later in the year, Suntech exceeded its own record with an aperture area conversion efficiency measured at 16.53% by the Fraunhofer Institute for Solar Energy Systems. The world record breaking multi-crystalline silicon module was powered by Pluto PV cells utilizing solar grade silicon with each PV cell having a conversion efficiency well over 17%. With this value increasing as more production experience is gained, Suntech expects to exceed 17% efficiency at the module level during 2010.
COMMERCIALISATION OF LUMINESCENCE IMAGING BY BT IMAGING

UNSW Centre spin-off company BT Imaging continued the successful commercialisation of the luminescence imaging technology that was developed by Centre researchers Thorsten Trupke and Robert Bardos. The first product, the LIS-R1™ is a flexible offline R&D tool that allows fast and highly spatially resolved characterisation of silicon bricks prior to wafering, silicon wafers at any processing stage and fully processed silicon solar cells. It incorporates measurement techniques such as minority carrier lifetime imaging and series resistance imaging and has by now been deployed to several leading wafer and solar cell makers and top research institutes worldwide. Commissioning of a LIS-R1™ tool at UNSW is planned for April 2010.

Significant progress has also been made with the development of a range of inline characterisation tools. The first figure shows the LIS-W1™, a PL imaging system that can be integrated at any point of a solar cell production line. The second figure shows a fully automated sorter that uses PL imaging analysis in combination with standard inspection methods such as optical inspection, resistivity and thickness measurements for classification of raw wafers. Significant hardware improvements made at BT Imaging allow full resolution (Megapixel) luminescence inspection of as-cut wafers at in-line speed with measurement times below one second in both the LIS-W1™ and the sorter. This tool will be presented by BT Imaging for the first time at several trade shows in 2010.
NEW MAJOR EQUIPMENT

The Centre has added new capability to its research laboratories with major equipment additions totalling over $2M in uninstalled replacement value. A common feature of the equipment, where relevant, is the ability to handle large area 156 mm x 156 mm wafers that are becoming the production standard for solar cell manufacturers.

An 8.2 metre long, commercial fast firing metallization belt furnace funded by the NSW Department of State and Regional Development was installed to provide our first in house capability to fire 156 mm x 156 mm wafers on the same equipment as used by industry. A new custom integrated mirror steered scanning 532 nm laser and dopant spinner was commissioned to support laser doping research.

The Centre acquired its first commercial spectral response system capable of extended range measurements on cells with either double or single side contacts. This allows for spectral response measurements on conventional, rear contact and thin film on glass cells. One of the first of a new breed of commercially available silicon wafer characterization tools, a Luminescence Inspection System was sourced from Centre "spin off" company, BT Imaging, to obtain both non invasive Photoluminescence (PL) and Electroluminescence (EL) measurements from the one tool. A new aerosol deposition system capable of very fine scale patterning was purchased to build on research related to deposition by inkjet systems. Other major equipment additions include a high speed flash cell tester, spectrophotometer and the purchase of a Deep Level Transient Spectrometer (DLTS).
SUNSWIFT SOLAR CAR BLITZES DARWIN TO ADELAIDE

UNSW's solar racing team won a major victory in the Global Green Challenge from Darwin to Adelaide. Sunswift IV was the first Australian car to cross the finish line and the top-placed silicon cell car, a double win for the elated members of the student-led team.

This was the debut race for Sunswift IV, a three-wheeled, hand-built carbon fibre solar vehicle. The car cruises at 90km/h and can reach a top speed of 115km/h using just 1,300 watts, the same amount of power it takes to toast two slices of bread.

Team Leader Clara Mazzone, who is a student in the Centre's Renewable Energy Engineering program, said the Sunswift team had put in an extraordinary effort to prepare the new car and raise the $280,000 needed to fund the project and race campaign. She thanked the main University sponsors – UNSW Engineering, NICTA and UNSW Global – for their support, along with the team’s other major sponsors, aircraft maker Boeing and sustainable marketing agency Sunshine n Water.

In the overall results, the team was fourth on the road. The 3000km endurance test for eco-friendly vehicles draws competitors from around the world, including big-budget solar racing teams from the US and the Netherlands.

BEST PAPER AWARD AT WORLD’S LARGEST PHOTOVOLTAIC CONFERENCE

PhD Student Zi Ouyang - Principal Author.

PhD Student Zi Ouyang and his co-authors have been selected as the winners of the 24th European Photovoltaic Solar Energy Conference’s Poster Award in Hamburg, Germany in the area of “Thin-Film Photovoltaics”. Their paper was entitled Enhanced Photocurrent in Evaporated Solid-Phase-Crystallised Poly-Si Thin-Film Solar Cells Using Rear Surface Plasmons by Z. Ouyang, F. Beck, O. Kunz, P. Campbell, K.R. Catchpole, S. Varlamov, S. Pillai, M.A. Green.

“Surface Plasmons, as a novel light-trapping method, have the potential to significantly improve solar cell performance with little add-on cost and are especially viable for thin-film solar cells”, said Zi Ouyang. “At the conference there were six topics and eight best posters awards among 1,081 accepted posters (991 of them were presented at the conference as award candidates). Our poster was in the “Thin-Film Solar Cells” topic area.”

STUART WENHAM RECEIVES MULTIPLE PRESTIGIOUS AWARDS

Professor Stuart Wenham in a Centre teaching lab next to a commercial solar module using one of his early inventions, the “buried contact” solar cell.
The Green Globe Prize awarded to Prof Wenham.

Centre Director Professor Stuart Wenham was presented with another major international award at the 34th IEEE Photovoltaic Specialists Conference in Philadelphia - the IEEE William R. Cherry Award - the most highly valued international award for photovoltaic researchers. “This award is named in honour of William R. Cherry, a founder of the photovoltaic community”. “The purpose of the award is to recognize engineers and scientists who devote a part of their professional life to the advancement of the technology of photovoltaic energy conversion. The nominee must have made significant contributions to the science and/or technology of PV energy conversion, with dissemination by substantial publications and presentations”.

Later in the year, Professor Stuart Wenham was presented with the Green Globe Award. The Green Globe Awards are the leading environmental awards in New South Wales. Now in its tenth year, the NSW Government's Green Globe Awards showcase outstanding achievements in the sustainable use of natural resources in NSW and leadership in tackling climate change.

Professor Stuart Wenham also won the top prize at the 2009 Inventor of the Year awards hosted by New South Innovations, the UNSW technology commercialisation company. In a career spanning more than a quarter of a century, Professor Wenham has invented or co-invented eight suites of solar cell technologies that have been licensed to solar cell makers around the world, including Suntech-Power, BP Solar and Samsung. These companies have annual production volumes valued at hundreds of millions of dollars in an industry that is now the world’s fastest-growing energy sector.

MARTIN GREEN HONOURED BY SEVERAL AWARDS

Professor Martin Green, Centre Executive Research Director, was again recognised for his achievements in the world's richest science prize, the inaugural Zayed Future Energy Prize presented in January 2009 in Abu Dhabi. Professor Green, one of the two finalists, was awarded the US$350,000 prize by the Crown Prince of Abu Dhabi, Sheik Mohamed bin Zayed Al Nahyan, for his groundbreaking work to make photovoltaic technology more efficient and affordable. Professor Green's prize was given in recognition of his research on high-efficiency third-generation solar cell technology – which has the potential to drastically reduce the cost of solar power. “I firmly believe that many of our future energy needs can be addressed by photovoltaic technology,” Professor Green said. “I’m proud that as one of the first recipients of this award, photovoltaic technology and its importance in the renewable energy mix is also being recognized as a commercially viable solution.”

Professor Martin Green was honoured by another award just two months later. In March, ENI, the major Italian energy company, announced the winners of the 2009 ENI Award, its competition to promote research and technological innovation in sustainable energy. Professor Green was awarded the 2009 ENI Award for Renewable and Non-Conventional Energy, presented for advanced R&D results in renewable and non-conventional energy sources. The award was presented in the La Scala, the historic opera theatre in Milan and was followed by a lecture series across Italy.

Eco-ambassador … Professors Green (left) and Garnaut (right) in “The Alternative Ambassadors” by Giles Alexander (foreground).

Professor Green’s pioneering solar cell research has earned him some of the world’s most important prizes in science and engineering such as the two above awards. Now he, or at least his image, is in the running to win one of Australia’s biggest art prizes. Sydney artist Giles Alexander has reached the finals of the 2010 Archibald Prize with a portrait of Professor Green and leading economist Professor Ross Garnaut. The imposing double portrait featuring the country’s leading solar scientist alongside the author of the influential Garnaut Climate...
Change Review is called *The Alternative Ambassadors*, in recognition of a 16th century artwork, *The Ambassadors* by Hans Holbein, which Giles Alexander used as his inspiration. Giles is the husband of Dr Anna Bruce, of the School of Photovoltaic and Renewable Energy Engineering, and decided Professor Green was an ideal subject for his debut Archibald entry.

"Obviously, being married to Anna I’m pretty aware of the climate change debate – she’s a very passionate advocate of climate science," Giles said after his painting became one of 34 finalists selected from nearly 900 submitted works. "I had met Martin a few times before – he’s such an outstanding figure in the solar community."

Mr Alexander said he had wanted to avoid using a media celebrity as his subject. "There are far more interesting people out there as far as I’m concerned – I feel that the sciences are the most creative realm of humanity now."

**BOOKS IN TRADITIONAL CHINESE**

Following the publication of the Centre’s first book in simplified Chinese in 2008, in 2009, the Centre published for the first time in the Traditional Chinese language, targeting photovoltaics growth in Taiwan, Hong Kong and Macau. Two books were published:


**High Profile Visitors:**

**PRESIDENT OF SOUTH KOREA VISITS UNSW PHOTOVOLTAICS LABS**

The Centre’s world-leading solar cell technology has generated interest at the highest level of the Korean government, with President Lee Myung-bak visiting campus visiting the Photovoltaics Laboratories on 5th March 2009.

"We are honoured to have President Lee as a guest at the University," the Vice-Chancellor Professor Fred Hilmer said during the official welcome. "This visit is high-level acknowledgement of our leadership position and we are keen to strengthen and deepen our connection to industry and education in Korea."

Dr Richard Corkish, Head of the School of Photovoltaic and Renewable Energy Engineering, led the President on a tour of the Centre’s labs where the world’s most efficient silicon solar cells are produced. Dr Corkish applauded the President’s statement that the importance of developing clean energy solutions overrode the current economic challenges presented by the global financial crisis. "Our research team is conscious that Korea is a rapidly emerging producer in this field and we are currently in discussions with Korean companies about new manufacturing technologies," he said.

The President later told reporters that he hoped the two countries can work together in developing clean energies. "Korea and Australia are in a unique position to bridge the gap between developing and developed countries on climate change," President Lee said.

“This was a very successful event,” Dr Chung-Sok Suh, Director of the Korea-Australasia Research Centre (KAREC) at UNSW said. “With our leadership in two key areas on the President’s agenda – clean technologies and Korean studies – it’s appropriate that UNSW is the only Australian university to host the president on this visit.”
CHINESE GOVERNOR VISITS UNSW PHOTOVOLTAICS LABS

The ARC Photovoltaics Centre of Excellence was honoured by the visit of His Excellency Mr. Guo Geng Mao, Governor of Henan Provincial Government and delegates on 3rd February 2009. “We are most pleased to show His Excellency thorough our photovoltaics laboratory,” says Dr. Richard Corkish. “We have very strong academic and industrial links with many Chinese Universities and PV manufacturing groups. Visits such as these are instrumental in fostering collaborative activities.”

JULIA GILLARD TURNS FIRST SOD FOR NEW ENERGY BUILDING

Triumphant bid team: Nicole Kuepper (PV Centre), Jason Coombs (Chancellery), Martin Green (PV Centre), Graham Davies (Dean, Engineering), Peter McGeorge (Chancellery), Rose Amal (Director, CERPA) and David Jordan (PV Centre/Engineering). (Another bid team member Prof Stuart Wenham, also from the PV Centre, is missing from the photo). Inset: Deputy Prime Minister of Australia Julia Gillard.

In December 2009, Deputy Prime Minister of Australia Julia Gillard opened the site for the new Tyree Energy Technologies Building at UNSW. This new $155 million building will be the new home for many of the Centre’s educational and research activities. The project has received $75 million from the Australian Government’s Education Investment Fund (EIF) and will be a carbon-neutral design due to be completed by early 2012. As well as housing the ARC Photovoltaics Centre of Excellence, the building will also be the focal point of the University’s new Centre for Energy Research and Policy Analysis (CERPA), bringing together the capabilities of nine UNSW faculties to develop solutions to future energy challenges. As well as research in photovoltaics, other work under the umbrella of CERPA includes research into carbon capture and storage, oil and gas reservoir characterisation, nanomaterials and policy and market analysis. The building will also house learning space for 300 engineering students. The photo shows the bid team who successfully presented the case for funding to the Australian Government. In a very competitive funding environment, the UNSW bid emphasised the past achievements of the PV Centre and the way the new building would boost PV Centre activities. The inset shows the Deputy Prime Minister presenting the well-received opening speech.
3. Staff List
DIRECTOR
Stuart Ross Wenham, BE BSc PhD UNSW, FTSE, FIEEE, FIEAust
(Scientia Professor)

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Anita W.Y. Ho-Baillie, BE PhD UNSW (until January 2009)
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Ashraf Uddin, BSc (Hons) MSc Dhaka U, Bangladesh; PhD
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Sergey Varlamov, PhD Moscow

BUSINESS, TECHNOLOGY & OPERATIONS MANAGER
Mark D. Silver, BE UNSW, GMQ AGSM

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Merlinde Kay (P/T)
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Santosh Shrestha, PhD UNSW

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Sergey Varlamov, PhD Moscow

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Mathew Edwards, BE PhD UNSW
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Prof. Hans Queisser (October 2009)
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Mines, MSc UNSW
Prof. Bingqing Zhou, Inner Mongolia Normal University,
China (since August 2009)

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Yong Heng So
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Robert Patterson
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Binesh Puthen Veettil
Yong Heng So
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Yuguo Tao
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Long Seng To
Lara Treiber

**MASTERS STUDENTS**

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Do Soon Jung (since July 2009)
Anahita Karpour
Kenneth McLean
Gerald Parnis
Yang Michael Song (until October 2009)
4. Research
4.1 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 is funded until December 2010.

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. 4.1.1) 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 the technological emphasis upon 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, to save on material use.

![Figure 4.1.1: “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).](image1)

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. 4.1.1), 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.

Wafers are 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 commercialising “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. 4.1.2). 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. CSG Solar, a partner in the Centre, has commercialised an approach pioneered by Centre researchers that is unique in that it is based on the use of the same high quality silicon used for first-generation production, but deposited as a thin layer onto glass.

![Figure 4.1.2: Example of “second-generation” thin-film technology (module fabricated on CSG Solar’s German production line, based on thin-films of polycrystalline silicon deposited onto glass, again UNSW-pioneered technology).](image2)

As well as its collaborative activities with CSG Solar, the Centre currently maintains a largely independent program addressing alternative solutions to those adopted by CSG Solar for producing high-performance “silicon-on-glass” solar cells. The main emphasis of both is the development of lower-cost approaches (such as deposition by evaporation rather than PECVD). The Centre also commenced activities on carbon-based, organic solar cells during 2009.

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 completely different manufacturing cost structure. However, costs again are increasingly becoming 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 is possible by increasing energy-conversion efficiency. This leads to the notion of a third-generation of solar cell distinguished by the fact that it is both high-efficiency and thin-film. To illustrate the cost leverage provided by efficiency, Fig. 4.1.3 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 (12-20%). The dotted lines in Fig. 4.1.3 show the corresponding cost/watt, the market metric. Values as low as US$1/watt may be feasible by increasing the efficiency while reducing manufacturing cost, but this is close to the limit for the first-generation approach.

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 (5-15%). Overall, this trade-off produces costs/watt estimated as about 2 times lower than those of the wafer product, in large production volumes.

The third-generation is specified as a thin-film technology, which therefore results in 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 these). 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. 4.1.3 suggests that third-generation costs 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 implementation in the Centre’s timescale (Fig. 4.1.4). 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. Photon up-conversion as a way of “supercharging” the performance of relatively standard cells forms a second line of research. A third is the investigation of schemes for implementing hot-carrier cells. Both of the latter are well suited to organic solar cells.

The fourth “spin-off” 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. 4.1.5). Developing this approach to its full potential has formed an increasingly large part of the Centre’s photonics program.

Figure 4.1.3: Efficiency and cost projections for first-, second- and third-generation photovoltaic technology (wafers, thin-films and advanced thin-films, respectively).

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Figure 4.1.3: Efficiency and cost projections for first-, second- and third-generation photovoltaic technology (wafers, thin-films and advanced thin-films, respectively).

Figure 4.1.4: 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.

Figure 4.1.5: 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 a Centre “spin-off” during 2008.
4. Research continued

4.2 Facilities and Infrastructure

The ARC Photovoltaics Centre of Excellence is located at the Kensington campus of the University of New South Wales, about 6 km from the heart of Sydney and close to its world famous beaches including Bondi, Coogee and Maroubra (Fig. 4.2.1).

Organisationally, the Centre of Excellence is located within the new School of Photovoltaic and Renewable Energy Engineering (SPREE) within the Faculty of Engineering. The Centre of Excellence has a large range of laboratory facilities (Fig. 4.2.2). These include the Bulk Silicon Research Laboratories, the Device Characterisation Laboratory, the Optoelectronic Research Laboratories, the Thin-Film Cell Laboratory, the Industry Collaborative Laboratory and Inkjet Processing Laboratory. Off campus the Centre has a Thin-Film Cleanroom facility at Botany, 5km south-west of the main campus. Another important resource is the Semiconductor Nanofabrication Facility (SNF) jointly operated by the Faculty of Science and the Faculty of Engineering.

Additional equipment commonly used for solar cell work is found at the new MicroAnalytical Research Centre (MARC) 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.

During 2009, the development and acquisition of laboratory equipment and infrastructure continued with specific details about significant additions found under the laboratory headings which follow.
computational power of 960 Gigaflops for Density-Functional-Hartree- 
Fock and molecular dynamical computations. A second 128 core cluster 
has been installed for complementary investigations of energy efficiency 
and renewable energy via computational fluid dynamics techniques.

The Student Computer network comprises of two computer 
laboratories of total 83 m² with 5 servers, a UNSW custom CSE 
computer based IPQ router and 34 workstations. Students enrolled in 
the Undergraduate Degree Courses use these computers for computer-
related coursework and Internet access. There is also an Internet 
capable web-server that gathers and displays data collected from solar 
arrays on the roof of the building. These data can be viewed using a 
web browser and can be made available for Internet access.

Students also have access to over 200 additional workstations made 
available through collaboration with the School of Computer Science 
and Engineering.

The Laboratory Development and Operations Team develops and 
maintains core Centre and laboratory facilities. During 2009, the 
team, under the leadership of Mark Silver, comprised of an additional 
5 equivalent full-time and 12 casual 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 Cell Laboratories. Total laboratory processing space 
of over 580 m² (including the Industry Collaborative, InkJet Processing 
Development, Device Characterisation and Optoelectronic Research 
Labs) is located in the Electrical Engineering Building and is serviced 
with filtered and conditioned air, appropriate cooling water, processing 
gases, de-ionized water supply, chemical fume cupboards and local 
exhausts. There is an additional 819 m² area for the accommodation of 
staff, research students, school office and laboratory support facilities. 
Another 480 m² of combined roof space accommodates fixed PV arrays 
and 361 m² of accessible outdoor experimental space. Off site, areas 
totalling 200 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 23 tube diffusion furnaces, 6 
vacuum evaporation deposition systems, a laser-scribing machine, 
two laser doping machines, rapid thermal annealer, four-point sheet-
resistivity probe, quartz tube washer, silver/nickel and copper plating 
facility, visible wavelength microscopes, 3 wafer mask aligners, spin-on 
diffusion system, photoresist spinner, electron beam deposition system, 
metalization belt furnace, manual and automatic screen printers and a 
laboratory system control and data acquisition monitoring system.

**Figure 4.2.3: CNC Laser Scribe Tool.**

The laser scribe tool, shown in Figure 4.2.3, 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 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. 
DEVICE CHARACTERISATION LABORATORY

This laboratory is located on the lower ground floor of the Electrical Engineering Building. Associated with it is the Optoelectronic Research Laboratories, reception area, seminar room, offices for Centre staff interacting with the public and industry, including the Business & Technology Manager, Finance Officer, External Relations and Design Assistance Division Manager.

The Device Characterisation Laboratory 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 4.2.4, 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 156mm square wafer capability as shown in Fig 4.2.5, a replacement UV/VIS/NIR spectrophotometer and a commercial Luminescence Inspection System (LIS) from spin off company BT Imaging.

OPTOELECTRONIC RESEARCH LABORATORIES

This facility has six optical benches and several visible and near-infrared semiconductor diode lasers along with other optical and electrical instrumentation. The facility is used for photoluminescence (PL) and electroluminescence measurements in the visible and infrared spectral range up to wavelengths of 2500nm, luminescence experiments with simultaneous two-colour illumination, quasi steady state photoluminescence lifetime measurements and Sinton lifetime testing with the conventional flash-light replaced by a high-power light emitting diode array.

This facility also houses the Centre's world-leading first photoluminescence imaging system. Other equipment includes a silicon CCD camera (for sensitive PL measurements), spectroscopic PL systems, PL lifetime measurement unit, and LBIC measurement system. Areas separate from the Device Characterisation Laboratory were necessary in order to meet stringent standards for safe laser use. It shares cryogenic cooling equipment with the Device Characterisation Laboratory.
**THIN-FILM CELL LABORATORY**

This 40 m² laboratory is equipped with a range of equipment for thin-film deposition and patterning, including a plasma-enhanced chemical vapour deposition (PECVD) system, a sputtering system, larger area plasma etcher, a reactive ion etcher (RIE), a resistively heated vacuum evaporator, helium leak detector and an optical microscope with digital image acquisition system. Also used by the laboratory is an electron-beam vacuum evaporator for silicon which is physically located within the Bulk Silicon Research Laboratory. This Si evaporator is also equipped with an ionizer unit and a sample heater, enabling fast-rate Si homoepitaxy at temperatures of about 500-600°C by means of ion-assisted deposition (IAD). The IAD is also equipped with a residual gas analyser to permit real time process monitoring. Other equipment of use in thin-film projects is located within the Semiconductor Nanofabrication Facility.

The PECVD system, shown in Fig. 4.2.7, 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) 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.

In 2008 the thermal evaporator was upgraded to also support e-beam evaporation. This capability greatly expands the range of materials which can be deposited and is of great interest to 3rd generation researchers. In 2009 a new 4 point probing station was added to the laboratory.

**INDUSTRY COLLABORATIVE LABORATORY**

This 120 m² laboratory houses equipment needed for many of the industry-collaborative research activities including the Buried-Contact Solar Cell group. The laboratory equipment includes a belt furnace; a state of the art laser micromachining tool; a new PECVD deposition system (located in the adjacent thin film solar cell laboratory); a TiO₂ spray deposition station; a high temperature semiconductor muffle furnace, manual screen printer and a fully automatic production scale screen printer. In 2008 a new 532 nm green laser was added and customised in-house to increase the capability for processing laser doped solar cells.
In 2009 new additions included a fast metallization firing furnace capable of processing 156mm square wafers, a light induced plating system, spin on doper and mirror steered scanning laser for laser doping.

**INKJET PROCESSING DEVELOPMENT LAB**

This 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 inkjet material deposition printing systems, capable of depositing a wide range of materials onto different substrates, a surface tension meter and viscometer. In 2009 a commercial aerosol deposition system capable of very fine scale patterning was purchased.

**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 are being expanded to house the, NCRIS funded, Australian National Nanofabrication Facility.
THIN-FILM CLEAN ROOM FACILITY IN BAY STREET, BOTANY

In 2003, the Centre added a 120 m² cleanroom facility in Bay Street, Botany to its infrastructure, greatly improving its experimental capabilities in the area of thin-films. This cleanroom is equipped with several fume cupboards, two tube furnaces, an electron-beam vacuum evaporator, a thermal vacuum evaporator, a glass washing machine, a rapid thermal processing (RTP) machine and a 5-chamber cluster tool. The cluster tool presently features four plasma-enhanced chemical vapour deposition (PECVD) chambers and one lamp-heated vacuum annealing chamber. The PECVD chambers enable the low-temperature deposition of dielectric films (silicon oxide, silicon nitride, etc) and amorphous silicon films (either n- or p-doped or undoped). Furthermore, samples can be hydrogenated by PECVD using hydrogen plasma at substrate temperatures of up to 480°C. During 2004 the Centre purchased a low-pressure chemical vapour deposition (LPCVD) system, an infrared NdYAG laser scriber and a box furnace for sample annealing. The LPCVD system is capable of depositing doped crystalline silicon on glass and with its additional remote plasma source is currently engaged in hydrogenation work. The NdYAG laser is used for scribing silicon films and other suitable metal and dielectric materials.

In 2006, a state of the art multi-target sputter machine was installed. In 2008 this vacuum tool was upgraded from four to five separate targets. Each target is able to be operated independently of one and other, allowing users to cosputter 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 system can handle substrates up to 150mm x 150mm. Excellent film purity is assured as the system incorporates a load-lock. Computer control can be used for most operations, including substrate heating, allowing precise multilayers to be deposited repeatedly.

During 2007, a new computer controlled multi pocket, multi source UHV electron beam evaporator system was delivered. This equipment provides the capability for high "industrial" rate silicon and other thin film deposition.

In 2009 an optically assisted IV measurement system was installed for the determination of static hot carrier distributions. The LPCVD computer control system was also upgraded to provide enhanced throughput.
4.3 First Generation Wafer Based Projects

RESEARCH TEAM:

UNIVERSITY STAFF
- S. Wenham (Centre Director)
- M. A. Green (Executive Research Director)
- A. Ho-Baille (Deputy Director – High Efficiency Cells)
  (until Jan 2009)
- T. Trupke (Deputy Director – Photoluminescence Imaging)

POSTDOCTORAL FELLOWS
- Dr H. Mehrvarz
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POSTGRADUATE RESEARCH STUDENTS AND RESEARCH ASSISTANTS
- L. Mai (Research Assistant and PhD student)
- B. Tjahjono (Research Assistant and PhD student)
- M. Lenio (Research Assistant and PhD student)
- Z. Hamieri (PhD student)
- A. Lennon (Research Assistant and PhD student)
- N. Kuepper (Research Assistant and PhD student)
- M. Lenio (Research Assistant and PhD student)
- Z. Hamieri (PhD student)
- A. Lennon (Research Assistant and PhD student)
- S. Wang (PhD student)
- N. Borovjevic (Research Assistant and PhD student)
- S. Zamani Javid (Research Assistant and PhD student)
- P. Hamer (Research Assistant and PhD student)
- A. Sugianto (Research Assistant and PhD student)
- B. Hallam (Research Assistant and undergraduate thesis)
- A. Wenham (Research Assistant and undergraduate thesis)
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- A. Han (Research Assistant)
- C. Chan (Research Assistant)
- G. Xu (PhD student)
- K. Valliappan (Research Assistant)
- L. Zhang (Research Assistant)
- M. Eadie (Research Assistant)
- Y. Yao (PhD student and Research Assistant)
- L. Gu (Research Assistant)
- N. Western (Research Assistant)
- Mattias (Research Assistant)
- Xi (Research Assistant)
- X. Bai (Research Assistant)
- Yang Yang (PhD student) (since Aug 2009)
- Y. Yeung (Research Assistant)

TECHNOLOGY TRANSFER TEAM:

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- S. Wenham (Technical Director)
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TEAM MEMBERS
- N. Kuepper
- A. Sugianto
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- B. Tjahjono
- L. Mai
- C. M. Chong

NEWSOUTH INNOVATIONS
- N. Simpson
- A. Prib

4.3.1 High Efficiency Silicon Cells

43% EFFICIENT SOLAR CONVERSION

During 2008, the Centre achieved one of its major long-term milestones, the first silicon solar cell to convert 25% of incident sunlight into electricity. The passivated emitter, rear locally diffused (PERL) cell structure leading to this achievement is shown in Fig. 4.3.1.1.

During 2009, the Centre provided such a cell as the key contribution to a multi-cell combination that has set a new outright record of...
43% efficiency for converting sunlight into electricity by any possible approach, irrespective of complexity or cost [4.3.1.1]. One way of improving the efficiency of solar cells is to subdivide the broad solar spectrum into smaller energy ranges and to convert each range with a cell of appropriately matched bandgap. This idea (Figure 4.3.1.2) seems to have been first suggested in 1955 by Jackson [4.3.1.2]. However, it was not until 1978 that this idea was first demonstrated experimentally by Moon et alia [4.3.1.3], with an efficiency of 28.5% measured in outdoor sunlight using a 17-layer dichroic reflector stack to steer the light of energy above 1.65 eV onto an AlGaAs cell and below 1.65 eV onto a silicon cell.

Subsequent interest has been in monolithic stacks of cells as in Fig. 4.3.1.2 (b) for thin-film, space cell and concentrator cell use. However, the greater flexibility in cell choice made possible with the spectrum splitting approach combined with the low losses associated with dichroic reflectors makes it likely that higher efficiency will always be possible than with the monolithic approach, at the expense of greater system complexity.

This potential has recently been demonstrated with a composite cell efficiency of 42.7% reported for split-spectrum cell combinations involving a total of five cells of different bandgap [4.3.1.4]. The Centre extended this work by increasing composite efficiency to beyond 43%, the highest reported to date for any combination of photovoltaic devices, and by putting measurements on a more rigorous footing.

The improved efficiency was measured under concentrated sunlight. Minimal additional boosts occur in reporting split-spectrum results. If losses in concentrating optics are ignored, as in normal concentrator cell measurements, the only additional losses in the scheme of Figure 4.3.1.2 (a) arise from any non-ideal performance of the dichroic reflectors. The dichroic reflectors involve dielectric stacks that are essentially lossless at visible and near infrared wavelengths. In the work of Moon et alia [4.3.1.3], the dielectrics ZnS and Na₃AlF₆ were used. The main non-ideality involved is not absorption in the filters, which is negligible as noted, but the non-ideal reflection and transmission properties of these filters. The transition from reflective to transmissive behaviour occurs over a finite wavelength range rather than abruptly and filters do not always partition their response between reflection and transmission as exactly as desired for other wavelengths of interest. For example, in the experiment described by Moon et alia [4.3.1.3], about 5% of the light that would ideally be transmitted to the AlGaAs cell was instead reflected onto the silicon cell. Here it was converted at 0.6 V rather than 1.1 V. This is the main component of a total 2-2.5% relative performance loss attributable to the non-ideal properties of the dichroic reflectors in this case. Additional effort in improving filter design would further reduce this loss.
This loss is small compared to other unavoidable losses involved in using concentrator cells, including the lens, light uniformity and thermal losses previously mentioned. It is also small compared to the normal 6% measurement uncertainty in measuring the performance of a monolithic concentrator cell stack [4.3.1.5]. Moreover, there are compensating operational advantages expected from spectral-splitting as opposed to cell stacking. The larger cell footprint would allow better thermal control. Interestingly, in the work of Moon et alia [4.3.1.3], wasted infrared wavelengths were directed at the AlGaAs cell which had a lower temperature coefficient of performance, an additional advantage. The larger cell footprint also means better response to diffuse and stray light [4.3.1.6] that will, to first-order, depend on the ratio of cell to aperture area. Operationally, there will be less spectral mismatch loss if cells are connected in voltage-matched assemblies [4.3.1.7] rather than current-matched as normally for monolithic tandem cells.

Unavoidable losses involved in the practical use of either scheme of Fig. 4.3.1.2 are therefore similar in magnitude. There are likely increases in system complexity and component cost with the split-spectrum approach, although substantially higher efficiency could more than offset these at the system level. Monolithic tandem cells represent a subcategory that may have practical advantages, in the same way that silicon may have practical advantages over III-V cells, but would not be expected to be able to match the efficiency of a similarly well-developed split-spectrum combination, as the present work has shown.

Table 4.3.1.1: New composite split-spectrum concentrator cell result (Global ASTM G173-03 spectrum).

<table>
<thead>
<tr>
<th>Cell</th>
<th>Supplier</th>
<th>Spectral Range (nm)</th>
<th>Cell Area (cm²)</th>
<th>Irradiance (kW/m²)</th>
<th>Aperture (cm²)</th>
<th>Current Density (mA/cm²)</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaInP/ GaAs (2 terminal stack)</td>
<td>Emcore [4.3.1.4]</td>
<td>280 - 890</td>
<td>0.1245</td>
<td>24.2</td>
<td>3.0</td>
<td>27.6</td>
<td>31.7</td>
</tr>
<tr>
<td>Si</td>
<td>UNSW</td>
<td>890 - 1100</td>
<td>4.00</td>
<td>4.21</td>
<td>16.8</td>
<td>9.7</td>
<td>5.7</td>
</tr>
<tr>
<td>GaInAsP/GaInAs (3 terminal stack)</td>
<td>NREI [4.3.1.4]</td>
<td>1100 - 4000</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>7.8</td>
<td>5.6</td>
</tr>
<tr>
<td>GaInAsP</td>
<td>NREI</td>
<td>1100 – 1350</td>
<td>N/A</td>
<td>40.1</td>
<td>N/A</td>
<td>6.7</td>
<td>3.7</td>
</tr>
<tr>
<td>GaInAs</td>
<td>NREI</td>
<td>~1350=1800</td>
<td>N/A</td>
<td>41.7</td>
<td>N/A</td>
<td>1.9</td>
<td></td>
</tr>
<tr>
<td>5 Cell Combination</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>51.9</td>
<td>43.0 ± 1.9</td>
</tr>
</tbody>
</table>

When results for the Centre's high performance silicon cell over the 890-1100 nm range were combined with previously reported results (Table 4.3.1.1), this gave a self-consistently summed conversion efficiency of 43.0% ± 1.9% under the ASTM G173-03 global spectrum. Note that the uncertainty in this measurement (about 4% relative) is smaller than in measurements of monolithic tandem cells (typically 6% relative) since current matching issues are relaxed. The efficiency of the silicon cell in converting its assigned energy in the 890-1100 nm range is a very creditable 44.3%, showing this cell's role in boosting the efficiency of the combination. Figure 4.3.1.3 shows the layout of high performance cells on a 10 cm diameter silicon wafer.

Figure 4.3.1.3: Dr Anita Ho and Professor Martin Green showing the layout on a silicon wafer of silicon cells of the type used to set the 43% record.
4. Research continued

REFERENCES


4.3.1.6 A. Goetzberger, private communication, circa 1990.


4.3.2 Industry Collaborative Research and Commercialisation

4.3.2.1 Introduction

The Centre's Technology Transfer team (TTT) was established in 2008 to accelerate the developments of the Centre's commercially significant technologies and to carry out technology transfers to industry. This includes assisting companies to establish and optimise the large scale production of UNSW photovoltaic technology. With the high demand for UNSW technology and new licences, the TTT grew significantly during 2009 with the inclusion of Dr. C. Chong, Dr. A. Lennon and C. Chan. The already strong academic record of the TTT was also further enhanced with an additional two team members being awarded University Medals for being placed first in their respective university programs. This included Dr Lennon who received the University Medal for being placed 1st in her Chemistry Degree at Sydney University and B. Hallam who received the University Medal for being placed 1st in Photovoltaic Engineering at UNSW. This takes the number of University Medalists within the TTT to five at the end of 2009, but with another university medalist Dr Emily Mitchell set to also join the team from the Fraunhofer Institute in Germany during 2010. Figure 4.3.2.1 shows the TTT with members from left to right being D. Jordan, A. Sugianto, S. Wenham, A. Lennon, B. Hallam, L. Mai, B. Tjahjono and N. Kuepper.

Figure 4.3.2.1: TTT photo with M. Edwards overseas at the time.

4.3.2.2 Industry Collaborators and Licensees of Technology

The Centre has a large number of collaborators and licensees including many cell manufacturers working with the Centre to improve or develop new solar cell technology for commercialisation. Some of these fund the Centre quite generously and interact strongly with 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 2009 despite the international financial downturn in late 2008. 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, Optomec, Global Sunrise Energy, BP Solar, Sunergy, CSG Solar, E-ton Solar, Spectraphysics, Hyundai Heavy Industries, China Light, Corum Solar, Advent, Shinsung, JA Solar and Yunnan Tianda. Several of these companies are amongst the world’s largest solar cell and equipment manufacturers.

4.3.2.3 Commercially Relevant Technologies

INTRODUCTION

With screen-printed solar cells continuing to dominate commercial manufacturing, 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.

![Figure 4.3.2.2: Standard screen-printed solar cell.](image)

Despite the dominance of this technology, this solar cell design shown above 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 range of 40-50 ohms per square, which inevitably give significantly degraded response to short wavelength light. Good work in recent years by partners Dupont and Ferro has improved paste formulations, allowing ohmic contacts to be formed to more lightly doped emitters in the vicinity of 60 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 the contact resistance at the metal to n-type silicon interface.

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, the cells will have the potential for improved open circuit voltages, but only provided the surfaces, including under the metal, are well passivated.

LASER GROOVED 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, such a close spacing is not possible without shading well over 10% of the cell surface. The concept of semiconductor fingers is therefore introduced as shown in Figure 4.3.2.3. These semiconductor fingers are formed by laser scribing the silicon surface and then heavily diffusing the walls of these grooves as shown in the schematic in Figure 4.3.2.4. Using this design, semiconductor fingers can be spaced less than 1mm apart to avoid excessive resistive losses in the lightly diffused emitter while metal lines can be spaced further apart than in conventional screen-printed solar cells due to the superior conductivity of the semiconductor fingers compared to a homogeneous emitter. The top surface can therefore be diffused to above 100 ohms per square, while the heavily diffused grooves act as semiconductor fingers to carry the current to the screen printed silver fingers that run perpendicular to the grooves as shown. Also not shown in the figure is the surface passivating dielectric that 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
4. Research continued

saturation current. Importantly, the silicon is only exposed within the grooves, 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 4.3.2.3: Screen-printed fingers running perpendicular to the heavily diffused grooves where electrical contact is made. A dielectric/AR coating passivates the top surface and isolates the metal from the lightly diffused top surface.

Fill factors of 79-80% have been demonstrated with this structure on large area devices of approximately 150cm², 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 Jsc values of 36-37mA/cm². Even though commercial p-type substrates are not capable of voltages above about 640mV, Voc values approaching this have been achieved in pilot production with this technology, with corresponding efficiencies as high as 18.3%.

Figure 4.3.2.5: Spectral response of semiconductor finger cell.

In pilot production, the grooves are typically spaced less than a millimetre apart so as to minimise resistive losses within the lightly diffused emitter, while the screen-printed metal lines can be spaced significantly further apart than in normal screen-printed cells due to the comparatively excellent lateral conductivity of the emitter achieved by the very heavy doping within the grooves. This concept of semiconductor fingers does not appear to have ever been used in commercial solar cells, 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.

A weakness in this cell design and fabrication approach results from the requirement for the prolonged high temperature solid state diffusion of the semiconductor finger grooves. This thermal treatment is detrimental to some high oxygen CZ material as well as most multicrystalline silicon wafers. The highest efficiency achieved for the latter is 16.2%, but with the average only being 15.3% which is no better than achieved with conventional screen-printing approaches. In particular, Voc values fall to below 600mV while the long wavelength response deteriorates indicating degraded minority carrier lifetimes. The solution to this problem involves eliminating the prolonged high
temperature exposure of the wafer which can be done by replacing the laser grooved thermally diffused semiconductor fingers with ones that are formed by laser doping in localised areas as discussed in the next section.

LASER DOPED SEMICONDUCTOR FINGER SOLAR CELLS

A significant simplification of the proposed emitter design in the previous section is to apply a phosphorus doped passivating dielectric after lightly diffusing the top surface. The laser scribing conditions for groove formation are then modified so as to melt the silicon rather than ablate it, thereby allowing large amounts of phosphorus to penetrate into the molten silicon, producing heavily doped channels rather than grooves. This avoids the need for etching the grooves and subsequently diffusing the groove walls. An important benefit of this approach for multicrystalline silicon wafers is that the heavily doped regions are able to be formed without heating of the entire wafer. Some multicrystalline silicon wafers are known to degrade significantly if heated to temperatures above about 900°C. The performance of these devices with CZ silicon however does not currently match that of the devices produced using the emitter design based on the use of laser grooving due to the inability with conventional Q-switched lasers to achieve sheet resistivities as low as 5 ohms per square. In the most recent work however, using the latest laser technology, laser doped sheet resistivities of only 1-2 ohms per square have been achieved, with the expectation that cell efficiencies using laser doping will at least match if not surpass that of the laser grooving approach.

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.

ADVANCED N-TYPE SCREEN-PRINTED SOLAR CELLS:

A) 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+n+p 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.4.3.2.6 (b) can be achieved.

Figure 4.3.2.6: 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 15-20 mV 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. Figure 4.3.2.7 shows the improvement in the photoluminescent (PL) response resulting from the improved firing and formation of the rear contact and junction.
4. Research continued

4. Research continued

A common problem with the manufacture of conventional screen-printed solar cells is minute amounts of aluminium paste accidentally 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 emphasizes 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.

B) 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 4.3.2.8: 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 18% 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 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 18.6% have been achieved on large cell area of 148.6cm² using commercial grade CZ n-type wafers.
In this work, the cells were fabricated using industrial sized (125x125mm) phosphorous-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 75 nm was subsequently deposited using 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 532 nm wavelength Q-switch diode laser to create locally heavily diffused lines. The wafers were rinsed and submerged in 1% HF solution for 30 sec 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 400°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 650 mV), 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 580 nm to 960 nm. However, there was a slight drop in the short wavelength range, indicating that the front surface passivation can be further improved.

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.

Never-the-less, 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 Fig. 4.3.2.12 although in more recent years the interdigitated rear contact design applied to n-type wafers shown
in Fig. 4.3.2.11 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.

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 the schematic. 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 metallisation 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.
Contact resistances below 0.001 ohmcm² have been demonstrated, leading to fill factors as high as 80% being achieved on devices of approximately 150cm² in area. This has facilitated the achievement of efficiencies as high as 18.6% 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 TT 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 has been achieved in pilot production at Sunrise Global Energy in Taiwan on standard solar grade p-type mono wafers, with Nicole Kuepper and Adeline Sugianto from UNSW working closely with the talented Sunrise research team during 2009 to bring about these results.

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 standard commercial grade p-type CZ wafers, based on laboratory results it appears this technology will achieve comfortably over 20% efficiency on full sized commercial wafers when established in pilot production in early 2010 with impressive open-circuit voltages in the vicinity of 660mV.

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 is achieving significantly higher efficiencies in the range 18-19% compared to 17% 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 b) above 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 of 18-19% 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. Never-the-less, 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
INKJET TECHNOLOGY FOR SOLAR CELL FABRICATION

A) 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 is 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.

Figure 4.3.2.15: 30-40 micron diameter holes formed by ink-jetting.

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 of textured surfaces and light trapping schemes. Examples of the latter are shown below as well as corresponding reflectance curves.

Figure 4.3.2.16: (a) Optical Microscope photograph of ink jet patterned holes in a SiO₂ layer and (b) Scanning Electron Microscope photograph of the inverted pyramids formed in the silicon surface following KOH etching of (a).
Figure 4.3.2.17: (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 4.3.2.18: 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 4.3.2.19: (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 4.3.2.20. Such techniques appear to have significant commercial appeal.

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\textsubscript{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 4.3.2.21) were cleanly etched in a 260 nm thick SiO\textsubscript{2} layer using aerosol and sheath gas flow rates of 21 and 50 cm\textsuperscript{3}/min respectively and depositing 10 layers of aerosolized 10% NH\textsubscript{4}F solution. These grooves were ~35 microns wide at the surface but only ~20 microns wide at the Si/SiO\textsubscript{2} interface.
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.

We have also been able to etch grooves 20-25 microns wide in 75 nm thick SiN_x 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. These further reductions in etched feature size may enable high-efficiency silicon solar cell designs, such as the PERL cell, to be commercially realised.

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.

**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 17% to 19%. These efficiencies have been independently confirmed by the Fraunhofer Institute in Germany. The main contributors to these increased efficiencies are: reduced shading loss (3%); improved short wavelength response due to selective emitter (3%); improved Voc due to lightly diffused emitter and well passivated surfaces (3%); and improved fill-factor due to reduced resistive losses (3%).

"inverted" pyramids

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**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 17% to 19%. These efficiencies have been independently confirmed by the Fraunhofer Institute in Germany. The main contributors to these increased efficiencies are: reduced shading loss (3%); improved short wavelength response due to selective emitter (3%); improved Voc due to lightly diffused emitter and well passivated surfaces (3%); and improved fill-factor due to reduced resistive losses (3%).

"inverted" pyramids

We have also been able to etch grooves 20-25 microns wide in 75 nm thick SiN_x 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. These further reductions in etched feature size may enable high-efficiency silicon solar cell designs, such as the PERL cell, to be commercially realised.

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.

**PLUTO TECHNOLOGY**

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"inverted" pyramids
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 4.3.2.25 and 4.3.2.26 respectively.

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.
Suntech has publicly announced that it increased the manufacturing capacity of the Pluto technology in mid 2009 to 100MW. This will be scaled to 450MW by mid 2010 with the full 1GW production capacity to be retrofitted to the Pluto technology during 2011.

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. It is expected to take efficiencies to the 20-23% range depending on wafer quality. 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 in about 1-2 years.

The PLUTO technology has been also successfully applied to multicrystalline silicon wafers and implemented into large scale production with efficiencies of 17-18% also independently confirmed by the Fraunhofer Institute. In mid 2009, Suntech beat the 15.5% multicrystalline silicon pv 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 pv module, this time beating the recently achieved ECN world record in the Netherlands.

**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.

![Luminescence image of a completed multicrystalline silicon solar cell.](image)

A prototype bench-top system established at the Centre two years ago continues to be in heavy demand by various UNSW research groups and for consultancy projects. 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 2009.

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.

### 4.3.2.4 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>Antireflect Coating</th>
<th>Jsc (mA/cm²)</th>
<th>Voc (mV)</th>
<th>FF (%)</th>
<th>Effic %</th>
<th>Area (cm²)</th>
<th>Wafer type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 BCSC</td>
<td>SiO2</td>
<td>36.8</td>
<td>619</td>
<td>79.0</td>
<td>18.0</td>
<td>148.6</td>
<td>(p-type CZ)</td>
</tr>
<tr>
<td>1 BCSC</td>
<td>SiN</td>
<td>33.4</td>
<td>604</td>
<td>77.4</td>
<td>15.6</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>35.8</td>
<td>614</td>
<td>76.1</td>
<td>17.5</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>36.2</td>
<td>635</td>
<td>79.5</td>
<td>18.3</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>37.3</td>
<td>636</td>
<td>78.6</td>
<td>18.6</td>
<td>148.6</td>
<td>(p-type CZ)</td>
</tr>
<tr>
<td>5 LDSE</td>
<td>SiN</td>
<td>35.0</td>
<td>628</td>
<td>77.9</td>
<td>17.1</td>
<td>156</td>
<td>(p-type multi)</td>
</tr>
<tr>
<td>5 LDSE</td>
<td>SiN</td>
<td>36.0</td>
<td>645</td>
<td>79.9</td>
<td>18.6</td>
<td>148.6</td>
<td>(n-type CZ)</td>
</tr>
<tr>
<td>6 Pluto</td>
<td>SiN</td>
<td>38.1</td>
<td>640</td>
<td>79.5</td>
<td>19.4</td>
<td>148.6</td>
<td>(p-type CZ)</td>
</tr>
<tr>
<td>6 Pluto</td>
<td>SiN</td>
<td>38.6</td>
<td>638</td>
<td>81.9</td>
<td>20.2</td>
<td>4.0</td>
<td>(p-type CZ)</td>
</tr>
<tr>
<td>6 Pluto</td>
<td>SiN</td>
<td>35.5</td>
<td>633</td>
<td>78.1</td>
<td>17.5</td>
<td>156</td>
<td>(p-type multi)</td>
</tr>
<tr>
<td>7 PERL</td>
<td>ZnS/MgF2</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>
4. Research

4.4 Second Generation: Silicon and Organic Thin-Films

4.4.1 Silicon Thin Films

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4.4.1.1 Summary

Significant progress has been made by the thin-film group in its key area of research on polycrystalline Si (poly-Si) on glass solar cells. After recent demonstration of enhanced light-trapping with advanced Al-induced-textured (AIT) glass, which achieved the theoretical limit for fully randomised light [4.4.1.1], an improved cell metallisation scheme using point-contacted SiO2/Al back-surface reflector (BSR) [4.4.1.2] and wire-bonding for cell interconnection [4.4.1.3] was demonstrated. High crystal and electronic quality poly-Si films with Voc ~510 mV were also made by high rate PECVD at ~5 nm/s [4.4.1.4]. The research focus in the PECVD cells area has been on combining all the above in one advanced device targeting efficiencies above 10%. Although the implementation of this approach required re-development and re-optimisation of the major cell fabrication processes and turned out to be more challenging than originally thought, steady progress with efficiencies is being made.

Additional research efforts have been in the area of further development of poly-Si cells made by electron beam (e-beam) evaporation, which is also the major strand of the ARC linkage grant project between UNSW and industry partner, CSG Solar, started in 2009. Small area (2 cm²) e-beam cells with efficiency above 5% (Voc 422 mV, Jsc 19.2 mA/cm², FF 65%) were initially developed [4.4.1.5]. Large area (~50 cm²) mini-modules with efficiency up to 5.4% (Voc 458 mV, Jsc 17.29 mA/cm², FF 71%) were fabricated using a “hybrid” cell structure with PECVD emitter and e-beam absorber and back-surface field (BSF) on planar glass. To address the problem of poor compatibility of the evaporated Si films with textured substrates [4.4.1.6, 4.4.1.7], a new light-trapping approach based on the localised surface plasmon resonance on metal nanoparticles has been investigated. Application of Ag nanoparticles over an intermediate dielectric layer on the rear (air) side of the planar poly-Si thin-film cells results in Jsc and efficiency enhancement of 13% [4.4.1.8]. To ensure precise and repeatable doping control during Si evaporation the e-beam evaporation tool (IAD tool) has been upgraded with a more reliable boron high temperature source (HTS) with a W filament.

Progress has been made in better understanding of the solid-state crystallisation (SPC) of a-Si to form poly-Si and how SPC conditions affect the poly-Si properties. A comparative study of the SPC of the PECVD and e-beam a-Si films has been conducted, which shows that the crystallisation kinetics depend more on the particular film structure, such as doping concentration and profile, than on the film deposition method. The activation energies (Ea) for the incubation and growth are estimated to be respectively 2.7 and 3.0 eV for the PECVD films and 2.9 and 3.3 eV for the e-beam films. Although the crystal grain size is smaller and the crystal quality is slightly worse at the higher SPC temperatures, the Voc stays similar for the temperatures between 600 ºC and 640ºC.

To support a new research strand on a transient heating defect anneal a line beam diode laser (LIMO450-L12x0.3) has been commissioned.

Further insight has been gained in better understanding of mechanisms limiting the performance of poly-Si thin-film cells. Experimental evidence points to the presence of thermally activated shallow levels, which can act as recombination centres and/or traps (becoming active particularly at lower temperatures contributing into the \(n=1\) recombination in the quasi-neutral region which particularly become significant at lower temperatures).

A close collaboration with CSG Solar has been established since the start of the ARC Linkage Project Grant to combine resources and expertise in developing crystalline Si on glass (CSG) technology.
4.4.1.2 Introduction

The technology of thin-film poly-Si on glass solar cells is developing steadily and it is expected to become cost-competitive with other thin-film technologies. [4.4.1.9, 4.4.1.10]. The presently best developed poly-Si on glass PV technology is that of CSG Solar AG where an approximately 1.5 μm thick PECVD amorphous silicon (a-Si) precursor diode is solid-phase-crystallised to form a poly-Si film, which is annealed and hydrogenated to remove and passivate defects, and then processed into metallised modules [4.4.1.11]. The highest achieved efficiency for 94 cm² mini-modules produced by CSG technology is 10.5% [4.4.1.12], and full scale 7-8% efficient modules have been commercially manufactured in Thalheim, Germany since 2006.

Research in the thin-film group at UNSW focuses on critical cell fabrication processes and explores a range of advanced approaches to improve the performance and manufacturability of poly-Si thin-film cells. The group’s work over the past years has led to innovative solutions for the key steps of the cell fabrication process, including Al induced glass texturing (AIT) and localised surface plasmons (LSP) for enhanced light trapping, silicon deposition by high rate PECVD and e-beam evaporation, defect anneal and passivation, and cell metallisation and interconnection. The following sections summarise the thin-film cell research projects and their results.

4.4.1.3 Solar cell fabrication sequence

The thin-film group research in 2009 has been focusing on two different solar cell types: cells deposited by PECVD and by e-beam evaporation. A schematic representation of a poly-Si thin film cell is shown in Fig. 4.4.1.1 and Fig. 4.4.1.2 shows its fabrication sequence.

![Diagram of poly-Si solar cell on planar glass](image1.png)

Figure 4.4.1.1: Structure of a p-type poly-Si solar cell on a planar glass (layer thicknesses and grain size not to scale).

![Diagram of solar cell fabrication sequence](image2.png)

Figure 4.4.1.2: Process sequence of the four types of poly-Si thin-film on glass solar cells under development in UNSW. All cells are designed for the superstrate configuration (i.e., the sunlight enters the cell through the glass).

Additionally hybrid cells combining the PECVD emitter with the e-beam absorber and BSF were produced in collaboration with CSG Solar. The substrate used for all cells is 3.3 mm thick borosilicate glass (Schott Borofloat33). Both planar and textured glass substrates are investigated: typically e-beam and hybrid cells are fabricated on the planar glass while PECVD cells are fabricated on textured glass. The texture on the Si facing glass surface aims to reduce the reflection losses and to enhance the light trapping in a weakly absorbing poly-Si thin-film. The texture is typically prepared by the UNSW-developed AIT method [4.4.1.13] described below consisting of an irregular rough array of sub-micron sized dimples. The next step is the deposition of an approximately 75 nm thick SiN film (refractive index ~2.1 at 633 nm) by
PECVD at about 400°C or by reactive sputtering at 200°C. The SiN film acts both as an AR coating and a barrier layer for contaminants from the glass. An a-Si n+pp+ or p+nn+ precursor diode is then deposited by either e-beam evaporation or PECVD on planar or AIT glass respectively, followed by SPC at 600°C in a nitrogen atmosphere. The resulting as-crystallised poly-Si diodes have Voc of only about 200 mV. A high temperature treatment is then performed at 1000-1100°C for 30-60 s to activate the dopants and to anneal defects, which increases Voc up to 350-400 mV. The final step of the material preparation is hydrogenation in a remote hydrogen plasma to passivate the remaining defects resulting in Voc of ~500 mV typical for the finished cells.

The cells are metallised using a combination of photolithographic patterning with dielectric and metal deposition processes to create an interdigitated electrode structure on the rear, or Si side, of the cells. Typically, the BSF electrode of the PECVD cells covers the whole rear cell surface and the cells can only be illuminated from the glass side [4.4.1.14, 4.4.1.15]. The BSF electrode of the e-beam cells consists of thin Al fingers covering only 3-5% of the rear surface, thus allowing bifacial (i.e. illumination from both glass and Si side) operation of the cells [4.4.1.16, 4.4.1.17, 4.4.1.18]. The details of the cell metallisation are described in respective sections below.

The hybrid cells are made on planar glass with the SiN layer and the emitter deposited in the CSG large area KAI PECVD tool and the absorber and BSF layers - in the UNSW IAD evaporator. The films are processed into solar mini-modules using the proprietary CSG metallisation technology described elsewhere [4.4.1.11, 4.4.1.12].

### 4.4.1.4 Glass Texturing

A unique glass texturing process was developed at UNSW and it is referred to as “aluminium induced texture” (AIT) [4.4.1.13, 4.4.1.14]. A thin sacrificial Al film is deposited onto planar glass, followed by annealing at about ~600°C in an inert atmosphere. The anneal initiates a red-ox reaction whereby Al is oxidised to Al₂O₃ and SiO₂ from the glass is reduced to silicon, as follows:

\[
4\text{Al} + 3\text{SiO}_2 \rightarrow 3\text{Si} + 2\text{Al}_2\text{O}_3
\]

A surface texture is imparted to the glass according to the nucleation conditions provided during this anneal. Subsequent wet-chemical etching removes the reaction products from the glass surface and reveals the glass texture.

A typical atomic force microscope (AFM) image of the bare AIT glass surface with the RMS roughness of 800 nm and an SEM image of the AIT glass coated with a 2 μm thick poly-Si film are shown in Fig. 4.4.1.3.

The reflection dark field mode microscopy was identified as the most effective, quick, and convenient tool for characterising the light trapping properties of the bare textured glass. Fig. 4.4.1.4 shows the images of the bare AIT glass surface prepared by different etching processes. To examine the light trapping effect of different textures, 2.7 μm thick poly-Si thin films were fabricated on these AIT glass samples by PECVD of a-Si:H films followed by SPC, rapid thermal annealing, and hydrogenation. The optical properties of the poly-Si films on the AIT glass were characterised by optical absorption (1-R-T) measurements.
When the AIT glass is prepared with evaporated Al and by HF: HNO₃ etching, the poly-Si films have the highest optical absorption (Group-III) while those prepared by KMnO₄:HF etching (Group-I) have the lowest absorption (Fig. 4.4.1.5). It is also found that the optical absorption in the poly-Si films is closely correlated with the number of bright sidewalls of the textured features observed for the uncoated AIT glass in the optical microscope reflection dark field mode images. The higher number of bright sidewalls, the higher the optical absorption.

As shown in Fig. 4.4.1.6, the absorption in the 2.7 μm thick poly-Si films on the best AIT glass in the 500–1000 nm wavelength interval is very close to the calculated random scattering absorption limit, based on Monte Carlo ray tracing. It should be noted that the significantly higher absorption than the theoretical limit at 1000 nm and above can be explained by the enhanced parasitic absorption in the glass and/or measurements errors as discussed elsewhere [4.4.1.14]. The poly-Si films on the AIT glass fabricated by using in-line Al sputtering have optical absorption similar to that of the films on the AIT glass fabricated by using the thermally evaporated Al proving the scalability of the AIT process.
4. Research

4.4.1.5 Solid Phase Crystallisation

Solid phase crystallisation (SPC) is a thermally activated process of transformation of a-Si into poly-Si, which is used for poly-Si thin-film cell fabrication. The SPC parameters, such as the exact temperature profile, as well as the film structure, such as the composition and thickness of the individual layers, have effects on the resulting crystal and electronic quality of poly-Si film and thus on the cell performance. During 2009 a detailed study of the SPC kinetics was conducted to clarify such effects. A few techniques – Optical transmission microscopy (OTM), Raman, UV reflection (UV-R), and X-ray diffraction (XRD) spectroscopies, Scanning electron microscopy (SEM) – were used to characterise the SPC kinetics and the crystal quality of the films. External Quantum Efficiency (EQE) and Suns-Voc measurements were used to characterise the cell performance.

Representative SPC kinetics for the e-beam cell structure at different temperatures based on the Raman data are shown in Fig. 4.4.1.7. Similar so-called “S-curves” were obtained by the other characterisation techniques mentioned above. The summary of the incubation and full crystallisation times based on all film characterisation methods is given in Table 4.4.1.1.
Table 4.4.1.1: Incubation and crystallisation times for the e-beam and PECVD Si films (cell structure).

<table>
<thead>
<tr>
<th>Incubation, min</th>
<th>Crystallisation, min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ebeam</td>
<td>PECVD</td>
</tr>
<tr>
<td>T, ºC</td>
<td>600</td>
</tr>
<tr>
<td>OTM</td>
<td>300</td>
</tr>
<tr>
<td>Raman</td>
<td>300</td>
</tr>
<tr>
<td>UV-R</td>
<td>270</td>
</tr>
<tr>
<td>XRD</td>
<td>270</td>
</tr>
<tr>
<td>Ave.</td>
<td>285</td>
</tr>
</tbody>
</table>

Based on the data from the table it is possible to estimate the activation energies (Ea) for the incubation and crystal growth processes using the Arrhenius law. Arrhenius plots are shown in Fig. 4.4.1.8. The Ea calculated from the plots are 3.0 and 3.2 eV (e-beam films) and 2.8 and 3.0 eV (PECVD films) for the incubation and crystal growth respectively. The Ea for the crystal growth falls within the reported 3.1-3.4 eV range, but the Ea of 2.9 eV for the incubation is significantly smaller than ~3.4 eV previously found [4.4.1.19]. Most likely it is because the nucleation rate, to which the incubation time is closely related, is enhanced by particular film deposition conditions and/or the particular film structure, such as the presence of the heavily doped layers and interfaces.

The average grain size in the e-beam poly-Si films crystallised at different temperatures was estimated from the SEM images shown in Fig. 4.4.1.9, where the grain boundaries were enhanced by Secco etching. The grain size decreases from 2.3 μm to 1.5 μm and 1.0 μm as the SPC temperature rises from 600ºC to 640ºC and 680ºC. The Raman peaks for the respective films are slightly shifted to the left of the c-Si peak, and their FWHM are larger for the higher SPC temperatures similarly indicating a slightly poorer crystal quality of the films crystallised at higher temperatures (Fig. 4.4.1.10).

![Incubation Arrhenius plot](image1)

![Crystallisation Arrhenius plot](image2)

Figure 4.4.1.8: Arrhenius plots and respective activation energies for incubation and crystallisation processes of the e-beam (blue) and PECVD (pink) Si films.
4. Research continued

Fig. 4.4.1.9: SEM images of the fully crystallized and Secco etched e-beam poly-Si films for different SPC temperatures.

Figure 4.4.1.10: Raman spectra of the fully crystallised e-beam films at three SPC temperatures (c-Si as a reference). The peak intensities are normalised.

However, according to Suns-Voc measurements the electronic quality of the poly-Si diodes is similar for all SPC temperatures: 451, 450, 455 mV for 600, 640 and 680°C respectively, which is only slightly lower than the Voc of 472 mV recently reported for the best e-beam poly-Si cells [4.4.1.20]. Thus, the Voc values alone do not show any disadvantage of the higher SPC temperatures suggesting that most defects, possibly associated with the high temperature SPC, can still be annealed or passivated, which also suggests that the lower Voc is more likely due to intragrain defects rather than the smaller average grain size estimated from the SEM images.

4.4.1.6 Transient heating defect anneal

As was mentioned in section 4.4.1.3, the defect annealing in poly-Si films after SPC is a very important process for improving cell Voc. Finding the best conditions for this process is complicated due to conflicting trends. On one hand, higher annealing temperatures and longer times are preferred because of better dopant activation and more complete defect dissolution; on the other hand, the same conditions cause excessive dopant diffusion and glass distortion, which need to be avoided. Typically, for any given annealing temperature, there is an optimum time balancing favourable processes with unfavourable ones. For example, at 950°C such an optimum time is about 4 min, while a similar Voc effect can be achieved at 1050°C for only 60 s. Following this trend, it can be estimated that at temperatures near the Si melting point (around 1400°C), the optimum annealing times can be of order of a few milliseconds only. Very importantly, for such short times the thermal diffusion length in glass is of an order of tens of microns only [4.4.1.21], which means the bulk of the glass stays mostly cold resulting in less distortion and lower thermal budget of the annealing process.

Two recently available techniques, which allow heating a few micron thick Si film up to its melting point within a few millisecond long time are flash lamps [4.4.1.22] and diode lasers. With the diode lasers in particular, the exposure time can be easily controlled in the CW mode from about 1 ms to 100 ms by the laser beam scanning speed, while the degree of Si film heating is controlled by adjusting the laser power.

To support development of a low thermal budget defect annealing process a line beam diode laser LIMO450-12x0.3 has been commissioned in 2009 (Fig. 4.4.1.11). Experiments have started to identify effects of the various laser treatment parameters and conditions on the electronic properties of poly-Si films and cells.
4.4.1.7 PECVD cells

PECVD CELL STRUCTURE AND PERFORMANCE

The poly-Si thin-film cells made with the use of the PECVD are the most technologically advanced and have achieved the highest efficiencies compared to other cell types. The progress with the PECVD cell efficiencies is shown in Fig. 4.4.1.12.

The cells are made on 3.3 mm thick textured Borofloat glass, have about 2-2.5 μm thickness, an area of 4.0 cm², and an intended structure of glass/SiN/n+p-p+. The standard processing sequence includes SPC at 600°C for ~ 15 hrs; rapid thermal defect annealing and dopant activation at ~1000°C for ~ 1 min; remote hydrogen plasma defect passivation at 600°C for ~30 min; followed by metallisation using the interdigitated contact scheme shown in Fig. 4.4.1.13 and described elsewhere [4.4.1.14].

One of our recent advances in improving the PECVD cell performance was the development of an optimised metallisation scheme with a superior BSR made of a combination of a thin silica layer and evaporated Al. The rear Al electrode makes a contact to the cell back-surface-field (BSF) layer through small vias photolithographically defined in the silica film. When the PECVD cells are fabricated on the AIT glass (the textures from Group II in Fig. 4.4.1.5), and metallised using such a point contacted rear-surface structure (Fig. 4.4.1.14 and [4.4.1.15]), they possess enhanced light-trapping and achieve both high Jsc of 29 mA/cm² and record efficiency of 9.3%.

The measured I-V curve of the record cell together with the other important cell parameters is illustrated in Fig. 4.4.1.15. The measurements were apertured to 4.0 cm² area and a NREL calibrated cell was used as a reference.
HIGH RATE PECVD OF A-SI FILMS FOR POLY-SI CELLS

The manufacturing of poly-Si thin-film solar cells is a commercially viable process [4.4.1.9]. However, the deposition of the precursor a-SiH films by currently conventional PECVD has been indentified as having the high cost and a low throughput due to its low deposition rate (25-35 nm/min) and the high equipment cost [4.4.1.11]. E-beam Si evaporation has been investigated as a higher rate and lower cost alternative. A challenge with e-beam evaporation is its directional nature ("line-of-sight" deposition), leading to non-conformal coating of textured surfaces, which results in microstructural defects causing to the poor textured cell performance [4.4.1.6, 4.4.1.7]. Another high rate process, which in contrast to the evaporation can provide a conformal coating of textures, is hot-wire CVD. However, no performance results have been reported for the SPC hot-wire CVD solar cells, and it is also known that the hot-wire CVD a-SiH has very high nucleation rates [4.4.1.23], which may lead to poor crystal and electronic quality of SPC poly-Si.

A major part of research conducted on PECVD of a-Si:H has been traditionally focused on minimising the defect density for a-Si:H solar cell applications. However, the device-grade a-Si:H, which performs well for a-Si:H cells, is not necessarily the best precursor material for making poly-Si cells by SPC and a higher rate PECVD a-Si:H may also be suitable for producing a good electronic quality poly-Si.

Using a conventional 13.56 MHz PECVD system and a process optimised for the SPC application, much higher deposition rates up to 230 nm/min have been demonstrated as shown in Fig. 4.4.1.65. By further optimisation of the deposition conditions, i.e. by increasing the deposition pressure from 800 to 950 mTorr, a deposition rate of 265 nm/min has been achieved [4.4.1.4].

Raman microprobe characterisation of the poly-Si films obtained after SPC from the high rate PECVD a-Si:H material reveals an identical crystal quality to that of the standard rate poly-Si as shown in Fig. 4.4.1.17.

The poly-Si cell structures were fabricated with the thin emitter and BSF layers deposited at the standard rate and the ~2 μm thick absorber deposited at the high rate of 250 nm/min in a different PECVD chamber. After the standard material processing sequence described above, the Voc of the high rate cell was higher than the Voc of the standard rate cell as shown in Table 4.4.1.2.
Table 4.4.1.2: Suns-Voc results (the average of five points) after RTA and hydrogenation of 10-cm² SPC poly-Si diodes on AIT glass with PECVD a-Si:H absorber deposited at 35 nm/min (“low rate”) and 250 nm/min (“high rate”).

<table>
<thead>
<tr>
<th>Absorber deposition rate nm/min</th>
<th>1-Sun Voc mV</th>
<th>n=1 Voc mV</th>
<th>n=2 Voc mV</th>
</tr>
</thead>
<tbody>
<tr>
<td>35</td>
<td>494.6±8.9</td>
<td>496</td>
<td>666</td>
</tr>
<tr>
<td>250</td>
<td>512.4±4.5</td>
<td>513</td>
<td>711</td>
</tr>
</tbody>
</table>

The current research in PECVD poly-Si cells is focusing on developing advanced cells, which combine the best AIT glass for enhanced light trapping with the high rate PECVD Si films to achieve efficiencies exceeding 10%.

**PECVD CELL METALLISATION – CELL INTERCONNECTION**

During fabrication of large size thin-film PV modules the as-deposited films are divided into smaller area unit cells, which are then interconnected in series to reduce the resistive ohmic losses. A novel approach allowing a low loss interconnection of individual thin-film cells into a minimodule using wire-bonding was recently developed in the UNSW thin film group [4.4.1.3]. Fig. 4.4.1.18 shows a sample containing four individual PLASMA cells prior to the interconnection process.

The interconnection method consists of laser scribing an isolation groove along the glass side aluminium busbar to define the cells. Wire-bonds are then placed over this groove, connecting the air-side BSF busbar to the glass side emitter busbar of the adjacent cell as shown in Fig. 4.4.4.19. This method can be expanded by applying a conductive material (with a non-conductive adhesive) to the surface of the cell, and wire-bonding the first and the last cell busbars to the surface of the conductive material as also shown in the figure.

**Table 4.4.1.3: PECVD thin-film cell (prior to interconnection, encapsulation) and module (after interconnection, encapsulation) electrical properties.**

<table>
<thead>
<tr>
<th>Cell A Before</th>
<th>Cell B Before</th>
<th>AB interconnected</th>
</tr>
</thead>
<tbody>
<tr>
<td>Voc (mV)</td>
<td>508.7</td>
<td>507.9</td>
</tr>
<tr>
<td>Isc (mA)</td>
<td>96.4</td>
<td>97.6</td>
</tr>
<tr>
<td>FF (%)</td>
<td>69.78</td>
<td>68.45</td>
</tr>
<tr>
<td>Eff (%)</td>
<td>7.8</td>
<td>7.7</td>
</tr>
</tbody>
</table>

**Figure 4.4.1.18: Metallisation on cell level completed: top view of a 5x5 cm² sample showing 4 individual cells plus cross sectional view (SiN and silica layers not shown) with the emitter and air side busbars.**

**Figure 4.4.1.19: A schematic air-side top view of a mini-module using wire-bonded cell interconnection.**

**Figure 4.4.4.19: A schematic air-side top view of a mini-module using wire-bonded cell interconnection.**

**Figure 4.4.4.19: A schematic air-side top view of a mini-module using wire-bonded cell interconnection.**

**Figure 4.4.1.20: I-V curves of the individual cells and the wire-bonded minimodule.**
4. Research continued

4.4.1.8 E-Beam evaporated Si cells

E-Beam Cell Structure, Fabrication, and Performance

Deposition of Si using an e-beam evaporator can be performed at a very high rate of up to 1 μm/min. Other advantages of the method include absence of toxic gases, good Si source material usage, and compatibility with a continuous in-line deposition mode. Thus, if performed in a non-UHV environment (base pressure > 1×10^{-8} Torr, pressure during Si evaporation > 1×10^{-7} Torr), e-beam evaporation is potentially a cost effective Si deposition method for thin-film PV applications.

The thin-film group at UNSW has been researching e-beam Si thin-film cells for several years, and significant progress has been achieved in advancing the cell technology from a few square millimetre area mesa devices at the start to recent fully functional 6 cm² area 5% efficient cells. Fig. 4.4.1.21 illustrates the progress with the efficiencies of the e-beam cells and Table 4.4.1.4 summarises the design features of the cells typically fabricated at UNSW. The cells are also made with the reverse polarity structure, i.e. p-type glass side emitter, and n-type absorber and air-side BSF layers.

![Figure 4.4.1.21: Evolution of e-beam cell efficiencies at UNSW (in-house measurements).](image)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass</td>
<td>3.3 mm planar Borofloat33</td>
</tr>
<tr>
<td>AR coating</td>
<td>SiN (~75 nm, n ~2.1)</td>
</tr>
<tr>
<td>Emitter</td>
<td>n⁺ (<del>100 nm, P, 5e19</del>1e20 cm⁻³, 400~500 Ω/sq)</td>
</tr>
<tr>
<td>Base</td>
<td>p (1.5<del>2 μm, B, 1e16</del>1e17 cm⁻³)</td>
</tr>
<tr>
<td>BSF</td>
<td>p⁺ (<del>150 nm, B, up to 1</del>5x10¹⁹ cm⁻³, ~1000 Ω/sq)</td>
</tr>
<tr>
<td>RTA</td>
<td>10~20 s at 1000°C or ~4 min at 900°C</td>
</tr>
<tr>
<td>Hydrogenation</td>
<td>15~20 min at ~600°C, remote plasma</td>
</tr>
<tr>
<td>Metal</td>
<td>0.5-1.5 μm thick interdigitated Al fingers on front &amp; rear</td>
</tr>
<tr>
<td>Back reflector</td>
<td>Commercial white paint</td>
</tr>
</tbody>
</table>

During the previous years the focus of the e-beam cell research was on improving the poly-Si material quality and optimising the cell structure and post deposition treatments (RTA, hydrogenation) to achieve better voltages. Respectable Voc in the range of 500 mV were measured by the Suns-Voc technique on non-metallised cells. More recently the focus shifted to developing a working metallisation scheme, improving the cell currents and fill factors (FF), i.e. producing functional e-beam cells with appreciable conversion efficiencies.

E-Beam Cell Metallisation

It was found that the metallisation schemes developed for PECVD cells [4.4.1.14, 4.4.1.15] are not suitable for the similarly structured e-beam cells. As soon as a relatively significant fraction of the BSF layer is metallised, the cell performance as measured by Suns-Voc severely deteriorates, which is characterised by a large reduction in Voc, the pseudo-FF, and the shunt resistance Rsh. Different contacting schemes such as full area contact, point-contact, and self-aligned line-contact, were tried and all resulted in the unsatisfactory cell performance once the BSF area contacted with the metal was more than 10% of the total BSF area [4.4.1.17].

With the help of Dark Lock-In Thermography (DLIT) combined with the optical and Focused-Ion-Beam (FIB) microscopy, wet-chemical and plasma etching, it was shown that this type of device shunting is caused by numerous submicron pinholes believed to be inherently present in the e-beam evaporated Si films as shown in Fig. 4.4.1.22. When Al is deposited over such pinholes it forms a conducting path between BSF and the emitter layers, which shunts the cell.
Figure 4.4.1.22: (a) DLIT image of e-beam test structure after metal deposition and grid finger definition; (b) DLIT close-up of the framed section in (a); (c) DLIT image of the same region after phosphoric acid etch; (d) schematics of the used test structures (total area 1 cm²); (e) optical microscope images of two gridline shunts (x100 magnification, transmission and reflection modes respectively) from (b) directly after phosphoric etch (‘before HF’), and after extended etch in 15% HF (‘after HF’), which opens a large cavity in the glass, respectively; (f) cross-sectional FIB image of the shunt from (b) and from the left column of (e) after Si plasma etching and second Al deposition. (DLIT images were taken by J. Bauer and Dr. O. Breitenstein at the Max Planck Institute of Microstructure Physics in Halle, Germany).

Additionally, shunting occurs during emitter contact formation. Typically contacting is done by etching emitter grooves through the whole Si film and then filling with Al. This approach works well for PECVD cells but in the e-beam cells it leads to non-linear (Schottky-type) shunting that develops between the metal and the sidewalls of the lightly doped absorber layer as described elsewhere [4.4.1.16]. This non-linear shunting causes a large reduction of Voc after the contacts formed in the described way are baked.

A new cell metallisation scheme, illustrated in Fig 4.4.1.23, was developed in 2008, which avoids both described shunting problems. It features interdigitated Al line contacts for both heavily doped layers, the emitter and BSF. The BSF electrodes only cover about 4% of the area to minimise the number of pin-hole related shunts. To completely eliminate the BSF shunting the metallised cells undergo a brief phosphoric acid etch, which removes Al from the pinhole sidewalls. The emitter electrode is formed in a way that it avoids contact with the absorber layer entirely. Instead of plasma etching the grooves through the whole Si thickness, a time etch stop is used such that a thinned emitter layer still remains at the bottom of the grooves. Then, the glass-side comb-like electrode is centred in the grooves leaving significant space (>10 μm) between the edges of the electrodes and the groove sidewalls. After metallisation the entire cell rear surface is then coated with a white paint layer serving as a diffuse back-surface reflector (BSR). The typical cell performance parameters obtained with the new metallisation are listed in Table 4.4.1.5.
Table 4.4.1.5: Measured 1 sun J-V results of e-beam cells with aligned bifacial metallisation ([4.4.1.5, 4.4.1.16]). The shunt resistance of the cells is > 2000 Ωcm² and has a negligible effect on the performance. The pseudo fill factor (pFF) was determined from Suns-Voc measurements.

<table>
<thead>
<tr>
<th>Cell</th>
<th>Voc (mV)</th>
<th>Jsc (mA/cm²)</th>
<th>pFF (%)</th>
<th>FF (%)</th>
<th>Eff (%)</th>
<th>Rs (Ωcm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>436</td>
<td>15.62</td>
<td>72.7</td>
<td>62.5</td>
<td>4.25</td>
<td>3.63</td>
</tr>
<tr>
<td>B</td>
<td>458</td>
<td>14.01</td>
<td>72.9</td>
<td>59.6</td>
<td>3.82</td>
<td>5.52</td>
</tr>
<tr>
<td>C</td>
<td>462</td>
<td>12.26</td>
<td>71.1</td>
<td>61.8</td>
<td>3.5</td>
<td>4.88</td>
</tr>
</tbody>
</table>

E-BEAM CELL ABSORBER DOPING DENSITY AND THE EFFICIENCY

The electronic properties of the absorber layer, mainly the effective minority carrier diffusion length and life-time, are expected to depend strongly on its doping level, which thus can have a large effect on the cell performance. After introducing the working metalisation scheme, an absorber doping optimisation experiment was conducted in order to estimate this effect. All cells in the experiment were intended to be nominally identical but with the different doping densities in the absorber all were about 2 μm thick, made on planar glass with SiN barrier, and with the metallisation and the white-paint BSR as described in the previous section. The dopant concentration was determined using the Z-analysis technique described elsewhere [4.4.1.24]. This technique has an advantage of yielding the electrically active dopant density, which is most relevant to the cell performance. The cells were characterised by Suns-Voc, EQE, light J-V measurements and the results are shown in Table 4.4.1.6. To account for the spectral mismatch between the light I-V tester and the AM1.5G solar test spectrum, which causes measurement artifacts, a conservative approach was used where the short-circuit current density during the J-V measurements was adjusted to match those determined from EQE measurements.
Table 4.4.1.6: Performance parameters of e-beam cells with different absorber doping densities.

<table>
<thead>
<tr>
<th>N (at/cm²)</th>
<th>Eff (%)</th>
<th>Voc (mV)</th>
<th>Jsc (mA/cm²)</th>
<th>pFF (%)</th>
<th>FF (%)</th>
<th>Rsh (Ωcm²)</th>
<th>Rs (Ωcm²)</th>
<th>Neff</th>
</tr>
</thead>
<tbody>
<tr>
<td>2e15</td>
<td>5.23</td>
<td>422</td>
<td>19.21</td>
<td>73.1</td>
<td>64.5</td>
<td>820</td>
<td>1.99</td>
<td>1.39</td>
</tr>
<tr>
<td>5e15</td>
<td>5.20</td>
<td>435</td>
<td>18.46</td>
<td>72.8</td>
<td>64.7</td>
<td>415</td>
<td>2.09</td>
<td>1.37</td>
</tr>
<tr>
<td>9e16</td>
<td>2.16</td>
<td>444</td>
<td>7.79</td>
<td>72.7</td>
<td>62.5</td>
<td>930</td>
<td>7.92</td>
<td>1.46</td>
</tr>
<tr>
<td>6e17</td>
<td>1.3</td>
<td>417</td>
<td>5.09</td>
<td>66.6</td>
<td>61.3</td>
<td>1113</td>
<td>6.82</td>
<td>1.83</td>
</tr>
</tbody>
</table>

The major observed effect of the doping density is a sharp reduction of the cell current with increased doping. It dominates a weaker effect on the cell voltage, where Voc rises slightly up to dopant density of about 1e17/cm³ before falling sharply at the higher densities. The best cell efficiencies are obtained at the lowest active dopant concentrations in the range between 2e15/cm² and 5e15/cm². The first e-beam cells with efficiencies above 5% have been fabricated with the described approach [4.4.1.5]. Fig. 4.4.1.24 shows the I-V curves of one of the 5% cell with the lowest doping density of 2.1e15/cm² together with the curves for the heavier doped absorber cells for comparison and illustration of the doping effect.

Figure 4.4.1.24: Measured I-V curves of the metallised e-beam cells from Table 4.4.1.4 with three different absorber doping densities.

LIGHT-TRAPPING IN E-BEAM POLY-SI THIN-FILM CELLS

All e-beam cells described in this section have been made on planar glass superstrates and they possess relatively modest light-trapping properties, mostly provided by the diffuse white-paint BSR. Poor light-trapping seriously limits the amount of light absorption in the cells and therefore the cell current. To improve the evaporated cell efficiencies further through better light-trapping, they need to have at least one textured Si interface, either on the glass or air side, as the CSG cells and UNSW PECVD cells do.

However, the increased light absorption in the textured e-beam cells does not result in better performance but makes it worse compared to the planar cells. The Voc pseudo-FF of non-metallised textured e-beam cells measured by Suns-Voc are lower than those for the planar e-beam cells, see Table 4.4.1.7. After metallisation both the voltages and pseudo-FF of the textured cells completely collapse due to severe shunting. Poor performance of poly-Si e-beam cells on the typically used textures ("bead" and "abrade") was also reported by CSG Solar [4.4.1.20].

Table 4.4.1.7: The Voc and pseudo-FF for e-beam cells on AIT glass.

<table>
<thead>
<tr>
<th></th>
<th>Voc (mV)</th>
<th>pFF (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Planar</td>
<td>435</td>
<td>73</td>
</tr>
<tr>
<td>Mild AIT</td>
<td>420</td>
<td>74</td>
</tr>
<tr>
<td>Medium AIT</td>
<td>349</td>
<td>68</td>
</tr>
</tbody>
</table>

A cross-sectional FIB investigation of the evaporated Si films on the textured glass reveals noticeable morphological differences with the films on the planar glass. Depending on the degree of the glass roughness a number of defects are observed in the films (Fig. 4.4.1.26). On relatively smoother textures the Si film has apparently vague areas of lower material density, or high defect density, extending from the inflexions in the texture features. Such defective areas further develop into microcracks or voids either after the thermal treatment (SPC, RTA) or on the rougher textures. When the glass texture has vertical or overhanging features the extended discontinuities in the evaporated Si film are found.
Most described defects are believed to be related to the columnar microstructure, which is typical for evaporated films [4.4.1.25]. In particular, for evaporated Si "a continuous network ... of interconnected cylindrical voids" was observed. A clear experimental evidence for the columnar microstructure and the low density void network present in the SPC poly-Si films was recently reported [4.4.1.7]. Such a defective structural morphology is formed due to two inherent characteristics of the evaporation, high directionality of the arriving atomic flux and the adatom low surface mobility. The deposition only takes place on the surface areas in direct line-of-sight of the evaporation source resulting in discontinuities in the areas shaded from the source either by the surface topographical features or by the previously deposited atoms themselves. The earlier arrived adatoms cast "shadows" for subsequently arriving adatoms, thus creating a network of parallel high density columns surrounded by lower density material, as it is schematically shown in Fig. 4.4.1.27. Besides, in contrast to PECVD deposition, the evaporated adatoms have a sticking coefficient close to unity. They do not have or receive the excessive energy to move in any way from the place of their initial landing to find a more thermodynamically favorable position, thus leading to morphological and possibly electronic defects.

Possible approaches to reducing the extent of the defect formation during deposition by evaporation is using smoother glass texturing and/or to texture the Si film surface instead of, or in addition to, smooth glass textures, which both have been chosen by CSG Solar [4.4.1.20] with encouraging results. At UNSW a completely different approach, the localized surface plasmon (LSP) enhanced light-trapping, has been tested and shown to result in significantly higher cell currents. The excitation of LSP in Ag nanoparticles for light-trapping has been previously reported for a number of thin-film cells without a need for surface texturing [4.4.1.26, 4.4.1.27]. The Ag nanoparticles excited at their SP resonance can scatter a large fraction of the incident light into a neighboring Si thin-film at significant angles, by which means the light-trapping in the film is enhanced as shown in Fig. 4.4.1.28.
The Ag nanoparticles can be relatively simply prepared by depositing a 10-30 nm thin Ag film on already metallised and characterised poly-Si e-beam cells followed by annealing at about 200°C leading to formation of 50-200 nm wide irregular shape particles as shown in the figure. Typically, a thin intermediate dielectric layer (such as silicon oxide or nitride) is also placed between the poly-Si film and the Ag nanoparticles. Changing the nanoparticle size and the dielectric film thickness and refractive index allows optimising the SP effect for better light-trapping. Having the same cells characterised with and without the nanoparticles allow the accurate comparison and estimation of the light-trapping effect.

After the Ag nanoparticles were fabricated on the rear (air) side of the fully metallised e-beam poly-Si cells, the cell performance was characterised by the EQE and I-V measurements. As shown in Fig. 4.4.1.29 and 4.4.1.30 the plasmonic cells have an improved spectral response at the wavelength from 500 nm and above. The best Jsc enhancement of about 13% was achieved with the Ag nanoparticles on the nitride dielectric [4.4.1.8].

The work is in progress on further developing the SP technique to achieve higher currents than those typical for the planar non-plasmonic e-beam cells with the standard white paint BSR (~19 mA/cm²).

HYBRID PECVD/E-BEAM SOLAR CELLS

There are two difficulties in controlling the exact structure of the e-beam cells, which are related to very high volatility (high partial vapour pressure) of phosphorus: 1) depositing a very thin (15-35 nm) heavily doped n-type emitter because of the high P flux from its source even after it is switched off; 2) maintaining very low p-type doping (<1e16 cm⁻³) in the absorber because of the very high residual P background vapour pressure in the evaporation chamber leading to unintentional P doping of the absorber up to the concentration of 3-5e16 cm⁻³, thus, to maintain the required p-type polarity, the absorber has to be B doped at about 5e16 cm⁻³ level.

An approach allowing to overcome both problems is to deposit a thin heavily P doped emitter by the PECVD in a separated tool followed by
evaporation of a B doped absorber and BSF [4.4.1.28]. Cells made with this approach are called the hybrid cells, and their fabrication at UNSW started in 2009. The doping structure of the hybrid cells is typically the same as for the standard e-beam cells, which is shown in Table 4.4.1.4, and the post-deposition treatment is no different as well. The first hybrid cell structures made from the films evaporated at UNSW and processed into CSG minimodules easily achieved efficiency exceeding 5%. The performance parameters of a few hybrid minimodules with different absorber dopant (B) concentration are given in Table 4.4.1.8 and the I-V curves are shown in Fig. 4.4.1.31. A relationship between the absorber doping and the cell current and voltage similar to such for the standard e-beam cells (Table 4.4.1.6) is observed: the higher absorber doping, the lower the current and the higher the voltage. The highest efficiency is achieved for an optimum current-voltage combination at the absorber density of about 1e16 cm\(^{-3}\) (B). It should be noted that the IAD tool where the absorber layers were evaporated still had a relatively high residual P background from previous depositions and that the absorbers with the two lowest doping (sample 1 and 2) might have actually been n-type instead of the intended p-type. This may have resulted in the rear- (air) side junction location leading to the lower overall efficiencies (the C-V analysis only measures the active carrier concentration, not the type).

### Table 4.4.1.8: The hybrid cell performance (from Light I-V) and the absorber doping (from C-V analysis).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Doping ((1 \times 10^{15})) cm(^{-3})</th>
<th>(J_{sc}) mA/cm(^2)</th>
<th>(V_{0.1}) mV</th>
<th>(Voc) mV</th>
<th>Eff %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.3</td>
<td>19.4</td>
<td>315</td>
<td>435</td>
<td>5.04</td>
</tr>
<tr>
<td>2</td>
<td>5.6</td>
<td>19.0</td>
<td>349</td>
<td>444</td>
<td>5.07</td>
</tr>
<tr>
<td>3</td>
<td>12.3</td>
<td>17.7</td>
<td>355</td>
<td>456</td>
<td>5.13</td>
</tr>
<tr>
<td>4</td>
<td>19.5</td>
<td>17.0</td>
<td>360</td>
<td>470</td>
<td>4.98</td>
</tr>
</tbody>
</table>

Figure 4.4.1.31: Light I-V curved for the hybrid (PECVD emitter – e-beam absorber/BSF) CSG minimodules with different absorber active dopant density (from C-V analysis). The mininodule area is about 15 cm\(^2\).

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4.4.1.9 **Recombination processes in thin-film Si on glass solar cells**

The current output of poly-Si thin-film solar cells is approaching the so-called Lambertian limit, which serves as a gauge for quantum efficiencies. However, there is little understanding about how high the Voc could be – the lowest foreseeable practical limit is the \(V_{oc}\) of multicrystalline Si wafer based solar cells. Thus, the voltage of poly-Si cells as an academic topic is still a research frontier where the fundamental limits are unknown and speculations abound. In previous years many researchers have attributed the lower lifetimes of poly-Si solar cells to their small grain size, a view which holds merits if the grain boundaries are not well passivated [4.4.1.29], but in more recent years it is becoming clear that intragrain defects are also potent enough to limit the lifetime to the nanosecond range [4.4.1.30]. Problematically, whereas the grain boundary recombination has been successfully mitigated by enlarging the grain size or optimising the passivation of dangling bonds within the grain boundaries, so far there has not been an effective method to circumvent the detrimental effects of intragrain defects. The goal of our research is to elucidate the dominating recombination pathway in the poly-Si thin-film solar cells so that the attainment of higher Voc becomes a more tractable problem.

Following the work in 2008, which showed the impact of shallow levels on the Voc characteristics of poly-Si thin-film cells on glass [4.4.1.31], subsequent studies has been focusing on the bulk lifetimes as a function of temperature in order to gain a more detailed understanding of the behaviour of these shallow levels in the device quasi-neutral, bulk regions. Minority carrier diffusion lengths in the absorber layers of various poly-Si thin-film cells were extracted by fitting the device EQE simultaneously with its optical reflectance, a procedure, which has become a routine for poly-Si thin-film cells whose short lifetimes precludes quantification by the standard techniques such as the quasi steady state photoconductance (QSSPC). Following the temperature-dependent quantum efficiency (TQE) method introduced by Wagner and Rau [4.4.1.32], the EQE measurement and fitting procedure was repeated for each sample at different temperatures ranging from 120K to 320K. Fig. 4.4.1.32 shows an example fitting to the front (light...
incident from the glass side) and rear-side (light incident from the air side) EQE of a bifacial poly-Si thin-film cell at room temperature, using a MATLAB code developed at UNSW. Fig. 4.4.1.33 superposes the front-side EQE curves of the same cell at different temperatures (note that the heights of the curves are reduced slightly due to additional reflectance by a quartz window on the cryostat in which the sample is placed). Clearly the quantum efficiency of the cell varies strongly with temperature.

Figure 4.4.1.32: Screenshot of MATLAB code used for EQE fitting.

Figure 4.4.1.33: Typical sequence of EQE curves at different temperatures ranging from 120K to 320K

Figures 4.4.1.34 a) and b) plot the extracted lifetime $\tau$ against $q/kT$ for p- and n-type cells respectively. Although the actual lifetime values at a given temperature differ greatly from cell to cell, all the lifetime curves exhibit Arrhenius law with the activation energy (Ea) of 0.17-0.21 eV near room temperature. The lifetimes in p-type cells seem to attain lower Ea at the low temperatures, which is reminiscent to the observations by Wagner and Rau for p-type poly-Si cells deposited epitaxially by ion-assisted deposition (IAD) on (100) oriented Si wafers. This type of behaviour indicates that the carrier recombination pathway might involve the interaction of more than one shallow level – the change in the Ea marks the temperature, at which one such levels cease to emit carriers at a significant rate. It is unlikely that there are two parallel recombination pathways operating independently because, if it were true, the lower Ea process would determine the lifetime at higher temperatures, in contrast to the trends observed in Fig. 4.4.1.34a.

Figure 4.4.1.34: Lifetime vs $q/kT$ plots for a) p-type, and b) n-type poly-Si thin-film cells.

Figure 4.4.1.35: Lifetimes at 232K for various poly-Si thin-film cells plotted against dopant concentration.

The large scatter in the lifetime values can be rationalised when one plots, at a certain temperature (say at 232K where all cell diffusion lengths are shorter than the absorber width and thus EQE fittings are accurate), the lifetimes of the samples as a function of the absorber dopant concentration (determined from the capacitance-voltage measurements) shown in Fig. 4.4.1.35. Clearly, there is a rough inverse relationship, which has been previously observed for a wide variety of Si materials. The origin of this inverse law is not clear but is invariably one of two possibilities: 1) none of the defect levels participating in the dominant recombination pathway are saturated with the majority carriers, or 2) the concentration of active defect levels, which are rate limiting in the recombination pathway, increases proportionately with doping concentration. More experimental work is required to determine the relative plausibility of these two scenarios.
Amongst the n-type cells in Fig. 4.4.1.34b, three are made from small grained (~1 μm) poly-Si (circle or square data points), and three are made from large grained (~5 μm) poly-Si epitaxially grown on the Al induced crystallised (AIC) seed layer (triangle data points). The similarity in the temperature behaviour of the lifetime, regardless of the grain size, indicates that large and small grain materials have a common lifetime limiting mechanism. Also, in Fig. 4.4.1.35 one readily sees that the AIC cells (triangles) can take on the lifetime values either above or below the power law trend line, indicating that they do not have consistently superior lifetimes just by virtue of their larger grain size. It was found that the predominant grain orientation plays a greater role in determining the Voc of AIC cells [4.4.1.33] – in fact, of the two rightmost triangle data points representing AIC cells at about 5x10^{16}/cm^3 doping in Fig 4.1.1.35, the higher lifetime point originates from (100) preferentially oriented material and the lower lifetime point comes from (111) preferentially oriented material. All this evidence points at intragrain defects as a likely reason that limits the poly-Si thin-film cell lifetimes. In particular, dislocations are plausible candidates because they provide the strain fields necessary to create split-off states from the band edges that can act as shallow levels [4.4.1.34]. Therefore, future work will be directed towards confirmation of dislocation-related recombination in poly-Si, reconciling experimental data with existing theories, and understanding the unique role that these intragrain defects play in poly-Si solar cells.

### 4.4.1.10 References


4.4.1.16 O. Kunz, Z. Ouyang, J. Wong, and A.G. Aberle, Advances in evaporated solid-phase-crystallized poly-Si thin-film solar cells on glass (EVA), Advances in Optoelectronics, 2008, article ID 532351.

4.4.1.17 O. Kunz, J. Wong, J. Janssens, J. Bauer, O. Breitenstein, A.G. Aberle, Shunting Problems Due to Sub-Micron Pinholes in Evaporated Solid-Phase Crystallised Pol-Si Thin-Film Solar Cells on Glass, PIP, 20009, 17, p.35.


4. Research continued
4.4.2 Organic Thin Films

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4.4.2.1 Introduction

Although not part of the originally planned activities of the ARC Photovoltaics Centre of Excellence, new staffing appointments encouraged the initiation of organic photovoltaic (OPV) activities at the Centre during 2009 [4.4.2.1]. This resulted in the award of an ARC Discovery Project in this area for the next three years. We have started to build-up our OPV research lab with moderate facilities such as glove box, spin-coater, thermal evaporator, fume cupboard, etc. Two PhD students and several honours students are already working on OPV materials and devices. We are also expecting additional PhD and honours students will start working on OPV devices in 2010. Dr Ashraf Uddin has responsibility for implementing the experimental device program, taking advantage of his recent practical experience in the organic LED field. He is also co-ordinating the experimental programs of postgraduate students and postdoctoral researchers involved on device aspects of the project as well as contributing to device and material characterisation. Professor Martin Green is primarily involved in device and optical design, analysis and modelling. He is also targeting innovative light-trapping schemes suitable for low-index organic materials and is contributing to device characterisation. Prof. Gavin Conibeer is taking responsibility for characterisation of polymer properties and for synthesis of required materials, either in-house or in conjunction with collaborators. He is also responsible for investigating the applicability of third generation approaches to organic cells, particularly multijunction devices, up-conversion and hot carrier concepts. Dr Dirk König is primarily responsible for ab-initio simulations of candidate materials using Density-Functional Hartree-Fock (DF-HF) real space methods for ground state electronic structures and Quadratic Convergence Configuration – Interaction with Single and Double Excitations (QCISD) for excited states. The goal is to identify molecular species with low exciton dissociation energy, reasonable carrier mobility and high optical activity with photochemical stability as a constraint. He is also contributing to the electrical and optical characterisation either directly or in collaboration with external partners, as well as being responsible for the on-going development of the dedicated 960 Gigaflop Linux cluster.

4.4.2.2 OPV Conversion Efficiency

Interest in OPV with increasing conversion efficiency has grown exponentially over recent years. OPV devices have benefited greatly from the OLED and OTFT developments and offer a potentially low cost alternative to the traditional inorganic counterparts made from materials such as silicon, gallium arsenide, cadmium telluride, copper indium diselenide and other compound semiconductors. The key development in the OPV device area has been the bulk heterojunction cell [4.4.2.2] obtained by blending donor and acceptor layers, a device structure well suited to the associated short excitonic diffusion lengths. The workhorse for OPV research has become polymer-fullerene bulk heterojunction devices fabricated by coating a thin layer of PEDOT-PSS on the top of cleaned ITO substrates followed by a blend of PCBM/P3HT (or other donor polymer), followed by vacuum evaporation of Al and annealing. 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 [4.4.2.3]. Using the above workhorse, Konarka, USA established 4.8% efficiency for a small 0.14 cm² cell in July 2005. Konarka increased this to 5.15% in December 2006 with 5.24% posted for a 0.7 cm² cell in July 2007. Companies such as Plextronics have reported roughly comparable results using similar materials with 5.4% efficiency confirmed in July 2007 for a 0.1 cm² device, 6.0% in August 2008 for an even smaller 0.04 cm² cell and 2.0% as recently as 28 January 2009 for a 224 cm² module. OPV device developer Solarmer Energy has achieved the highest conversion efficiency record so far for a plastic OPV champion cell—7.9% in December 2009 [4.4.2.4]. The history of OPV conversion efficiency is shown for small area (≤1cm²) cells in the following Figure 4.4.2.1.

Figure 4.4.2.1: Recent improvements in independently confirmed efficiency for small area (≤1cm²) organic solar cells (extracted from Green et al. [4.4.2.3]).
4. Research continued

4.4.2.3 UNSW Challenges

The UNSW Photovoltaics group is well-known internationally for its world-leading work on first generation silicon wafer-based photovoltaics, most recently setting a new world record of 25% for a silicon cell in late-2008. The aim of the present OPV project is to build on this established expertise and infrastructure and the relevant, but as yet untapped, experience of new and existing staff members to establish a world-class capability in the area of OPV, a field still in its relative infancy. A multi-pronged approach is planned involving fundamental investigation of new polymeric material options for improved efficiency/stability by ab-initio simulation using the group's dedicated 960 Gigaflop Linux mainframe, synthesis of new materials as required, either locally or internationally depending on the required level and location of the relevant expertise, experimental cell fabrication, cell performance characterisation and modelling, cell design improvement, implementation of a range of new ideas relevant to recombination reduction and improved light trapping in cells and exploration of the potential of a range of "third generation" options as a means of significantly boosting performance. While retaining the advantages of OPV, the hybrid approach offers additional advantages including the potential for higher conversion efficiency and improved stability. The approach also allows control of bandgap in a stable material system. This opens the opportunity for fabricating optimised tandem stacks of OPV-based cells, with much higher efficiency potential than 10%. Many new ideas and much new technology will be required before competitive products eventuate. The Centre aims to contribute to this development in the same way it has contributed to silicon cell development. There are three main challenges to making this type of technology a reality:

- low conversion efficiency of present OPV cells
- poor stability and durability of OPV devices
- present expense of some OPV materials.

The OPV cell needs to be protected from oxygen and water vapour to increase the stability and durability, which is difficult to achieve using permeable organic material. Barrier coatings containing multiple thin blocking layers of optically transparent inorganic material are the most promising option. It is also very important to identify the key degradation mechanisms to improve the device lifetime and performance. Much work needs to be done, both in cell material selection and in low cost encapsulation, before a level of durability required for mainstream product is obtained.

Finally, even though the low cost of OPV is often stressed, the fullerene-based materials used in all the cells reported are very expensive to synthesise at present. Even though minute amounts (0.01g/watt) are used, present costs would preclude the economic viability of OPV. It is expected that fullerene costs will reduce greatly as production volumes increase. Counteracting this expected trend to some extent is increasing interest in larger and more complex fullerene molecules, even more costly to synthesise.

4.4.2.4 Standard OPV structures

The fullerene based acceptor material (PCBM) is interspersed with a donor polymer, commonly P3HT, with line-bond diagrams for these materials as shown in Fig. 4.4.2.2(b) and the standard "bulk heterojunction" cell structure is shown in Fig. 4.4.2.2(a). From this baseline of device structure, the Centre believes it has several strengths that will allow it to contribute to the ongoing cell efficiency evolution documented in Fig. 1 and to the development of more stable and durable devices. 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 an acceptor and donor materials will increase the photocurrent of the solar cell [4.4.2.5]. 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 up to 10% 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.
The interface barrier between electrodes and active layer (D/A layer) is also playing an important role to increase the OPV output current. Typical energy band diagram of an OPV device is shown in Figure 4.4.2.3. The hole can see the interface barrier between indium tin oxide (ITO) and active layer and the electron can see the interface barrier between active layer and Al electrode. Among many other electrode metals Al is a desired material as it is relatively stable and resistant to oxidation. Aluminium has a higher work function as an electrode with an organic layer compared to other metals. The improvement in Al performance as an electrode is achieved by the use of a thin LiF interlayer at the Al/organic interface [4.4.2.6]. The effect of LiF in improving device efficiency is still not fully understood.

Figure 4.4.2.3: Typical energy band diagram for an ideal organic solar cell [4.4.2.7].

ITO is highly conductive and transparent to visible light. Based on these characteristics, ITO is widely used as a transparent electrode in optical devices including solar cells. The work function of the ITO is critically importance as it sets the energy barrier height at the hetero junction interface. The schematic energy band diagram in Figure 4.4.2.3 shows the work function of ITO. Another factor affecting the ITO work function is surface morphology. It is seemingly important to have a smooth surface on which the device may be built upon. This can be tested and identified using atomic force microscopy. There is little current literature on the surface morphology of the ITO layer. To improve the hole transporting performance of the ITO, often, a layer of Poly (3,4-ethylenedioxythiophene) (PEDOT) doped with Poly(styrene sulfonate) PSS is added. This layer has a high conductivity; however, it can have negative impacts on the lifetime of the device. It also adds another step to production. Ideally, the ITO surface would be prepared in such a way that it can be an efficient hole transport layer.

The indium tin oxide substrate surface consisted of grains 20–50 nm in diameter and ~5 nm in height as shown in Fig. 4.4.2.4(a), which is also showed molecular sized sub-grain features. Due to the ambient the ITO surface was covered by a ~1 nm thick hydrocarbon layer which serves as the actual surface on which an organic layer is deposited for device fabrication. A structural model for the indium tin oxide surface, on which the small molecules were deposited, was suggested in Fig. 4.4.2.4(b). It shows the granular nature of the surface and the layer of organic contamination. The amount of organic contamination on the ITO surface affects the performance of the layer. The substrate surface was chemically treated to study the relation between the surface manipulation and the hole injection barrier. Such surface modification of ITO has the potential to significantly improve the performance of OPV.
4. Research continued

The Centre is purchasing an upgrade of the Gaussian DFT program package to Gaussian09. We then 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.4.4.2.5) presently rated at 960 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.

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 [4.4.2.9].

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.
4.4.2.5 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. 4.5.5.9. 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.

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. 4.4.2.6.

Figure 4.4.2.6: Si nanoparticle encapsulated with organosilanes.

Progress to date is reported elsewhere [4.4.2.10] (see also Section 4.5.3.4.2 of this report). 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.

4.4.2.6 References

4.4.2.4 http://www.solarmer.com
4.4.2.9 S. Pillai, K.R. Catchpole, T. Trupke, and M.A. Green, “Surface Plasmon Enhanced Silicon Solar Cells”, Journal of Applied Physics 101, 093105 (2007).
4. Research continued
4.5 Third Generation Strand – Advanced Concepts

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Summary
The major project in 2009 has remained the Si nanostructure tandem cells project (the “all-Si” tandem cell) with completion of the Global Climate and Energy Project (GCEP). The Hot Carrier solar cell project has seen a very large increase in activity with continuing funding from GCEP. There has also been an increase in work on Up-conversion.

The Si nanostructure work has seen refinement of fabrication of rectifying p-n homo-junctions. A greater knowledge has been gained on the requirements for higher $V_{oc}$ with values still close to 500mV. The increase in the effective band gap has been demonstrated using both optical and electronic techniques. Progress on understanding the experimentally observed doping behaviour and on a theoretical understanding of modulation doping have both been made. There has been a continuation of work on Si QDs in SiN, and SiC and progress on Ge and Sn QDs in SiO$_2$ and SiN, respectively, with PL energy in Ge QDs demonstrated to increase with decrease in QD size.

On Hot Carrier cells there has been continued development of Energy Selective contacts with improved control of Si QD size and size.
uniformity in double barrier structures. On the absorbers there has been modelling work on a range of compound bulk materials and an important proof of concept of longer time-resolved PL time constants for bulk III-V materials with large phononic band gaps. Further modelling of QD nanostructures has been carried out for a range of material and superlattice configurations. Further progress has been made on the fabrication of QD arrays using colloidal dispersion.

The up-conversion project has made significant progress with first luminescence and then UC of 1500nm light demonstrated in Er doped porous Si.

This progress in all the main Third Generation project areas is leading to new understanding of the mechanisms involved and to improved materials and device designs.

4.5.1 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 [4.5.1]. Thus these “third generation” technologies will be compatible with large scale implementation of photovoltaics. The aim is to decrease costs to below US$0.50/W, potentially to 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 of the three PV generations) [4.5.1, 4.5.2]. 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" indicated in Fig. 4.1.3 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 devices [4.5.1, 4.5.3].

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. 4.5.1), and thermalisation of photon energy exceeding the band gap, (2 in Fig. 4.5.1). These two mechanisms alone amount to the loss of about half of the incident solar energy in solar cell conversion to electricity. Multiple threshold approaches can utilise some of this lost energy. Such approaches do not in fact disprove the validity of 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. 4.1.3, of 67% or 86.8% (again depending on concentration).

In the Third Generation Strand, we are implementing strategy (a) 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 also tackling strategy (b) by investigating the “Hot Carrier solar cell” in which carrier cooling is slowed such that carriers can be extracted before thermalisation. This requires both an absorber with slowed carrier cooling properties and collection of carriers over a limited range of energies, such that cold carriers in the external contacts do not cool the hot carriers. Finally we are investigating implementation of strategy (c) by up-conversion in a layer behind the Si cell. Rare earth doped phosphors in the up-converter absorb below band gap photons and up-convert two or more to above band gap photons which are then incident on the Si cell. Hence all Third Generation approaches are based on tackling one or both of the “below band gap” or “thermalisation” loss mechanisms mentioned above.

![Figure 4.5.1: 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.](image-url)
4.5.2 Si nanostructures

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4.5.2.1 The “all-Si” Tandem cell

We are developing a material based on Si (or other group IV) quantum dots, from which we can engineer a wider band gap material to be used in tandem photovoltaic cell element(s) above a thin film bulk Si cell, see Fig. 4.5.2.

In previous work we have demonstrated the fabrication of an engineered band gap in a Si based material through the use of quantum confinement in quantum dot (QD) nanostructures to produce an enhanced band gap [4.5.4]. 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 [4.5.5].

2009 saw the completion of the GCEP program on fabrication of an “all-Si” tandem cell with successful demonstration of doping of these layers with both phosphorous and boron to create a rectifying p-n junction which exhibits a photovoltaic open circuit voltage of 490 mV [4.5.6, 4.5.7, 4.5.8].

Formation of Si (or Ge or Sn) quantum dots through layered thin film deposition of Si rich material which crystallises into uniform sized QDs on annealing.

Silicon is a benign readily available material, which is widely used for solar cell fabrication. Silicon also has a bandgap which is close to optimal not only for a standard, single p-n junction cell but also for the bottom cell in a 2-cell or even a 3-cell tandem stack. The fundamental efficiency limit for a single junction silicon cell is 29%, see Fig. 4.5.3.

This increases to 42.5% and 47.5% for 2-cell and 3-cell tandem stacks respectively. The optimal bandgap of the top cell is 1.7 eV – 1.8 eV for a 2-cell tandem with a Si bottom cell and 1.5 eV and 2.0 eV for the middle and upper cells for a 3-cell tandem.

A cell based entirely of silicon and its dielectric compounds with other abundant elements (i.e. its oxides, nitrides or carbides) fabricated with thin film techniques, is therefore 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.

In previous work we have demonstrated the fabrication of an engineered band gap in a Si based material through the use of quantum confinement in quantum dot (QD) nanostructures to produce an enhanced band gap [4.5.4]. 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 [4.5.5].

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Formation of Si (or Ge or Sn) quantum dots through layered thin film deposition of Si rich material which crystallises into uniform sized QDs on annealing.

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This increases to 42.5% and 47.5% for 2-cell and 3-cell tandem stacks respectively. The optimal bandgap of the top cell is 1.7 eV – 1.8 eV for a 2-cell tandem with a Si bottom cell and 1.5 eV and 2.0 eV for the middle and upper cells for a 3-cell tandem.

A cell based entirely of silicon and its dielectric compounds with other abundant elements (i.e. its oxides, nitrides or carbides) fabricated with thin film techniques, is therefore 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.

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Fabrication of silicon nanocrystals embedded in a dielectric matrix has attracted considerable interest in silicon optoelectronics [4.5.9,4.5.10,4.5.11] and in third generation photovoltaics [4.5.4,4.5.12-4.5.15,4.5.13,4.5.14]. When silicon nanocrystals are made very small (< ~7 nm in diameter), they behave as quantum dots (QDs) due to three-dimensional confinement of carriers [4.5.15]. Quantum confinement causes a material's effective band gap to increase. In indirect band-gap semiconductors optical transitions are allowed only if phonons are absorbed or emitted to conserve the crystal momentum. The localisation of electrons and holes inside a QD leads to reflections or folding of phonons in k-space. With increasing localisation this progressively relaxes the $k$-conservation requirement and creates a quasi-direct band gap. Our measurements of photoluminescence (PL) from Si QDs in silicon oxide has confirmed that we get a 1.7eV lowest energy transition from 2nm quantum dots; effectively a 1.7eV band gap [4.5.16]. They also show that there is a large increase in PL intensity as the QD size decreases, which is consistent with the increase in radiative efficiency with the onset of pseudo-direct band gap behaviour.

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 [4.5.15,4.5.16]. 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 [4.5.17]. To date, considerable work has been done on the growth and characterization of Si nanocrystals embedded in oxide [4.5.18,4.5.19] and nitride [4.5.20,4.5.21] dielectric matrices. However, little has been reported on the experimental properties of Si nanocrystals embedded in SiC matrix [4.5.22]. 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 [4.5.23]. As a result, sufficient carrier mobility can be obtained to satisfy device fabrication requirements.

In our work we have also observed that the photoluminescence peaks from Si QDs in nitride are more blue-shifted than that of Si QD in oxide. Fig. 4.5.4 shows the results of other workers for PL peak energies from Si QD dispersed in oxide [4.5.24,4.5.25,4.5.26] and nitride [4.5.20,4.5.27] together with our own PL data. Our PL results are in good agreement with the results from the other authors. PL peak energies of Si QDs in oxide are less than 2.0eV while Si QDs in nitride have peak energies less than 3.0eV. This is the opposite of what would be expected from the effective mass approximation calculation of confined energy levels [4.5.28]. The lower barrier height of Si QDs in SiN$_x$ would be expected to give a lower confined energy level rather than a higher one. Puzder et al. [4.5.29] claim that the main reason for the PL peak energy reduction in oxide matrix is the distortion of the local sp$^3$ network by double-bonded oxygen. Yang et al. [4.5.30] claim that the reason for the stronger blue-shift in nitride is better passivation of Si QDs by nitrogen atoms eliminating the strain at the Si/Si$_3$N$_4$ interface nearly completely. However our own work in this area using ab-initio modelling (HF-DF with Gaussian software) shows that the decrease in confined energy level, for a given size of Si nanocrystal, on going from nanocrystals terminated by H (equivalent to vacuum) to those terminated with –NH$_2$ groups ($\equiv$ to nitride) to those with –OH groups ($\equiv$ oxide) is due to the differing lowest local energy states of surface Si atoms [4.5.31]. The greater strain associated with QDs terminated with polar Si–O bond, as compared to the less polar Si–N bond, results in a larger number of surface states within the HOMO-LUMO gap and hence a lower confined energy level. This effect is greatest for small QDs in which the larger proportion of surface atoms meas thr surface states dominate [4.5.31].
4.5.2.2 Fabrication of Si QD nanostructures

Thin film techniques are used for nanostructure fabrication. These include sputtering and plasma enhanced chemical vapour deposition (PECVD). The deposition is a variation of the multi-layer alternating ‘stoichiometric dielectric / Si rich dielectric’ process, shown in Fig. 4.5.5, followed by an anneal during which Si nanocrystals precipitate limited in size by the Si rich layer thickness [4.5.16,4.5.18]. The most successful and hence most commonly used technique is sputtering, because of its large amount of control over deposition material, deposition rate and abruptness of layers. A multi-target remote plasma sputtering machine with two independent RF power supplies as well as additional DC power supplies is used in this work.

**Figure 4.5.5:** Multilayer deposition of alternating Si rich dielectric and stoichiometric dielectric in layers of a few nm. On annealing the Si precipitates out to form small nanocrystals of a size determined by the layer thickness. Nanocrystal or quantum dot size is therefore uniform.

RF magnetron sputtering is used to deposit alternating layers of SiO\(_2\) and SRO of thicknesses down to 2nm. [SRO refers to Si rich oxide, formed by co-sputtering Si and SiO\(_2\).] Deposition of multi-layers, consisting typically of 20 to 50 bi-layers, is followed by an anneal in N\(_2\) from 1050 to 1150°C. During the anneal the excess silicon in the SRO layer precipitates to form Si nanocrystals between the stoichiometric oxide layers.

For Si QDs in SiO\(_2\), the precipitation occurs according to the following:

\[
\text{SiO}_2 \xrightarrow{\Delta} \frac{3}{2} \text{Si} + \frac{1}{2} \text{SiO}_3
\]

Precipitation of excess Si from Si rich dielectrics in SiN\(_x\) and SiC follows a similar crystallisation reaction as Si precipitates from the amorphous matrix. The techniques has also been applied to growth of Sn QDs in SiN\(_x\) and Ge QDs in SiO\(_2\). Ge and Sn quantum dots can be precipitated at substantially lower temperature, as discussed below.

4.5.2.2.1 Carrier tunnelling transport in Si QD superlattices

Transport properties are expected to depend on the matrix in which the silicon quantum dots are embedded. As shown in Fig. 4.5.6 different matrices produce different transport barriers between the Si dot and the matrix, with tunnelling probability heavily dependent on the height of this barrier. Si\(_3\)N\(_4\) and SiC give lower barriers than SiO\(_2\), allowing larger dot spacing for a given tunnelling current.

**Figure 4.5.6:** Bulk band alignments between silicon and its carbide, nitride and oxide.

The wave function of an electron confined to a spherical dot penetrates into the surrounding material, decreasing exponentially into the barrier. The slope of this exponential decay and hence the barrier to tunnelling between quantum dots is reduced for a lower barrier height material. This is because - from transmission/reflection probability - the tunnelling probability \(T_e\) through a square potential well depends exponentially on three parameters, the barrier width \(d\) = the spacing between quantum dots; the square root of the barrier height seen by the electron \(\Delta E^{1/2}\) the energy difference between the CB edge of the matrix and the confined energy level of the quantum dots \(\Delta E = (E_c - E_n)^{1/2}\); and the square root of the effective mass \(m^*\) of the electron in the barrier. This gives the approximate relation (e.g. [4.5.32] p244):

\[
T_e \approx 16 \exp \left\{ -d \left( \frac{8m^*}{\hbar^2} \Delta E \right)^{1/2} \right\}
\]

Hence the important parameter in determining the degree of interaction between quantum dots is \(m^*\Delta E\). As barrier height decreases the barrier thickness for a given probability increases, thus requiring a lower dot density for a given conductivity or higher conductivity for a given dot density. As the dot size decreases \(\Delta E\) also decreases, thus increasing \(T_e\) and enhancing the effect further for smaller quantum dots [4.5.32]. The results suggest that dots in a SiO\(_2\) matrix would have to be separated by no more than 1-2 nm of matrix, while they could be separated by more than 4 nm of SiC. Fluctuations in spacing and size of the dots can be investigated using similar calculations. It is also found that the calculated Bloch mobilities do not depend strongly on variations in the dot spacing but do depend strongly on dot size within the QD material [4.5.23].
Fluctuations in spacing and size of the dots around their mean values can be investigated using similar calculations. Using this approach it is also found that the calculated Bloch mobilities do not depend strongly on variability in the dot position around a mean position, $\Delta d$, but do depend strongly on variation in the dot size within the QD material [4.5.23]. This is an important result for engineering a real thin film structure, because although it is necessary to minimise the mean spacing between QDs, $d$, to give high mobilities for a given matrix, the variation around this mean value, $\Delta d$, is less critical. Hence, transport between dots can be significantly increased by using alternative matrices with a lower barrier height, $\Delta E$. The spacing of dots would have to be closest in the oxide, nitride and carbide, in that order. Similar deposition and quantum dot precipitation approaches work for all.

4.5.2.2.2 Different materials for QD nanostructures

As described in section 4.5.2.2.1, different matrices are useful to modify both the tunnelling probability between adjacent quantum dots and the energy levels in the quantum dots themselves. Also alternative quantum dot materials such as germanium and tin offer the possibility of lower temperature precipitation of quantum dots and the potential for band gaps lower than that of silicon should these be required for tandem cell elements under a silicon cell. We have investigated a range of these quantum dot and matrix materials and with a view to optimising the properties of solar cell materials.

Table 4.5.1: Quantum Dot / Matrix combinations and current status of investigations.

<table>
<thead>
<tr>
<th>Matrix</th>
<th>SiO$_2$</th>
<th>Si$_3$N$_4$</th>
<th>SiC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>SPOED</td>
<td>SPOED</td>
<td>SPOE</td>
</tr>
<tr>
<td>Ge</td>
<td>SPO</td>
<td>P</td>
<td>-</td>
</tr>
<tr>
<td>Sn</td>
<td>SPO</td>
<td>PO</td>
<td>-</td>
</tr>
</tbody>
</table>

$S$ = Simulation (DFT - Gaussian 03)
$P$ = Physical (HRTEM, XRD, Raman)
$O$ = Optical (Photoluminescence, Absorbance)
$E$ = Electronic (Resistivity, activation energy)
$D$ = Devices (Diodes, Cells)

An overview of progress on the various combinations of quantum dot and matrix materials is shown in Table 1. Si QDs in SiO$_2$ and Si$_3$N$_4$ are furthest advanced, but significant progress has also been made on Sn QDs and Si QDs in SiC.

4.5.2.3 Structural and electrical characterization of SRO layers for device applications.

In order to fabricate a working device it was necessary to investigate a wide parameter space to optimize the material properties.

We investigated both thick and multilayered SRO structures varying their stoichiometry and doping. The effects of the variation were investigated by TEM, XRD, FTIR, PL and optical absorption spectra. The electrical characteristics of Boron and Phosphorous doped material were also studied.

4.5.2.3.1 The effect of stoichiometry of SRO on the properties of Si QD formed as multilayers in a SiO$_2$ matrix

The effect of stoichiometry of SRO on the properties of Si QDs formed as multilayers in SiO$_2$ matrix was investigated. The Si QDs formed as multilayers in a SiO$_2$ matrix were synthesized by a co-sputtering technique and subsequent high temperature anneal. The formation of Si QDs was confirmed by TEM. As shown in Fig. 4.5.7 and Fig. 4.5.8, the average Si QD diameter increases as the O/Si ratio decreases from 1.30 to 0.86. The Si QDs are approximately 4 nm in the SiO$_{1.3}$/SiO$_2$ multilayer, which decreases to a approximately 3 nm in SiO$_{1.0}$/SiO$_2$, and further decrease to approximately 2.5 nm in SiO$_{0.8}$/SiO$_2$.
Figure 4.5.7: Cross-section TEM images of SiQD/SiO\textsubscript{2} multilayer with various O/Si ratios (a) multilayer structure of annealed SiO\textsubscript{1.3}/SiO\textsubscript{2} (b) high-resolution image of annealed SiO\textsubscript{1.3}/SiO\textsubscript{2} (c) multilayer structure of annealed SiO\textsubscript{1.0}/SiO\textsubscript{2} (d) high-resolution of annealed SiO\textsubscript{1.0}/SiO\textsubscript{2} (e) multilayer structure of annealed SiO\textsubscript{0.86}/SiO\textsubscript{2} (f) high-resolution of annealed SiO\textsubscript{0.86}/SiO\textsubscript{2}

Figure 4.5.8: Si QD diameter as a function of O/Si ratio in annealed SiO\textsubscript{x}/SiO\textsubscript{2} multilayer films.

The measured optical absorption (Fig. 4.5.9) depends on the O/Si ratio of SRO and the absorption edge is blue-shifted as the O/Si ratio increases, consistent with the general perception of quantum confinement as expected from the size variation with the O/Si ratio as seen by TEM imaging. A strong increase in the absorption tail was observed for samples with O/Si=1.0 and 1.3 as compared to sample obtained at O/Si=0.86. This can be due to small amorphous clusters that would add a characteristic long tail in the density of states for O/Si=1.3 and 1.0.

Figure 4.5.9: Room temperature absorption co-efficient of annealed SiO\textsubscript{x}/SiO\textsubscript{2} multilayer films with various x (1100 °C, 1h). The inset is the estimated optical band gap (filled square: direct bandgap; empty circle: indirect band gap).

The PL spectrum (Fig. 4.5.10) of annealed SiO\textsubscript{x}/SiO\textsubscript{2} samples vary with the O/Si ratio both in peak position and intensity. PL intensity increases with O/Si ratio of the SRO. This PL intensity variation could be due to an increase in the oscillator strength with the QD size reduction. The position and the shape of the emission spectra depend on the
excitation wavelength. This effect is most probably related to the QD size distribution. The emission peak position does not completely follow prediction of quantum confinement. Our results suggest that the nature of the recombination process responsible for the observed emission for samples with O/Si = 0.86 is different from those with O/Si = 1.0 and 1.3. Similarities in PL (Fig. 4.5.10), absorption (Fig. 4.5.9) and decay time (Fig. 4.5.11) measurements for these two suggest that the recombination centre in samples with O/Si = 1.0 and 1.3 is very similar. The emission properties may be determined by small amorphous clusters with the long recombination time and long tails of density of states. The indications of the amorphous nature of QDs in samples (O/Si = 1.3 and 1.0) has been also observed from the absorption experiment as long absorption tails. On the other hand, when the O/Si ratio is equal to 0.86 we deal with mostly crystalline Si QDs for which the recombination lifetime is shorter (compared to amorphous QDs) and the emission peak position will appear at a position according quantum confinement predictions.

### 4.5.2.4 Silicon nanocrystal devices on quartz substrates

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Work was continued in our standard SiO$_x$/SRO/SiO$_2$ based structures aimed at improving the device performance using forming gas annealing on completed devices.

The fabricated p-n diodes consisted of sputtered alternating layers of SiO$_x$ and SRO onto quartz substrates with in-situ Boron and Phosphorus doping. The top B doped bi-layers were selectively etched to create isolated p-type mesas and to access the buried P doped bi-layers [4.5.7, 4.5.8, 4.5.33, 4.5.34]. Aluminium contacts were deposited by evaporation, patterned and sintered to create ohmic contacts on both p and n-type layers. The fabricated interdigitated solar cells have an effective area of up to 0.12 cm$^2$. Fig. 4.5.12 is a schematic diagram of a cross section of these devices.

![Figure 4.5.12: Schematic representation of the fabricated inter-digitated devices.](image)

Device modelling has been an integral part of the fabrication and significant efforts were spent developing a complete equivalent circuit of the devices previously fabricated. Based on this model it is possible to understand the limited short circuit current of these devices as well as the anomalous high diode ideality factor.

The successful fabrication of devices on quartz substrates reported in the previous year, opened the door to new device structures beyond the silicon dioxide (SiO$_2$) matrix. In order to improve the control of the nanocrystal (NC) size a new structure was thoroughly investigated which included silicon nitride (Si$_3$N$_4$) as the cladding layer. The new structure maintained an active layer composed of silicon rich oxide (SRO) sandwiched between thin Si$_3$N$_4$ layers. Due to the mechanical stability of Si$_3$N$_4$ compared to SiO$_2$, it is expected that the spatial confinement of the Si NC will improve whilst, due to the lower bandgap of Si$_3$N$_4$, the electrical conductivity between the active SRO layers will be increased. It is also expected that the nitride layer will impede or reduce the diffusion of dopants unavoidable during the high temperature required for the NC formation.
4.5.2.4.1 Forming gas annealing

Due to the insulating nature of the quartz substrates, our device fabrication requires reactive ion etching (RIE) to access the base of the solar cells. It is expected that some unavoidable defects, particularly at the surface and close to the junction, will occur during the RIE step. An effective way to remove this damage can be a high-temperature-anneal in forming gas (96% Ar, 4% H2) or a lower annealing temperature step in a hydrogen plasma. Due to the presence of the required metal contacts on the final structure, neither of these solutions is applicable. We investigated the effects of a post metallisation forming gas anneal in a quartz tube furnace at low temperature ranging between 250°C and 450°C. It was found that a temperature of 400°C is sufficient to improve both the short circuit current (Isc) and open circuit voltage (Voc), as shown in Fig. 4.5.13, without causing severe shunting effects. It was also found that both, Voc and Isc, show a dramatic improvement after the first 20 minutes of annealing time. This improvement then saturates and is practically unchanged even after 80 minutes. After 100 minutes annealing, a decrease in Voc is observed.

4.5.2.4.2 Equivalent circuit modelling

In order to better understand the limitation imposed by the device on the solar cell performance, it is necessary to find a good equivalent circuit model specific to our devices. The high resistivity of the base layer makes it imperative to consider the two dimensional effects of current flow. The following figure is a schematic drawing of the standard p-n structures we fabricate on a regular basis. Details of the fabrication can be found elsewhere [4.5.35].

The improvement in Isc is due to the reduced series resistance resulting from both an improved conductivity of the base layer and a reduced contact resistance, as determined from measurements using a transfer length method (TLM) after each annealing step. The underlying causes for the initial improvement of Voc have not been clearly identified. It is reasonable to assume that the hydrogen in the forming gas passivates defects in the bulk of the material. These defects may lie in the middle of the band gap, similar to those found in amorphous silicon. By reducing the density of defects, an improved lifetime, mobility and effective electronic band gap should result in an increase in Voc. After the 100 minute anneal, shunting is observed in the diode dark I-V characteristic which explains the reduction of Voc.

In order to analyse the I-V characteristics of these diodes we first generalised the model to include any number of diodes in series. The series connection of diodes is used to explain the ideality factors higher than two normally observed in our structures. We believe this is a reasonable model as the ideality factor observed is almost independent of the diode current. This type of behaviour has also been observed in multi quantum well laser diodes [4.5.36] where it has been proven to arise from an unintended series combination of diodes. Based on this series combination of diodes, it is possible to obtain an expression relating temperature dependent I-V measurements to the band gap [4.5.7]. It is further possible to linearise the expression around an average measuring temperature, T_avg, as follows:

\[
\sum \frac{kT}{q} n_i \exp \left( \frac{-E_g}{kT} \right) \sum \frac{kT}{q} n_i \exp \left( \frac{-E_g}{kT} \right) = \frac{1}{T_{nom}} \left( \frac{1}{I_{oi}} \sum \frac{kT}{q} n_i \exp \left( \frac{-E_g}{kT} \right) \right)
\]

Where \( k \) is Boltzmann’s constant, \( q \) is the electron charge, \( T_{nom} \) is the temperature at which the saturation current, \( I_{oi} \), is defined, \( n_i \) is the diode ideality factor, and \( \alpha_i \) is the saturation current temperature exponent. Notice that this equation shows that the I-V characteristics are related to a sum of band gaps.

As the current flows from the base contact to the emitter, a linear voltage drop along the base and under the diode isolation mesa causes an exponential change in the diode current. This crowding of the current at the edge of the diode mesa, depicted in Fig. 4.5.14, can be modelled adding a current dependence on the series resistance. This series resistance, \( R_s \), can be expressed as the sum of a current independent, \( R_{int} \), and a current dependent series resistance, \( R_{sat} \), arising from current crowding:

![Figure 4.5.14: Schematic diagram of the diodes investigated illustrating the effect of current crowding.](image-url)
4. Research

The value of this resistance can be found by numerically solving the following transcendental equation:

\[ R_s(T, I) = R_{s0} + R_s = \frac{R_{s0}(T)}{2L} + \frac{R_{s0}(T)}{2L} \ln \left( \frac{1}{\phi \tan(\phi)} \right) \]

The value of this resistance can be found by numerically solving the following transcendental equation:

\[ \phi \tan(\phi) = \frac{1}{K_n nV} \frac{q}{i_{ss}} \frac{1}{W} \]

Within this mathematical framework it is then possible to extract the value of the series resistance, remove its effect from the measured I-V characteristics to extract the actual ideality of the diode current. We normally observe an ideality factor of 3. Based on the proposed model of at least two diodes in series, without any assumptions, it is only possible to establish that the value of the band gap extracted from temperature dependent I-V measurements corresponds to a sum of the band gaps (or activation energies) of these diodes.

An interesting behaviour observed in these devices was the apparent lack of correspondence between the dark and light I-V characteristics.

The series resistance extracted from the diode dark I-V characteristic is too small to explain the limited short circuit current as well as the low fill factor measured under a simulated 1-sun condition. A more complete circuit model is necessary to explain this discrepancy. We propose a model where the observed behaviour is due to two distinct areas in the fabricated devices. The photocurrent is produced only in a small area of the device, this area being proportional to a fraction of the normalized diode area. In a Spice circuit model this area is given a value smaller than 1, that we denote as fraction. This will be a fitting parameter to reproduce the measured dark and illuminated I-V characteristics. The following figure shows the circuit proposed.

![Figure 4.5.15: Equivalent Spice circuit representation of the fabricated devices.](image)

A relatively large percentage of the device area is responsible for the measured characteristics in the dark. The current in this area is caused by the diffusion of minority carriers caused by the applied voltage (V1 in Fig. 4.5.15) from the p or n side to the opposite region. This current is expected to be large due to the low lifetime of the minority carriers (mostly recombination current in the depletion region). The observed series resistance will be proportional to the total series resistance, Rtot, and inversely proportional to the area, R2=Rtot/(1-fraction), where the diffusion current occurs. The dark I-V behaviour is modelled by the top branch of the circuit depicted in Fig. 4.5.15. D_QD1 and D_Sch represent the series connection of diodes whose band gaps are extracted using Eqn.(2). The series resistance, R2, has the temperature and current dependence detailed in Eqns.(3) and (4).

Only a small part of the diode area may have a large enough lifetime to produce a photocurrent. As this photocurrent flows only through this fractional area, the series resistance is inversely proportional to this fraction: R1=Rtot/fraction. Since the photocurrent, Iph, flows through R1, the illuminated I-V characteristics are limited by a larger resistance than that observed in the dark condition, as long as the fraction of the diode area is smaller than one half. The simulations depicted in the following figure show the reduction of ISC as the fraction, f, is varied from 99% to 1% of the total diode area.

![Figure 4.5.16: Spice simulations of 1-sun IV characteristics based on the circuit depicted in Fig. 4.5.15. The fraction, f, represents the normalized area of the diode where the photocurrent is produced.](image)

With the circuit model described, it will be possible to extract complementary information from dark and illuminated I-V measurements.

In view of these simulations, it is clear that the electrical characterisation of our devices needs to take into consideration previously overlooked limitations. For example, great care should be taken when interpreting the Quantum Efficiency extracted from a spectral response measurement as the assumed condition of short circuit current may be incorrect even if the device is externally short circuit (internally, the diode may be forward biased). Moreover, as the current is proportional to the photon flux, and the flux is generally different at each wavelength tested, the internal bias of the device can be different at each point of the spectrum investigated.
4.5.2.4.3 Si₃N₄/SRO bilayer structures

Having demonstrated working devices using Si and SiO₂, new structures were fabricated using SRO layers sandwiched by Si₃N₄ barriers as depicted in Fig. 4.5.17.

![Intended device structure of a Si QD solar cell with Si₃N₄ barriers.](image)

It is expected that the spatial confinement of the Si NC will improve whilst, due to the lower band gap of Si₃N₄, the electrical conductivity between the active SRO layers will be increased. The nitride layer will also impede or reduce the diffusion of dopants during the high temperature anneal required for the nanocrystal formation.

We have investigated some properties of this new structure previously used to assess the quality of the SiO₂/SRO layers employed in our working devices. We looked at the degree of crystallisation obtained from Raman spectra. The structures were deposited on quartz substrates and subsequently crystallized in a quartz furnace or by rapid thermal annealing (RTA), the later is investigated as an alternative method to produce Si nanocrystals but keeping the diffusion of dopants to a minimum.

![Raman measurements of SRO/Si₃N₄ samples.](image)

Figure 4.5.18: Raman measurements of SRO/Si₃N₄ samples. 40 sec RTA and 30 min furnace annealed samples show peaks at 515 and 516 cm⁻¹ respectively. 5 sec RTA sample peaks at 509 cm⁻¹. As deposited sample has a peak at around 465 cm⁻¹.

Having observed that the RTA method does result in the appearance of a crystalline phase, the photoluminescence (PL) signal was subsequently measured. The intensity and position of the PL peak were compared for different annealing times as well as after a hydrogen plasma passivation step.

![Photoluminescence data of RTA crystallized samples with and without hydrogenation.](image)

Figure 4.5.19: Photoluminescence data of RTA crystallized samples with and without hydrogenation. All three samples with different annealing conditions have the same peak at 1.38 eV.

It is clear that even after 5 seconds in the RTA process, a peak in the PL signal appears with an energy (1.38eV) larger than that of bulk Si. The peak position remains constant even after 40 seconds of RTA whilst the intensity increases. The peak intensity is further enhanced after hydrogen passivation.

It is now necessary to investigate the effects of doping and silicon concentration in the SRO layers. After this study is completed, a p-i-n structure will be deposited and fabricated aimed at improving our present record open circuit voltage of 490meV achieved by the SiO₂/SRO diodes.

4.5.2.5 Silicon QDs embedded in silicon nitride matrix

**RESEARCHERS**

Yong Heng So, Lei Shi, Ivan Perez-Wurfl, Shujuan Huang, Gavin Conibeer

The all-silicon tandem solar cell using silicon (Si) quantum dots (QDs) embedded in a silicon dioxide (SiO₂) matrix emerged to be a promising third generation photovoltaic approach to realise future high performance, thin film solar cell [4.5.4]. Silicon nitride (Si₃N₄) offers a more suitable host matrix due to its smaller band gap with respect to SiO₂, which enhance the carriers transport between QDs [4.5.23].

This work seeks to study the optical and electrical properties of Si QDs embedded in a Si₃N₄ matrix, in order to implement it as an alternative matrix to embed Si QDs for all-Si tandem solar cell application.

In earlier work on Si QDs in Si₃N₄ [4.5.37,4.5.38] PECVD was used to fabricate multilayer structures with subsequent formation of Si nanocrystals on annealing. This approach uses the same co-sputtering technique as used with the SiO₂ matrix to give a greater control of layer thickness. Si QD superlattices were obtained by depositing alternating layers of Si-rich Si₃N₄ (SRSN) and nominally stoichiometric Si₃N₄ by a co-sputtering technique and subsequent high temperature annealing.

Structural properties of Si nanocrystals (NCs) embedded in Si₃N₄ matrix were characterized [4.5.39]. Optical absorption and emission properties...
of Si NCs were studied using UV-visible-NIR and photoluminescence (PL), respectively. Circular transfer length measurement (CTLM) contact was applied photolithographically to the samples in order to measure the sheet resistance ($R_{\text{sheet}}$) and contact resistance ($R_c$) of the films (4.5.40).

A blue shift of the absorption edge was observed in Fig. 4.5.22(a) as the Si-richness in SRSN layer decreases, which indicates that reduction of dot size causes the widen of optical bandgap. This agreed with the blue shift observed in Fig. 4.5.22(b) for the decreasing SRSN thickness that governs the dot size. Also, quantum confinement effect was observed where decrease of Si-richness and thickness of SRSN cause PL blue shift that shown in Fig. 4.5.23(a) and Fig. 4.5.23(b). Measurements of CTLM (Fig. 4.5.24) show that $R_{\text{sheet}}$ decreases with the increase of Si-richness in SRSN, this can be attributed to the increase of dot density and distance between dots which enhance the conductivity. For similar Si-richness, $R_{\text{sheet}}$ of the 3nm SRSN thickness is higher than the 4nm one. As the thickness of the SRSN layer decreases, the dot formation process was hindered and became difficult thus causing the reduction of dot density and increase of dot separation (4.5.41).

Figure 4.5.20: TEM image of Si QDs superlattice of SRSN/SiN (5nm/3nm). The inset shows a Si QDs with Si (111) fringe.

Formation of a superstructure of Si QDs embedded in Si$_3$N$_4$ matrix has been confirmed using TEM, as shown in Fig. 4.5.20. The X-ray reflection spectra in Fig. 4.5.21 clearly show Bragg peaks, indicating that multilayer periodicity and thickness uniformity remain unchanged after high temperature annealing. This suggests that embedding Si QDs in nitride has several merits such as low variation in layer thickness throughout the multilayer film, low roughness at the interface of successive layers and a good barrier layer that hinders inter-diffusion of Si.

Figure 4.5.21: XRR spectra of a multilayer structure with SRSN/SiN (5nm/3nm).

Figure 4.5.22: Square root of absorption coefficients for Si QD superlattices with varying (a) Si-richness and (b) thickness of the SRSN layer.
4.5.2.6 Silicon QD nanocrystals embedded in silicon carbide matrix

RESEARCHERS
Zhenyu Wan, Dengyuan Song, Shujuan Huang

Silicon carbide (SiC) is thought a preferable matrix in which to embed Si QDs because of its lower barrier height compared to SiO2. In our previous reports, we have demonstrated that both Si and SiC QDs have been produced by high temperature annealing of a single Si-rich SiC (SRC) layer or in a Si1-xCxC/SiC multilayer structure. The PV device made from a n-type Si-QD-SiC/ p-type Si-QD-SiC homojunction grown on quartz has also been investigated and a Voc of 82mV at 1sun has been achieved [4.5.42,4.5.43]. We believe that the formation of β-SiC nanocrystals may hinder the formation of Si QDs. Also they may cause leakage via the SiC grain boundary traps to increase the shunt current in the solar cell. Therefore, the work in 2009 has focused on studying the mechanism of the crystallisation of SiC and optimising the materials by comparing the annealing methods, rapid thermal annealing (RTA) and conventional furnace annealing.

Furnace annealing was performed in nitrogen (N2) ambient at 1100°C for 1 hour, ramping from 600°C to 1100 °C over 40 mins. The RTA annealing was also performed in N2 ambient at 1100 o C, but with a very rapid ramping time of 30 sec and much shorter annealing time of 2 mins. The structural properties including the nanocrystal size, shape, and phase separation in the samples were studied using TEM (Phillips CM200) at 200 kV. The crystallization properties were evaluated by grazing incidence x-ray diffraction (GIXRD). Additional structural properties such as phase separation and crystallinity were studied by Raman spectroscopy.

Figure 4.5.25: TEM images of furnace (a) and RTA (b) annealed samples which contain 50 v% of Si.

Future work will concentrate on doping of Si QDs in Si3N4 matrix and realizing the implementation of Si QDs in Si3N4 for the all-Si tandem solar cell.
while the dash-line circled with a fringe spacing of 2.5 Å correspond to the [111] lattice planes of β-SiC. The nanocrystal size and shape are similar under both annealing conditions, with Si size 6-7 nm and SiC size 3-4 nm. We studied the crystalline property using XRD. For the sputtered stoichiometric SiC film, no Bragg peak was detected after annealed either by RTA or by furnace, which suggests that SiC does not crystallise under the 1100°C annealing condition. However, in our previous research Si and β-SiC nanocrystals started to form at 900°C annealing [4.5.42,4.5.43], and sputtered Si has elsewhere been reported to be able to crystallise around 900°C [4.5.44]. Therefore, in this work, β-SiC crystallization in SRC samples is directly related to Si nucleation. When the annealing temperature rises to 900°C, Si nanocrystals start to form, with some acting as nuclei heterogeneous nucleation of SiC nanocrystals. As a result, both Si and SiC diffraction peaks were observed in SRC samples.

![Figure 4.5.26: Comparison of nanocrystal sizes (nm) formed by RTA and furnace annealing, which were estimated from XRD peaks.](image)

Fig. 4.5.26 summarises the size as a function of Si concentration in the samples. We can see that the size of β-SiC nanocrystals remains the same ~3.5 nm in all samples. However, the Si nanocrystal size of the samples annealed by RTA is larger than that of the furnace annealed samples. This is more obvious when the samples contain more Si. The RTA annealing also results in a higher intensity Si diffraction peak than that of furnace annealing, as shown in Fig. 4.5.27. This indicates that RTA produces a higher volume of silicon nanocrystals.

![Figure 4.5.27: Comparison of the Si (111) XRD peak intensity for different anneals.](image)

The degree of crystallization of each sample has been evaluated by the ratio of the intensity of the crystalline Si peak and amorphous Si peak in Raman spectra: $I_c/I_a$ as shown in Fig. 4.5.28. The samples annealed by RTA show better Si crystallization and less amorphous Si remaining in the matrix compared to the furnace annealed samples at most Si concentration levels.

![Figure 4.5.28: Comparison of Si crystalinity ($I_c/I_a$) on RTA and furnace annealed samples.](image)

From these XRD and Raman results, the RTA annealed samples are seen to give a better degree of crystallization of Si QDs. This is because the shorter temperature ramping profile can prevent SiC from crystallization during the ramping process so as to leave enough space for Si atoms to precipitate. Future work will continue on material optimisation to improve PV device performance.
Alternative QD materials

4.5.2.7 Germanium Quantum Dots

Researchers
Santosh Shrestha, Bo Zhang, Pasquale Aliberti, Gavin Conibeer

4.5.2.7.1 Fabrication of Germanium quantum dots

Although our main focus has been on Si nanocrystals, other group of IV nanocrystals have also been studied. Since Ge has smaller electron and hole effective masses and a larger dielectric constant than Si, the excitonic Bohr radius of bulk Ge is larger than that of Si. This leads to a more prominent quantum confinement effect in Ge NCs. Furthermore the lower melting point of Ge at 938.3 °C implies that Ge NCs should be able to form at lower temperatures than Si NCs.

The current work builds on earlier work on Ge nanocrystals carried out in our group [4.5.45]. The new work uses a different approach to annealing of the samples which gives a wider range of control of Ge nanocrystal formation. Ge nanocrystal samples have been fabricated by RF magnetron sputtering using a combination of fused quartz disc and high purity Ge strips as a sputtering target. Sputtering of the Ge-rich oxide (GeRO) layer is achieved by Ar sputtering, whereas sputtering of the oxide layers, GeO₂/SiO₂, is performed by reactive sputtering with O₂. These layers are alternately deposited to obtain the desired multilayered structure. A thick oxide capping layer was deposited to prevent oxidation of the GeRO layers during subsequent annealing. Post deposition annealing of the samples was performed under a low pressure (in the growth camber) during which Ge NCs are formed. Results from structural characterization using TEM, Raman, XRD and PL have been obtained.

Fig. 4.5.29 shows a high resolution TEM image of a section of a typical sample containing GeRO layers between GeO₂/SiO₂ layers following annealing.

Figure 4.5.29: Cross-section HRTEM image of a typical sample containing GeRO layers between GeO₂/SiO₂ layers following annealing.

Figure 4.5.30(a) shows Raman spectra of the as-deposited and the annealed samples, including those for bulk Ge as a reference. For these samples, the sputtering times for each GeRO layer and GeO₂/SiO₂ layer were 8 minutes and 6 minutes, respectively, and the post deposition annealing was performed at 650°C for 40 minutes. A broad hump at around 270 cm⁻¹ is observed in the spectra of the as-deposited film which is attributed to the non-crystalline Ge phase. But in the annealed film, it is replaced by a sharp peak at 300.5 cm⁻¹, which is very close to the Ge-Ge optical phonon mode for bulk Ge (300.2 cm⁻¹), indicating the formation of Ge NCs with good crystallinity. Peak broadening and an asymmetric shoulder on the lower frequency side can be interpreted by the model of the optical phonon confinement effect in nanocrystals [4.5.46]. However, it seems that in our Ge system the high frequency side of the Raman peak does not show a shift to lower phonon frequencies which is usually the case for nanocrystals.

Figure 4.5.30(b) shows GIXRD patterns for this sample. In the as-deposited film there are no obvious peaks but only two broad bands at around 2θ = 26° and 28 = 49°. After annealing, the sample shows three sharp peaks at 27.12°, 45.13° and 53.21°, corresponding to the groups of planes (111), (220) and (311) of crystalline Ge, respectively. This observation confirms good crystallinity of the Ge phase in the film and agrees well with our Raman results. The average size of the Ge NCs, calculated from the (111) peak broadening using the Scherer equation, is about 4.5 nm. This value is slightly smaller than that estimated from the HRTEM image. The difference in Ge NCs sizes obtained from these two methods may possibly be due to spatial non-uniformity of the Ge NCs size; with TEM probing a much smaller sample region compared with XRD measurement. In addition, the penetration depth of the incident X-rays is larger than the thickness of our film, thus information obtained from XRD is averaged throughout the whole film.
4. Research continued

The crystallisation of Ge NCs with annealing duration has been investigated with Raman spectroscopy. Fig. 4.5.31 shows Raman spectra for identical multilayer samples with each GeRO and GeO$_2$/SiO$_2$ layers deposited for 6 minutes. The samples were annealed at 685°C for different durations as indicated in the diagram. The crystallization of Ge is found to take place within the first few minutes of annealing. However, the noticeable broad hump, which is attributed to small nanocrystals, suggests an early stage of the crystallization process at this annealing duration. As annealing duration increases, Raman peaks become sharper and narrower indicating increase in Ge crystallinity. It is also observed that the peaks show negligible difference for annealing durations longer than 10 minutes.

The average size of NCs, as calculated from XRD data, increases with annealing duration. This is consistent with the Raman results and agrees well with the growth dynamics by diffusion of neighbouring Ge atoms. Most importantly, the increase in the NCs size begins to level off after 15 minutes of annealing in this particular case. This is similar to the size confinement effect observed for the growth of Si NCs in SiO$_2$ matrix [4.5.14,4.5.18]. In our superlattice structure, Ge NCs are confined within the GeRO layers between GeO$_2$/SiO$_2$ layers, which work as barrier layers to the crystal growth. Hence, Ge tends to precipitate with a diameter approximately equal to the thickness of the GeRO layers. This control mechanism is more significant for thin layers with thickness of a few nanometers, within which there is 2D rather than a 3D growth.

Fig. 4.5.32 shows the Raman spectra of the samples annealed at different temperatures for 40 minutes, which is enough to complete the growth process as discussed above. As expected, the small nanocrystalline asymmetric hump is reduced with the increase in annealing temperature within the range of temperatures studies here, just as in the case of annealing durations. The results also illustrate the formation of Ge NCs in SiO$_2$ matrix at a temperature as low as 620°C.

A sample with the identical process sequence as those for structural characterizations was used for photoluminescence measurements, except that the film was deposited on quartz. Fig. 4.5.33 shows results of room-temperature PL measurement. The PL spectrum consists of a single broad band centred at 1.77eV (corresponding to a wavelength of 700 nm) which can be fitted with three Gaussian distributions. Measurement on GeO$_2$/SiO$_2$ film deposited on quartz under similar conditions did not show any observable PL in the range of wavelengths concerned. Thus the PL signal from the multilayer sample can be attributed to Ge NCs in the GeRO layers. Furthermore, a blue shift of PL energy with NCs size has been shown in the 2008 report. We tentatively consider that this is due to the band gap increase induced by the quantum confinement effect in Ge NCs.
4.5.2.7.2 Low temperature growth of Germanium quantum dots

In this section, a low temperature growth of Ge nanocrystals is discussed. This is advantageous because of the potential for reduced processing cost and suitability for low cost substrates. Samples were grown with rf magnetron sputtering as described earlier, except in this case the substrate was heated during the film growth and no post annealing process was used.

Figure 4.5.34 shows Raman spectra for a single layer GeRO film deposited at different temperatures as indicated in the diagram. For clarity, the graph has been divided into three different regimes. In regime I, the samples grown below 350°C are shown. In this case, the spectra show no Raman peaks related to nanocrystalline Ge, instead broad bands centred around 280 cm\(^{-1}\) are observed. The bands are shifted toward higher frequency by about 10 cm\(^{-1}\) compared with that of amorphous Ge (α-Ge) located at around 270 cm\(^{-1}\). This indicates that α-Ge coexists with very small particles (1~2 nm) \[4.5.47\].

For the sample grown at T\(_g\) = 320°C, the observation of a hump at ~ 280 cm\(^{-1}\) as well as a shoulder at ~ 298 cm\(^{-1}\) implies an increase in the number and size of small particles. The rapid growth of Ge NCs is found to happen in Regime II, in which samples grown at temperatures between 350°C and 400°C are shown. The Raman peak corresponding to the TO phonon mode of the crystalline Ge (c-Ge), near 300.4 cm\(^{-1}\), appears at T\(_g\) = 350°C and becomes sharper with increase in the growth temperature. This range of temperature is very close to the onset temperature for Ge crystallization reported in \[4.5.48\]. However, when the growth temperature T\(_g\) reaches 420°C (Regime III), a drastic degradation of Ge-Ge peak intensity and shape is observed. These phenomena indicate the absence of Ge crystallinity in this temperature range.

Based on the Raman results discussed above, it is expected that the growth temperature window is between 350°C and 420°C, in which Ge atoms or clusters can accumulate and eventually grow into highly crystallized nanocrystals. These temperatures are much lower than the usual post-deposition annealing temperatures used for Ge NCs fabrication.

A HRTEM image of a multilayered sample consisting of alternate layers of GeRO and GeO\(_2\)/SiO\(_2\) films is shown in Fig. 4.5.35. In this case the sample was grown at T\(_g\) = 380°C without further post-deposition thermal treatment. The TEM image shows close to spherical Ge NCs with fairly uniform size, separated by the barrier layers. The Ge NC sizes are in the range of 4.8 - 5.8 nm which is consistent with the average size (~ 4.8 nm) determined from XRD. The image in the inset shows clear lattice fringes inside one of the Ge-NCs (indicated by the arrow). The fringes are consistent with (111) planes of the Ge diamond structure.

Figure 4.5.33: Room temperature PL of a multilayer film containing Ge NCs in GeO\(_2\)/SiO\(_2\).

Figure 4.5.34: Raman spectra from Ge-NCs in single layer samples grown at different substrate temperatures.

Figure 4.5.35: A High resolution TEM image of multilayered Ge NCs in SiO\(_2\) matrix. The sample was grown at 380 °C.
4.5.2.7.3 Summary of Ge QDs

Germanium nanocrystals embedded in silicon dioxide films have been fabricated by RF magnetron sputtering by using combined germanium and quartz, followed by vacuum annealing. The formation of Ge nanocrystals has been confirmed by TEM, Raman, XRD and PL measurements. The results also show that the fraction of Ge crystallinity increases with both annealing duration as well as annealing temperature. Importantly, the size of NCs increases with the annealing duration and optimum size is reached after annealing for about fifteen minutes at 685°C. Investigation has shown that the size of Ge NCs is limited by the thickness of GeRO layer between the barrier layers and thus provides a mechanism for controlling NCs size.

Importantly, growth of Ge NCs at a temperature below 400°C has been demonstrated. This has been achieved with in-situ substrate heating during the film deposition. The fabrication of Ge NCs has been evidenced from HRTEM and Raman spectroscopy.

4.5.2.8 Tin nanocrystals embedded in Si$_3$N$_4$ matrix

RESEARCHERS
Shujuan Huang, Yong Heng So

In 2009, the work on Sn nanocrystals (NCs) in a silicon nitride (Si$_3$N$_4$) matrix continued. The principle aim being to avoid the oxidation problem occurred in oxide matrix [4.5.49]. We have developed a low temperature in-situ process to successfully produce Sn NCs in Si$_3$N$_4$ matrix [4.5.50], have studied the methods to control the NCs size and thoroughly investigated the growth mechanism. The co-sputtering process assisted by substrate heating was used. An example of the Sn NCs formed at 100°C in Si$_3$N$_4$ matrix is shown in Fig. 4.5.36. These TEM images clearly show the formation of β-Sn NCs with uniform sizes. We have studied the dependence of deposition temperature and Sn concentration in the co-sputtered films on the Sn NC size, as summarised in Fig. 4.5.37. In order to achieve more precise control on the NC size and tunnelling barrier layer, a multilayer structure composed of alternating layers of Sn-rich and nominally stoichiometric Si$_3$N$_4$ (Fig. 4.5.38) was also fabricated, which gave less than 10% size deviation.

Figure 4.5.36: TEM images of Sn-rich Si$_3$N$_4$ films deposited at 100 °C: cross-sectional TEM showing that uniformly sized Sn NCs evenly distribute in the film and HRTEM of an individual dot showing clear single crystalline structure of β-Sn.

Figure 4.5.37: Sn NC size dependence on substrate temperature and Sn concentration in the films. The size was estimated from XRD peaks.

Figure 4.5.38: Cross-sectional TEM of 20 bi-layer structure of Sn NCs and Si$_3$N$_4$ barrier layers.
We have carried out an experimental study on the growth mechanism of the above process. A series of Sn-rich layers was deposited at 100°C with different deposition time between a baffle and a capping layer of Si₃N₄. We studied the NC size as a function of the deposition time, as shown in Fig. 4.5.39. We can see that there are two growing stages: in the short deposition, which represents the early stage of the long deposition, the Sn NC size increases rapidly to about 4 nm, then, the size tends to be saturate at about 5 nm. We believe that the mechanism of this growing process is a truncated Volmer-Weber mode.

The conventional Volmer-Weber mode usually produces a bimodal size distribution: ultra small particles and comparatively larger coalesced ones [4.5.51]. In this work, the difference from the conventional Volmer-Weber mode is that we deposit two materials: Sn and Si₃N₄. When they are deposited on the heated substrate (100°C), there is sufficient energy for Sn to overcome the surface energy and form small particles diffusing freely across the surface in a two dimensional liquid-like mode. This results in Sn NC nucleation, similar to the early stage of the Volmer-Weber growth mode. However, the Si₃N₄ molecules tend to form a thin film because the melting point of Si₃N₄ is so high that the substrate temperature is not high enough for them to overcome surface forces and move freely in the Volmer-Weber mode. The diffusion of Sn nuclei is limited by the surrounding Si₃N₄ when the nuclei become larger than a certain size. In other words, there is no coalescence process similar to the latter stage of the conventional Volmer–Weber mode. As a result, uniformly sized Sn NCs form in the Si₃N₄ matrix.

Modelling of QD nanostructures:

4.5.2.9 Density Functional ab-initio modelling of nanocrystals

RESEARCHERS

Dirk König, James Rudd, Kristen Casalenuovo

Gaussian03 is a Density Functional – Hartree-Fock (DF-HF) program for calculating basic thermodynamic, electronic and phononic properties of approximants consisting of up to a few hundred atoms. The DF-HF approach together with the linear combination of atomic orbitals is an ab-initio real space method, delivering a spatial picture of magnitudes such as optimised atomic positions (variational principle), molecular orbitals (MOs) or vibrational modes.

Doping of group IV QDs is a research topic of vital interest, but may not be controllable to the required extent for thermodynamic reasons. Another approach is modulation doping as in III-V QWs, i.e. doping the dielectric barrier material such that the ionized dopants provide the respective carrier type in the QDs. We investigate donor and acceptor candidates in SiO₂ and Si₃N₄. Modulation dopants must have an energetic position above the confined electron (donor) or below the confined hole level (acceptor), they must not introduce defect levels in the QD band gap if located at the interface as an active dopant and as a completely saturated foreign atom, and they must have one single oxidation number. Results are expected to take a rather large amount of computation time due to the complex nature of modulation dopants in SiO₂ and Si₃N₄. Our findings indicate that Si and Ge QDs cannot be doped by modulation acceptors or donors in Si₃N₄. The high ionization energy and positive electron affinity of N together with the very polar bond between Si and dopant species does not yield occupied states near the Si₃N₄ conduction band or unoccupied states near the Si₃N₄ valence band. Another approach for modulation doping involves the use of excess Si in the Si-rich Si₃N₄ layer. An adjacent barrier layer with a wide band gap for maintaining quantum confinement, with Si working as a shallow donor is needed, see Fig. 4.5.40.

![Figure 4.5.39: Sn NC size as a function of deposition time for films containing 25 v% of Sn and grown at 100°C.](image)

![Figure 4.5.40: Schematic of modulation donor doping in a III-V QD structure [left]. Tellurium (Te) serves as a donor in the barrier (Aluminium Arsenide – AlAs) thus providing free electrons which are captured by the Gallium Arsenide (GaAs) QD. The principle of modulation doping with a Si-rich dielectric as the QD pre-cursor layer, with Si also serving as the dopant in the adjacent barrier layer [right].](image)
place as a precursor for Si NCs; no extra dopant has to be introduced. Si as a dopant cannot interfere with Si NCs as a defect. The amount required for doping is very small so that the growth of Si NCs should not be affected. Doping a barrier layer yields much higher doping probabilities as compared to small Si NCs. This shifts the search from suitable dopants to suitable barrier layers.

Si is a shallow donor in III-V compounds but the donor function is compensated at high doping densities, preventing donor densities above the high $10^{16}$ cm$^{-3}$ range. Choosing a III-V compound with a group V element with maximum electronegativity minimises this problem, pointing to group III Nitrides. The materials AlN, GaN and their ternary compound $\text{Al}_{x}\text{Ga}_{1-x}\text{N}$ ($0 \leq x \leq 1$) have appropriate band offsets to Si and Ge to maintain quantum confinement. By changing the ratio of Al to Ga, the band offset can be tuned as required for optimum carrier transport, see left graph of Fig. 4.5.41.

![Figure 4.5.41: Band offsets from Si to $\text{Al}_{x}\text{Ga}_{1-x}\text{N}$ and $\text{Al}_{x}\text{Ga}_{1-x}\text{N}$ band gap as a function of composition (left), together with experimental data from the literature of Si as a shallow donor (4.5.52). DFT data of Si and Ge as donors in pure AlN are shown in orange. Donor MOs of Ge in an Al$_{0.5}$N$_{0.5}$H$_{0.5}$ approximant (right) at the energy indicated by the orange star in the left graph. N, Al and H atoms are shown in dark blue, pink and white. The Ge atom is shown in cyan.](image)

Donor modulation doping of $\text{Al}_{x}\text{Ga}_{1-x}\text{N}$ can be accomplished by the segregation anneal required for Si QD formation, rendering the process *in-situ* doping during the Si nanocrystal formation, as shown schematically in Fig. 4.5.42.

![Figure 4.5.42: Principle of Si or Ge donor modulation doping of a Si or Ge QD SL in Si$_{1-x}$N$_x$ or Ge$_{1-x}$N$_x$ separated by $\text{Al}_{x}\text{Ga}_{1-x}\text{N}$ layers.](image)

For SiO$_2$, ongoing computations are investigating an acceptor candidate with a LUMO in doped SiO$_2$ below the HOMO of a Si$_{10}$ QD embedded in such an oxide shell.

### 4.5.2.10 CTEM and STEM Image Simulation to Detect Impurity Atoms

**RESEARCHERS**

Tom Puzzer

Transmission Electron Microscope (TEM) imaging is used extensively in our work on Si and other nanocrystals. A simple interpretation of the TEM data can be misleading and require some sophisticated techniques to extract the full information content. One of the key areas in which we are now employing TEM is in the detection and identification of dopant impurity atoms.

Many of the properties of materials are controlled by the distribution and motion of low concentrations of dopant and impurity atoms. Surface adatoms behave very differently to those in the bulk of a crystal and this is even more pronounced in the case of nanometre-sized particles. Computer simulation of images has become a routine tool to complement experimental high resolution transmission EM of materials. In order to determine the range of potential image contrasts that could be obtained from an impurity atom embedded in a silicon nanoparticle image, a range of model nanoparticle structures have been simulated. The goal of image simulation is to improve our understanding of the image structure and to examine the possible range of characteristic image features from experimentally produced silicon nanoparticles.

Bright-Field TEM multislice simulations have been performed for 3-nm diameter spherical Si nanoparticles for a range of potential particle orientations. To examine the contrast of a single heavy impurity atom a number of different atomic substitutions for Si are made (As, Sb, Au). It is found that orientations that are expected to show comparatively high-visibility lattice fringes in conventional Bright-Field phase-contrast images are not particularly useful to identify single impurity atoms. There appears to be very little phase contrast from the heavier impurity atoms to differentiate them from the contrast due to the regular crystalline lattice of the nanoparticle. With the particle aligned along low-index directions the Si atoms overlap one another in a
small number of columns containing a large number of atoms and the
electron scatter from these columns of Si atoms dominates over the
higher individual scattering due to the single impurity atom making
it necessary to rotate the particle to an orientation where there is a
small number of Si atoms in projection. Even under these conditions
appreciable contrast is only observed if the impurity happens to be
located around the periphery of the particle. The typical image contrast
that is observed is illustrated in Fig. 4.5.43(a) where an Au atom has
been located on the bottom of a particle aligned to the (012) zone
axis and Fig. 4.5.43(b) where an identically oriented particle has an Sb
impurity located on the periphery. Note the range of contrast from the
individual columns of Si atoms in the core of the particle. The image
resolution of high-resolution transmission electron micrographs of
materials are limited by the aberrations of the lenses in the microscope
and multiple scattering in the specimen. Multiple scattering influences
the image in unexpected ways such that the image intensity is no
longer related to the specimen structure in a simple manner.

An alternative imaging mode in high-resolution microscopy is Scanning
TEM (STEM), where a focussed probe is scanned across the specimen
in a raster and the image acquired sequentially. STEM is capable of
sub-Å spatial resolution in both of the main imaging modes employed
- Annular Dark Field (ADF) which employs an annular detector with
a small inner cut-off to detect electrons scattered elastically through
a large angles and Bright Field (BF) which employs a small axially-
mounted detector. STEM image calculations are significantly more
computationally intensive than phase contrast HREM images as the
paths of both the elastically and phonon-scattered electrons need to be
calculated at each pixel in the image. The same atomic coordinate files
as above are employed to calculate the STEM images. The thickness of
the slices used to determine the scattering potential is reduced and
the sampling resolution is suitably increased. Typical results are shown
in Fig. 4.5.44. Both BF and ADF STEM images show significant contrast – sufficient to identify the presence of an impurity in proximity to the
nanoparticle.

Figure 4.5.43: Conventional phase-contrast images (200kV, C_s = 1.0mm,
Scherzer defocus, FOV = 50Åx50Å). An Au atom located underneath
the particle is not visible. An Sb atom (indicated by the arrow) on the
periphery is just barely detectable.

Figure 4.5.44: ADF (a,c) and BF(b,d) STEM images for the same particles
as in Fig. 4.5.43. (200kV, C_s = 1.0mm, Scherzer defocus, FOV = 40Å x
40Å). In (a) and (b) the single Au atom on the lower surface of the
particle and in (c) and (d) the single Sb atom on the periphery of the
particle both produce quantifiable contrast compared to the
conventional HREM phase contrast images. (Note that the image
contrast has been expanded to improve clarity).

Phase contrast images showing fringes at atomic resolution
 correlations among the crystalline nanoparticles can only be achieved
from particles oriented to high symmetry zone axes. Under these
conditions, however, the comparatively weak phase contrast from
impurity atoms cannot be detected with any efficiency and cannot
be used to extract information regarding dopant or impurity atoms
around the particles. STEM images are found to be much more sensitive
to the projected atomic potential. This sensitivity arises because,
whereas bright-field HRTEM images are due to the interference
between the unscattered beam and Bragg diffracted beams, ADF-STEM
excludes the direct beam, generating contrast by interference between
different high-angle scattered electron beams. This higher sensitivity
may potentially be useful in characterising the surface structures of
the Si nanoparticles. With an optimum choice of STEM detectors and a
suitable sample geometry, impurities within and on the surface of the
nanoparticle may be identified. Work is continuing on quantifying, in a
statistically significant way, the likelihood of observing single impurity
atoms.
4.5.2.11 Summary of Si, Sn & Ge nanostructure work

2009 has seen a significant improvement in the understanding of Si and other QD superlattices materials. The mechanisms for formation of QD nanostructures are now better understood, with the effects on heterogeneous nucleation of crystallising sub-phases identified in SiC; the determination of a modified Volmer-Weber growth mode in formation of Sn nanocrystals; and greater understanding of the effects of substrate heating on the morphology of nanostructures. Optical and electrical characterisation of these nanostructures has also progressed with a better understanding of the transport and energy levels in these materials. Much still needs to be done, but a current crowding model seems to explain the non-linear effects observed in Si nanostructure devices and further evidence for a shift in absorption edge is seen in absorbance data. The importance of substrate heating has been identified in controlling crystallisation morphology and for Ge QDs has allowed in-situ formation of QDs. An understanding of doping is progressing with moves towards identifying the location of dopant atoms and hence of their exact doping mechanisms, with techniques such as STEM. Whilst theoretical modelling work is indicating potential materials for alternate modulation doping. Device design has improved in sophistication, with improved architecture and promising new hybrid structures with SiO$_2$ as a QD confinement layer with SiNx as a barrier layer allowing lower resistivities and hence leading to improved transport in devices. Future work will incorporate this new understanding and improved materials and device design to feed into improved devices with higher voltage and current outputs.

4.5.3 Hot Carrier cells

RESEARCHERS:
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Hot carrier solar cells offer the possibility of very high efficiencies (limiting efficiency 65% for un-concentrated 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 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 [4.5.3]. The limiting efficiency for the hot carrier cell is 65% at 1 sun and 85% at maximum concentration – very close to the limits for an infinite number of energy levels [4.5.1, 4.5.4-5, 4.5.55]. Fig. 4.5.45 is a schematic band diagram of a Hot Carrier cell illustrating these two requirements.

In 2009 modelling work on energy selective contacts now has a two dimensional model of tunnelling transport and experimental work has continued with improvements in materials quality for double barrier resonant contacts. Theoretical work on carrier cooling and interaction with phonons has developed into three dimensional modelling of phonon decay. There has also been a significant development in the measuring of slower carrier cooling in some III-V materials supporting the theoretical models for phonon decay. Other work on development of QD nanostructures using Langmuir-Blodgett deposition of nanoparticles has also made progress.

![Figure 4.5.45: Band diagram of the Hot Carrier cell. The device has two stringent requirements: a) To slow the rate of photogenerated carrier cooling in the absorber. B) To extract these ‘hot carriers’ over a narrow range of energies, such that excess carrier energy is not lost to the cold contacts.](image-url)
4.5.3.1 Modelling of Hot Carrier Solar Cell Efficiency

RESEARCHERS
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COLLABORATION WITH:
Yasuhiko Takeda (Toyota Central Research)

Earlier work has modelled the ideal limiting efficiency for HCSCs [4.5.1, 4.5.54, 4.5.55]. For a real device a number of the ideality assumptions must be given up. Indium Nitride (InN) has been suggested as a potential material for a HCSCs because of its narrow electronic band gap for absorption of a wide range of photon energies, whilst also having a wide phonon band gap, which is good for suppression of phonon decay – one of the main mechanisms for carrier cooling [4.5.56]. Some evidence for slowed carrier cooling is given in the literature, from transient absorption measurements [4.5.57].

The work presented here is on further development of the limiting efficiency of HCSCs with a bulk InN absorber modelled by removing most of the ideality assumptions previously used and also including in the calculation the real InN dispersion relations and thermalisation velocities.

Previous reports proposed two different approaches to calculate HCSCs theoretical efficiency; one is based on particle conservation (PC) [4.5.55] and the other assumes rapid rates of impact ionization and auger recombination (II-AR) [4.5.54] and is further expanded in [4.5.1]. These models are not suitable for describing the general behaviour of real materials for HCSC converters, but can only be applied under particular conditions. A third model [4.5.58] has recently been put forward uses finite II and AR rates in combining elements of both the PC and II-AR models. The current model described here also combines the PC and AR-II models, but in such a way that II and AR rates are determined by the specific band structure of the absorber material – this being another step forwards in realism. The detailed band structure of wurtzite bulk InN has been considered to perform computation of carrier densities, pseudo-Fermi potentials and II-AR time constants.

The HCSC has been treated as a system which can interact with the external environment through particles and energy exchange. Hot electrons and holes are extracted to the external circuit through energy selective contacts (ESCs) which are considered to be ideal. For simplicity a common temperature for hot electrons and holes has been assumed and energy distributions only differ for quasi-Fermi potential.

Fig. 4.5.46 shows energy and particle fluxes involved in the hot carrier device operation. The incoming particle flux from the sun can be approximated with blackbody radiation at 6000K; fluxes to the external environment are due to radiative emission and interaction with the lattice related to optical phonon emission.

The influence of AR-II on the efficiency of the HCSC has been taken into account by modifying the expression for the total current from the cell. Such a modelling approach allows consideration of the effects of II-AR for all operating conditions of the cell. AR-II rates have been calculated considering highly probable three particles processes for bulk InN (CCCH, CHHS, CHHL), and neglecting high k-vector mechanisms [4.5.60].

Fig. 4.5.47(a) shows the dependence of the calculated maximum efficiency as a function of the extraction energy ΔE, for the three different concentration ratios and the absorber thickness dabs = 50 nm. A thermalisation constant τth = 100 ps has been used, as a reasonable compromise between values recently reported [4.5.57].
4. Research continued

Figure 4.5.47: (a) HCSC efficiency as a function of carrier extraction energy level. Parameters used are: thermalisation time = 100 ps, concentration = 1000, lattice temperature = 300K and absorber layer thickness = 50 nm. (b) Current Density and a function of voltage for different extraction energies (ΔE) for ESCs.

We have found that for 1000 suns the efficiency curve reaches a peak value of 43.6% for a hot carrier extraction energy of 1.44 eV. Maximum efficiencies of 52% and 22.5% have been calculated for full concentration and non-concentrated spectra, respectively. Fig. 4.5.47(b) shows J-V relations for three different extraction energies. The value of $V_{oc}$ increases when the extraction energy is increased. In fact, as the carrier temperature $T_c$ is very high in open circuit conditions, the $V_{oc}$ is strongly related to $ΔE$. The short circuit current decreases monotonically as a function of extraction energy due to the increase in Auger recombination.

In summary results from this modelling work show that if a real material is considered, efficiency calculations of HCSC efficiency limits lead to considerably lower values than results obtained if ideal absorbers are considered. This implies that the gain in efficiency that can be achieved using bulk materials as absorbers in HCSCs is limited due to fixed phononic properties. The efficiency is found to depend critically on the thermalisation time. However the figure used of 100ps for thermalisation time, whilst based on a reasonable extrapolation of current experiment, is not necessarily the highest for InN. It is also quite possible that either higher quality or cubic InN or other bulk materials or nanostructures can have longer thermalisation times. Hence the fact that an efficiency of 43.5% can be obtained with a bulk absorber is a positive outcome which encourages further investigation on phononic properties of semiconductors to slow down carrier cooling and achieve a more significant efficiency gain.

4.5.3.2 Energy Selective Contacts

The requirement for a narrow range of contact energies can be met by an energy selective contact (ESC) based on double barrier resonant tunnelling. Tunnelling to the confined energy levels in a quantum dot layer embedded between two dielectric barrier layers, can give a conductance sharply peaked at the line up of the Fermi level on the ‘hot’ absorber side of the contact with the QD confined energy level. Conductance both below this energy and above it should be very significantly lower. This is the basis of the current work on double barrier resonant tunnelling ESCs.

4.5.3.2.1 Modelling of QD structures for Energy Selective Contacts

RESEARCHERS
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We have developed a robust 2D model within the effective mass approximation describing the transport properties through QD structures. The model uses the discrete Schrödinger equation for evaluating the filtering characteristics of ESCs.

During fabrication of the quantum dots in a dielectric matrix for ESCs there are various types of deviation from the ideal case, with major disorders being configurational (disorders in the position of the dots – CD) and morphological (disorders in the size of the dots – MD). The disorders are assumed to follow a normal distribution from the mean position and size, respectively. The results show the outcome of an average of 1000 simulation runs with different standard deviation ($σ$) values.
Figure 4.5.48: Peak at 1.205 eV of the conductance vs. energy plot for different values of $\sigma$ for CD (left). Conductance vs. energy plot with peak at 1.573 eV for different values of $\sigma$ for MD (right). Conductance given in units of $2e^2/h$.

The spread of the resonant peak increases with CD, reducing the efficiency of the QD array as an ESC.

A planar representation of the double barrier structure is shown as in Fig. 4.5.49 (left). The barriers are usually high band gap dielectric materials like SiO$_2$, Si$_3$N$_4$ or SiC. SiC barriers have advantages over SiO$_2$ barriers in that SiC barriers in the double barrier structure make a very good diffusion barrier for silicon while processing, which can yield a structure with uniform QD size in the transport direction thus ensuring sharp resonances at the resonant energies of the structure. Since the conductance of the structure is more in the case of SiC barriers because of the lower barrier height of SiC, thicker barriers can be used which give the same conductance as that of using SiO$_2$ whilst being easier to process [4.5.61].

Figure 4.5.49 [right] shows the I-V characteristics for the double barrier QD structure with SiO$_2$ dielectric and SiC barriers at temperatures of 10K and 300K. As can be seen, the structures with SiC potential barriers have higher current density at both low temperature and at room temperature. As the temperature increases, the current density as well as the width of the resonant peak increases. Also, the negative differential resistances appear at slightly lower voltages in structures with a SiC barrier than that in structures with a SiO$_2$ barrier. This is due to the increased leakage and thus the lower confinement energy in the former.
4.5.3.2.2 Fabrication of Selective Energy Contacts

**Researchers**
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Double barrier resonant tunnelling structures consisting of Si QDs were grown by depositing alternate layers of SiO₂, SRO (silicon rich oxide), and SiO₂ films with a single target RF-magnetron sputtering system. A combined sputtering target consisting of 4-inch quartz disc partially masked with a patterned silicon wafer was used to deposit the layers. SRO layers were deposited with argon sputtering and additional O₂ was supplied during the deposition of SiO₂ layers. Samples were generally grown both on quartz and highly doped silicon substrates to facilitate optical and electrical characterisations, respectively. Following the growth, the samples were typically annealed for 2 hours at 1100 °C in high purity nitrogen. During the high temperature annealing, the excess Si in the SRO layer segregates to form QDs between the two oxide layers as described in section 4.5.2.2.

The size of the QDs is expected to be limited by the thickness of the SRO layer between the two barrier layers. In order to investigate size-controlled growth of Si QDs, several SiO₂/SRO/SiO₂ structures with different SRO thicknesses were grown while keeping the composition of the films fixed. In this case the oxygen to silicon ratio of the films was kept at unity as determined from a thick layer of SRO with Rutherford backscattering spectroscopy. To facilitate comparison among different samples, thicknesses of the oxide layers were kept constant.

Fig. 4.5.50 shows a plan-view TEM image of a typical SiO₂/SRO/SiO₂ structure grown on a silicon substrate after annealing at 1100 °C for two hours. Silicon QDs in the oxide matrix are clearly visible. The size of the QDs is of about 5~nm which is similar to the thickness of the SRO layer, although a slight variation in the QD sizes is evident.

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Figure 4.5.49: Planar view of the double barrier structure formed by Si QDs in SiO₂ matrix, with SiC barriers of 2nm width [left]. Mean diameter of QDs is 1.8nm. I-V characteristics for the double barrier structure with SiO₂ and SiC barriers at temperature 10K and 300K [right].

Figure 4.5.50: Typical TEM image of a SRO layer in SiO₂ matrix after annealing at 1100 °C. Si QDs are clearly visible.
For the investigation of size-controlled growth of QDs, several samples consisting of single layer Si QDs in SiO2 matrix were prepared. The SRO layer thicknesses were in the range of 1.8 nm to 7 nm. Thicknesses of the oxide layers were about 6 nm for all the samples, except for the two samples with SRO layer thickness of 1.8 nm and 2.4 nm. For these samples a 30 nm capping oxide layer was deposited to prevent possible oxidation of the QD layer during the high temperature annealing. For comparison, all the structures were grown with the same sputtering target and under similar growth conditions.

Fig. 4.5.51(a) shows results of room temperature PL measurements on several samples and Fig. 4.5.51(b) shows the PL peak energy, derived from Fig. 4.5.51(a), as a function of the respective QD sizes. It should be noted that no distinct PL signature were observed from as-deposited samples. The signal-to-noise ratio is quite good, although PL is measured on a single layer of Si QDs, demonstrating a strong absorption by Si QDs. This ratio is similar for the samples with SRO layer thickness greater than 3 nm, however it is relatively weaker for the sample with smaller SRO layer thicknesses. A strong decrease in PL intensity for samples containing smaller nanocrystals is reported in the literature. This is attributed to a decrease in the density of nanocrystals and the smaller absorption cross section [4.5.18,4.5.25]. These could also explain the relatively weaker PL signal from our samples containing smaller QDs.

The full width at half maximum of the PL peaks are quite broad (>0.25 eV) suggesting a large size distribution of QDs in the samples. This is consistent with the TEM images where a slight variation in QD sizes has been observed. Large distributions of size of nanocrystals in multilayered structure or bulk film have also been reported [4.5.18, 4.5.25,4.5.26] and these are in reasonable agreement with our data (Fig. 4.5.51(b)). However, PL peaks from different samples are clearly separated which demonstrates that the average sizes of QDs are different for different samples. Importantly, a blue-shift of the PL peak is observed with the decrease in the SRO layer thickness. The shift is larger for the smaller QDs whereas it is smaller for the bigger QDs which is consistent with the quantum confinement model. This is a significant result which shows that the size of a single layer of quantum dots can be controlled with the SRO layer thickness. The solid curve in (Fig. 4.5.51(b)) is a best fit of PL peak energy with inverse square of QD diameter which is in good agreement with the data, both our own and those of other workers. Our data is also consistent with data for Si QDs in multilayered structure (SiO2/Si QDs/ SiO2/...Si QDs/SiO2), because it is grown with a similar technique, see section 4.5.2 [4.5.14]. This may indicate that Si QDs in single and multilayered structures have similar optical properties.

4.5.3.2.3 Annealing time and quantum dot formation

The double barrier structures are typically annealed for two hours at 1100°C for QDs formation. In order to investigate the optimum annealing duration, two sets of samples, one set with SRO thickness of 3.6 nm and another set with SRO thickness of 6 nm, were grown under similar conditions. Fig. 4.5.52 shows PL peak energy for two sets of samples as a function of annealing time. The annealing time indicated in the diagram refers to the duration at 1100 °C (the ramping up and ramping down time are not included).
4. Research continued

4.5.3.2.4 Summary of work on ESCs

A robust model for analysing deviations from an ideal resonant tunnelling structure. These deviations can be modelled as either Configurational variation in the positions of QDs in the resonant layer, or as Morphological variation in the sizes of these quantum dots. The Morphological variation is seen to have the strongest effect. Use of SiC double barriers instead of SiO\textsubscript{2} has also been investigated, in order to reduce diffusion – but this is seen to reduce the energy selection due to greater transmission at all energies. Experimental work has focussed on improvement in the Si QD layer size uniformity with improved control over the QD size and size distribution demonstrated. Data similar to multilayer QD samples are seen, except that size control can be controlled by annealing time, with longer times giving improved QD surface passivation. Future work will focus on the quality of the oxide and other double barrier layer materials. Improvement of quality here will be important to realise good energy selection.

4.5.3.3 Hot Carrier Absorbers: slowing of carrier cooling

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Carrier cooling in a semiconductor proceeds predominantly by carriers scattering their energy with optical phonons. This builds up a non-equilibrium ‘hot’ population of optical phonons which, if it remains hot, will drive a reverse reaction to re-heat the carrier population, thus slowing further carrier cooling. Therefore the critical factor is the mechanism by which these optical phonons decay into acoustic phonons, or heat in the lattice. The principal mechanism by which this can occur is the Klemens mechanism, in which the optical phonon decays into two acoustic phonons of half its energy and of equal and opposite momenta [4.5.64]. The build up of emitted optical phonons is strongly peaked at zone centre both for compound semiconductor due to the Frölich interaction and for elemental semiconductors due to the deformation potential interaction. The strong coupling of the Frölich interaction also means that high energy optical phonons are also constrained to near zone centre even if parabolicity of the bands is no longer valid [4.5.65]. This zone centre optical phonon population determines that the dominant optical phonon decay mechanism is this pure Klemens decay.
4.5.3.3.1 Suppression of phonon decay in bulk materials

In some bulk semiconductors, with a large difference in their anion and cation masses, there can be a large gap between the highest acoustic phonon energy and the lowest optical phonon energy, possibly large enough to block operation of this Klemens mechanism, which can be termed a ‘phononic band gap’. Work previously presented [4.5.66] using a simple 1D force constant model indicated that GaN, InN and InP all have large phononic band gaps, which are close to those found experimentally [4.5.67]. We are using time resolved photoluminescence (tr-PL) to investigate the carrier cooling rates in these materials.

This work has now been complemented by high accuracy DFT computation [4.5.68] of diatomic molecules consisting of the two elements forming attractive binary compounds for hot carrier absorbers. These diatomic molecules were H-terminated. The wave number of the standing symmetric vibration was then corrected for the attached H atoms, yielding the optical phonon wave number at the Brillouin zone centre. Despite the rather simple assumption of emulating a bulk phase with a H-terminated diatomic molecule, the match to experimental data is very close, see left graph of Fig. 4.5.53 and enables us to make more precise predictions about material candidates for hot carrier absorbers.

The accuracy of the results can also be seen at the high force constants for SiC, nitrides and borides, corresponding very well to the high Young’s modulus of these ultra hard materials and corresponding to the high values for these materials found previously with the 1D modelling. There are a few differences however, with the bismuth (Bi) and antimony (Sb) compounds looking promising candidates because of their large mass components. Carrier cooling rates will be measured using time resolved PL on Bi₂S₃ in the near future using material supplied thanks to a collaboration with the Fraunhofer Institute of Material Research in Dresden, Germany. There is also the possibility to obtain BBi samples at a later stage.

4.5.3.3.2 Time resolved photoluminescence measurements.

RESEARCHERS
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The potential efficiency boost, which can be achieved by Hot Carrier solar cells, is directly related to the possibility of extracting high energy carriers from the absorber layer before thermalisation, increasing the voltage and hence the conversion efficiency. The poor conversion efficiency of photons with energies above the band gap of the absorber is the main loss mechanism in conventional single junction solar cells. The investigation of thermalisation time constants of hot carriers is a crucial step towards the engineering of HCSCs. Monitoring the relaxation process of highly energetic carriers not only gives information on semiconductor materials which can be suitable as a absorber layers, but also helps to understand the physical mechanisms involved in the cooling process.

We have investigated the relaxation transients of hot carriers using femtosecond time resolved photoluminescence (tr-PL) spectroscopy in bulk GaAs and InP. These two materials have a very similar electronic band structure but different phononic dispersion relations [4.5.69].
The comparison of hot carrier relaxation times allows studying the role played by the “Hot Phonon Effect” which is enhanced by suppression of the Klemens decay of optical phonons into acoustic phonons. We investigated decay of hot carriers for different excitation wavelengths. This allows the population of different bands which is necessary to study the influence of Intervalley scattering mechanisms on carrier relaxation.

tr-PL experiments have been performed on GaAs and InP samples using a measurement configuration as in Fig. 4.5.54. In this technique a laser pulse acts as a switching gate relating the photoluminescence signal to the time domain. The PL signal is collected from the sample, after a femtosecond laser excitation, and focused in a non linear crystal. The gate signal is generated from the same laser and is focused on the same crystal after passing through an optical delay stage. The signal is detected using a monochromator and a PMT. Our system configuration provides 150 fs pulses with tunable wavelength over a range of 256 nm (4.84 eV) to 2.6 μm (0.48 eV).

Figure 4.5.54: 2 – Schematic representation measurement setup.

Fig. 4.5.55 shows the evolution of the PL signal for different wavelengths as a function of time in GaAs and InP. For this experiment an excitation energy of 1.7 eV was been used, which is below the side valley thresholds for both semiconductors. Thus, Intervalley-scattering (IVS) does not play any role and the hot phonon effect in InP is quite evident. InP, in fact, shows a longer transient compared to GaAs for the measured wavelengths. A very broad PL spectrum is observed during the first few picoseconds after photoexcitation, demonstrating fast carrier-carrier interactions (<100 fs). The spectrum red shifts towards the respective band gaps for InP and GaAs but with different time constants. The longer transient for InP, which is evident in Fig. 4.5.55(b), is proposed to be due to the maintenance of a hot phonon population which slows down carrier cooling, due to the wide phononic band gap suppressing Klemens decay of the optical phonons.

4.5.3.4 QD superlattice structures for slowed carrier cooling

4.5.3.4.1 Modelling of phonon band gaps

RESEARCHERS
Robert Patterson, Binesh Putten-Veettil, Gavin Conibeer

This work is on modelling a similar prevention of the Klemens’ optical phonon decay mechanism in less exotic materials (possibly based on elemental semiconductors), by exploiting the Bragg reflection that occurs at the mini-Brillouin zone boundaries of nanostructure superlattices. This reflection opens up mini-gaps in the phonon dispersion for those acoustic phonon energies which satisfy the Bragg condition. These gaps in the phonon dispersion or “phononic band gaps” refer to the disallowed phonon energies caused by a periodic modulation of atomic force constants. [This is directly analogous to the “photonic band gap” which arises from the disallowed photon energies caused by a periodic modulation of refractive indices.]

Studies of Quantum Dot (QD) superlattices (SLs) and other nanostructured materials using a semi-empirical force constant model within the rigid ion approximation are ongoing. Recent results from 2009 include the computation of phonon lifetimes in one symmetry direction from an arbitrary three-dimensional (3D) phonon dispersion, as well as the discovery of a few highly constrained geometries in which phonon decay via the Klemens mechanism is inhibited. In addition, lifetime computation shows that phonon band gaps of insufficient size to inhibit the Klemens mechanism also give rise to substantially increased phonon lifetimes if the band gaps force the phonon decay path into regions of the Brillouin Zone (BZ) with very low density of states. Both situations should slow phonon decay and in turn yield longer hot carrier lifetimes, which is a desirable property in the hot carrier solar cell absorber material.
Results were obtained for FCC or Diamond SLs with single element QDs and matrix materials. Force constants were scaled to match with literature values for group IV elements such as silicon out to third nearest neighbour interactions. Mass differences between the QD and matrix materials were set at 1:7 to simulate a bulk material with a large phonon bandgap such as InN. Typical QD sizes for solid state systems range from between 1-2 nm.

FCC SLs with heavy, overlapping QDs show phonon band gaps sufficient to inhibit first order (Klemens) phonon decay. Simulations of the "highly constrained" geometry, where QD overlap was large enough such that at superlattice interstitial sites the matrix material was reduced to only a few light atoms, produced a few high energy, highly degenerate phonon bands. The high energy bands are a result of these periodically placed light elements vibrating at high frequencies, largely decoupled from the heavier matrix. The degeneracy of the phonon bands appears to be the result of the symmetrical placement of the light elements in real-space, resulting in very similar energy and momentum states for each of these atoms in the BZ. Fig. 4.5.56 shows the large phonon band gap for the FCC SL arrangement in the three major symmetry directions, indicating a complete gap in reciprocal space. Simulations of the inverse situation, with small light quantum dots instead of interstitial sites, shows that this result is general and scalable to larger SL unit cell dimensions – a very important result for the possibility of fabricating such structures.

Similarly constrained Diamond SLs also show band gaps, though there is less degeneracy. In this case long phonon lifetimes are obtained since the fastest decay path that conserves energy and momentum is forced through some part of the BZ where the phonon density of states (DOS) is low. Typically the overall phonon decay path is made up of a few decay steps involving high and low energy phonons. In the simulations, any low energy phonon decay products were considered to be "lost." High energy phonon decay products, those still above significant phonon band gaps, were allowed to continue to decay. In the example case shown in Fig. 4.5.57, the first very fast phonon decay yields a high energy phonon for which only slow decays are possible. In detail the first stage is the decay of the LO phonon into a LA phonon (Step 1) and a TO phonon (Step 2), this is a Ridley decay event. Since these must happen simultaneously the rate is determined by the slow Step 2. This is slow because of the low DOS to which it couples. The next stage (Step 3) is further decay of the TO phonon to two LA phonons by an off centre Klemens decay. This is fast, but the overall rate is determined by Step 2 – 22ps in this case. Under these circumstances phonon lifetimes can be increased by two orders of magnitude [4.5.70].

Present modelling of phonons in nanostructures includes investigations of core-shell geometries and nano-porous materials. Phonon dispersions of simple cubic (SC) SLs of core-shell QDs show large phonon bandgaps for light shell thicknesses on the order of a monolayer. Nano-porous materials with gas filled pores also show potential as candidate hot carrier absorber materials. In these mixed-phase material the modulation of the force constant comes from difference in bond strength between the covalently bonded light absorber material and the gas phase interacting via dipole-dipole potentials. Fig. 4.5.58 shows some exploratory simulations for mixed phase absorber materials in a few different approximations.

Figure 4.5.56: FCC SL of QDs showing a complete phonon bandgap large enough to inhibit Klemens decay in all major symmetry directions (<100>,<110>,<111>).

Figure 4.5.57: HCP SL of QDs showing the rates of in-series phonon decay mechanisms, with their calculated rates.
4. Research continued

Hence the rate decay analysis shows that slow decay rates can occur even if complete gaps are not big enough to prevent Klemens decay. In addition core shell structures look promising in tailoring phononic properties further.

4.5.3.4.2 Fabrication and characterisation of highly ordered nanoparticle arrays for Hot Carrier absorbers

Researchers
Lara Treiber, Zekun Ren, Yukiko Kamikawa, Shujuan Huang, Gavin Conibeer

In parallel with the work on modelling phonon modulation in QD superlattices, methods are being investigated to fabricate highly ordered QD arrays. Colloidal dispersion of nanoparticles of very monodisperse size is a very promising way of doing this. It also offers the potential to incorporate core shell QDs. As discussed in section 4.5.3.3 and in [4.5.56] core shell QDs offer a way to significantly change the phonon modulation in a superlattice because the core and shell can be of materials of very different force constant, directly leading to a strong phonon confinement.

In 2009 experimental work has continued on methods to fabricate highly ordered QD arrays using Langmuir-Blodgett (LB) deposition of nanoparticles. The LB technique (Fig. 4.5.59) allows for the formation of ordered monolayers at an air-water interface using sophisticated apparatus while exploiting the self-organization mechanism of colloidal dispersion. Compression of the monolayer is monitored via measurements of surface pressure (SP) of the trough. This technique allows transfer of ordered monolayers and multilayers onto a wide range of solid substrates such as glass or Si wafers [4.5.71].

Figure 4.5.60: Surface pressure isotherm of Au nanoparticle on the water surface.

Work has focused on optimising the deposition parameters to achieve the required ordered monolayer of gold (Au) nanoparticles. The Au nanoparticles have been acuired from the Indian Institute of Science. They are 3.5±1.1 nm in diameter and functionalized with dodecanethiol molecules. Fig. 4.5.60 shows the full surface pressure of the trough with the Au nanoparticle as a function of the barrier position. This isotherm gives information on the interaction between the nanoparticles on the water surface, indicating the phase change of the monolayer. When the compression reaches the hump around 40 mN/m, the monolayer start to buckle and overlap. We have made a series of depositions at different surface pressures in order to study to nanoparticle arrangement. Fig. 4.5.61 shows the TEM images of the Au nanoparticle monolayer.
transferred at 20 and 30 mN/m, clearly showing the improvement of the nanoparticle order. The coverage of the nanoparticles was estimated from a number of TEM images, as shown in Fig. 4.5.61. We can see that the coverage increases significantly with increasing surface pressure. TEM image FFT has also been carried out to investigate the order of the nanoparticle monolayers. An example of the FFT from Fig. 4.5.61(b) is shown in Fig. 4.5.62 which clearly shows six spot-like features suggesting a highly ordered 2D hexagonal structure. The nearest centre-to-centre distance measured from this FFT is 5.9 nm, which give the average gap between the nanoparticles as 2.4 nm. This is in good agreement with the double length of the dodecanethiol molecules. The remaining defects in the arrangement are thought to be caused by the large deviation in nanoparticle size dispersion.

Figure 4.5.61: TEM images of Au nanoparticle monolayers deposited at surface pressures of 20 mN/m (a) and 30 mN/m (b).

Figure 4.5.62: FFT image from TEM image of Au nanoparticle monolayer deposited at 30 mN/m.

Future work will concentrate on the fabrication of highly ordered multilayer structures and the investigation on the phononic properties using Raman and tr-PL. Furthermore, other materials such as Si NPs will be investigated.

4.5.3.5 Summary of Hot Carrier Solar Cells

Significant progress has been made on making a more realistic model for hot carrier cell efficiencies. Incorporation of real material properties for InN as an absorber has allowed calculation of real II and AR recombination rates. The method is applicable to other materials perhaps with longer thermalisation times, such that the 43% limit found so far may well be able to be increased.

Modelling of ESCs is now able to include defects in either position or size of QDs in a double barrier resonant structure and concludes that size variation is more critical. The model is also able to include hybrid material combinations in ESCs. Experimental work on ESCs has focussed on improving the deposition and size uniformity of Si QDs as resonant centres, with improvements in the control of size and size uniformity.

Suppression of the Klemens decay of optical phonons remains the main focus to slowing carrier cooling. Modelling of bulk materials can now use ab-initio DFT methods to corroborate simpler 1D force constant models. The increased precision allows some extra materials to be predicted as being promising with Bi compounds in particular looking attractive because of their large potential mass difference. Time resolved PL has shown a slower cooling time for the large phonon gap InP as compared to GaAs, strongly supporting the claim of suppression of the Klemens decay mechanism.

Modelling of similar gaps in QD nanostructures is now able to calculate the rates of phonon decay in these nanostructures and to start to predict some real phonon lifetimes and hence soon predict carrier cooling time. Fabrication of highly ordered QD arrays tonachieve this has progressed with highly ordered 2D hexagonal arrays of Au nanoparticles fabricated by colloidal dispersion. Multilayer structures and other materials QD materials, possibly including core shell QDs, will be deposited in 2010 and tested for phonon modulation with high resolution Raman.
4. Research continued

4.5.4 Up-conversion

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**COLLABORATION WITH:**
Peter Reece (Physics, UNSW)

Up-conversion (UC) offers great potential as a Third Generation technique. If it can be made to work with only a few percent efficiency it can be applied to existing bi-facial Si cells and be incorporated into productions lines very rapidly. Longer term coupled to an optimised band gap of about 2eV, UC offers significantly higher efficiencies over all with a limiting efficiency of 48% under 1 sun [4.5.76].

Previous UNSW investigations [4.5.72] proved the feasibility of the UC concept in erbium-doped sodium yttrium fluoride (NaYF₄:Erₓ) layers, see Fig. 4.5.63. Although these layers demonstrate efficient UC luminescence at a UC quantum efficiency of up to 4% at wavelengths that are relevant to UC for crystalline silicon solar cells, absorption only occurs over a narrow band of the incident spectrum. We have shown that the UC effect can be enhanced by ‘sensitising’ Er absorption with the addition of a layer of luminescent semiconductor (PbSe) nanocrystals [4.5.73], though the material stability of such nanocrystals is a clear constraint on any such application.

Our recent work has been oriented toward the fabrication of low-cost erbium-doped layers as an alternative to expensive phosphors. In collaboration with the Optoelectronics Laboratory in the School of Physics, we have been exploring the etching and doping of thick (5-10 μm) meso- and microporous silicon layers. Such films have been reported to show strong room-temperature erbium-related luminescence [4.5.74]. A 1 μm-thick mesoporous silicon film is shown in a cross-sectional SEM image in Fig. 4.5.64(a); the columnar pores that are clearly visible as a result of the etching process allow for the infusion of chemical or biological species, resulting in considerable interest in porous silicon in several research areas [4.5.75].

![Figure 4.5.63: A schematic UC device under broadband illumination, showing (1) unabsorbed NIR photons passing from the solar cell into the up-converter; (2) the UC process and (3) emission of up-converted photons from the UC layer into the solar cell, where they are absorbed.](image)

![Figure 4.5.64: (a) Cross-sectional scanning electron micrograph of 1 μm-thick mesoporous silicon with long columnar pore morphology (b) porous silicon etching process (top) and electrodeposition process (bottom).](image)

Porous silicon is formed in an electrolytic anodisation process in a 1:1 solution of 50% aqueous hydrofluoric acid (HF) and ethanol as shown in Fig. 4.5.64(b). In the process described here, a section of pre-cleaned FZ or CZ boron-doped silicon is immersed in an electrolytic cell and biased at a constant current density (on the order of a few tens of mA/cm²) for approximately ten minutes. According to the chemical reaction shown in Fig. 4.5.64(b), the HF reacts with silicon atoms and holes at the surface of the wafer to dissolve the silicon into silicon hexafluoride ions and hydrogen. The samples we have produced by this process have a porosity of between 40 and 50 per cent when a lightly-doped substrate (1-10 Ωcm) is used.

Doping of these layers is achieved in a simple electrodeposition step: the porous silicon (PSi) samples are inserted into a cell filled with an...
electrolyte of 1g erbium chloride salt dissolved in 20mL ethanol. When the electrode is biased positively with respect to the silicon, erbium ions dissociate out of the solution and migrate toward the silicon substrate, where they bind with the oxygen on the pore walls of the PSi. The erbium concentration in the film can be controlled by varying deposition times and solution concentrations.

Following this step, samples are annealed at 900-1100°C in oxygen & nitrogen for an hour. Subsequent room-temperature photoluminescence measurements have shown strong erbium peaks (at 980 and 1540 nm) when excited by a 488nm laser operating at approximately 1W. This demonstrates that a significant portion of erbium remains in the film and is optically active after the annealing step. High-intensity excitation near 1530nm results in UC luminescence from higher excited states of erbium as shown in Fig. 4.5.65. The peaks at 980 and 810nm are likely from Energy Transfer Up-conversion in two neighbouring Er atoms, but the peaks at 660 and 550nm must be from three-photon absorption events and demonstrate that several UC mechanisms are occurring. In the next year we will optimise these structures by improving both material quality and device-level optical properties.

![Figure 4.5.65: Room temperature up-conversion photoluminescence spectrograph of erbium-doped microporous Si when excited with a 1523nm laser at varying power.](image)

### 4.5.5 Concluding remarks for the Third Generation section

2009 has seen an increase in both the breadth and the depth of the work on Third Generation projects.

The work on Si QD nanostructure tandem cells, has yielded a greater understanding and control of annealing conditions; in-situ growth; and transport mechanisms. This together with theoretical work on doping and analysis will allow a more targeted approach to optimisation of devices and hence to increases in current and voltage. Ge and Sn QD growth have both made progress, with Ge QDs now able to be grown in-situ without a subsequent anneal and the morphology of Sn QDs now much better understood and leading to improved growth to lead towards useful electrical properties.

Hot Carrier cells have seen significant steps forward on efficiency modelling using more realistic parameters and development of both the modelling and the materials understanding for Energy Selective Contacts. The theory of restricting the decay of optical phonon decay to slow the rate of carrier cooling has been improved for bulk materials and for QD superlattices alike, with new materials being predicted for the former and phonon decay lifetime computed for the latter. 2009 has also seen the first demonstrated evidence for slowed carrier cooling in time resolved PL measurements of the large phonon gap InN and progress on highly ordered 2D arrays of nanoparticles using colloidal dispersion.

Up-conversion has see the demonstration of a transfer of host for Er to porous Si, allowing much greater utility and ease of sample fabrication. Up-conversion of 1530nm light in this Er doped material has been demonstrated including higher order transitions.

The level of knowledge in these projects is now increasing very rapidly and informed choices of materials and methods for optimisation are now possible.

### REFERENCES


4.5.6 X.J. Hao, I. Perez-Wurfl, G. Conibeer, M.A. Green, 19th PVSEC, Korea, Nov 2009.


4.5.34 Y.H So et al., 19th International PVSEC, Jeju, 2009.

4.5.35 G. Scardera, E Bellet-Amalric, D Bellet, T Puzzer, E Pink and G Conibeer, “Formation of a Si-Si$_3$N$_4$ nanocomposite from plasma enhanced chemical vapour deposition multilayer structures”, Journal of Crystal Growth, 310 (2008) 3685.


4.5.51 D. König, G. Conibeer, M. Green, "Si-rich Si 3N4 for Si QD Formation and Simultaneous Donor Modulation Doping of Adjacent Barrier Material" , 24th European PVSEC, Hamburg (Sept. 2009) 1BO.8.3 on CD-ROM.


4.5.54 R. Patterson, M. Kirkengen, Binesh Putten Veettil, D. König, M.A. Green, G. Conibeer, "Phonon dispersion relations in Insulators", Springer-Verlag (1979).


4.5.58 B. Puthen Veettil, D. König, G. Conibeer, M.A. Green, “Theoretical analysis of energy selective contacts with Si QDs in SiO2 matrix and SiC barriers using a 2 dimensional model", 24th European PVSEC, Hamburg (Sept. 2009) 1CV.3.81 on CD-ROM.


4.6 Photonics: Photoluminescence based characterisation of silicon

4.6.1 Background

Luminescence imaging and its specific applications represent a rapidly expanding and developing research field. Using photoluminescence (PL) imaging for the characterisation of silicon wafers, cells and bricks was proposed and first demonstrated by the Photonics/Photoluminescence research group at UNSW [4.6.1-4.6.2]. An intense light source is used in that technique to illuminate large area samples homogeneously with up to one-Sun equivalent illumination intensity. A CCD camera captures a high resolution picture of the luminescent light that the sample emits as a result of that external excitation. Fig.4.6.1 shows a schematic diagram of a luminescence imaging system. The power supply that is shown on the bottom left can be used as an excitation source in electroluminescence (EL) imaging experiments on finished cells [4.6.3] and also for applications in which a solar cell is held at specific operating points under external illumination, such as the series resistance imaging methods that were introduced by our group [4.6.2, 4.6.4-4.6.5].

An appealing aspect of luminescence imaging is that high resolution (typical one to or up to several megapixels) images can be captured with a data acquisition time of below one second, which is much faster than other experimental techniques, allowing for measuring samples with a very high sample throughput. This high throughput is particularly advantageous for inline monitoring in industrial applications. The contactless nature of PL imaging allows such images to be taken on a wide range of samples, covering almost the entire PV value chain, starting with silicon ingots or bricks, via unprocessed or partially processed wafers, finished cells and solar cells encapsulated in modules.

The growing relevance of luminescence imaging applications in both R&D and in industrial production was recently acknowledged in a survey on luminescence imaging systems by leading PV industry journal Photon International [4.6.6]: "When it comes to quality consciousness, one technology for the solar industry that has gotten increased respect during the last year is luminescence imaging. Within a mere 12 months, this characterization principle has risen from a supporting role to take centre stage as the star of the show".

Our research at UNSW since the introduction of PL imaging in 2005 has contributed significantly to the identification and development of an increasing number of applications for luminescence imaging. This year the research by our group was focussed on an application of luminescence imaging for measuring the emitter sheet resistance on fully processed cells and on quantitative shunt imaging.

The commercialisation of PL imaging by UNSW spin-off company BT
Imaging Pty Ltd has also made significant progress, with a growing number of leading wafer and cell manufacturers and research institutes worldwide using the R1 offline R&D tool that was introduced into the market in 2008.

### 4.6.2 PL imaging on Si bricks

The contactless nature of PL allows PL imaging to be applied at an early stage in the PV value chain. Previous work on luminescence imaging on bricks showed excellent correlation between the as measured PL intensity and for example μ-PCD minority carrier lifetime maps [4.6.7].

Recent work by BT Imaging showed that a more detailed analysis allows a quantitative interpretation of the PL signal in terms of the bulk minority carrier lifetime $\tau_b$. Fig. 4.6.2 shows a calibrated PL image taken on the side facet of a p-type multicrystalline silicon brick. The colour scale in that image represents $\tau_b$ [4.6.8].

The ability to measure $\tau_b$ on an unpassivated surface is an important point, since most other techniques only provide information about the effective lifetime, i.e. a quantity that is strongly affected or dominated by surface recombination. The bulk lifetime is a more useful parameter, since it is the quantity that determines both the current and the voltage that a solar cell can achieve. Another important finding from [4.6.8] is that the bulk lifetime is determined at an injection level that is relevant for the operation of a solar cell and that is inaccessible to most other measurement techniques.

Figure 4.6.2: PL image measured on the side facet of a mc-Si brick. The colour scale represents the bulk minority carrier lifetime in microseconds.

PL imaging is therefore expected to be increasingly adopted by wafer manufacturers for process monitoring and inline inspection, for example to identify the areas of reduced lifetime near the top and bottom of an ingot or brick or areas of enhanced dislocation density.

### 4.6.3 Raw wafer inspection

Luminescence imaging on as cut wafers is a particular experimental challenge due to the exceptionally low luminescence quantum efficiency, which can be as low as $<10^{-8}$. This number indicates that more than one hundred million incident photons are required to generate a single luminescence photon that contributes to the measured signal.

Figure 4.6.3 shows two examples of PL images taken on as-cut multicrystalline wafers. Typical defects that are observed in these images are areas with high density of structural defects such as dislocation clusters (as shown on the right hand side) and also areas of enhanced impurity concentration near the wafer edges, which are found on a large fraction of wafers as a result of the proximity of the wafer edge to the crucible walls during ingot growth (see bottom edge on the left side). These defects can have a substantial impact on cell performance [4.6.9], indicating that luminescence imaging as an efficient quality control tool for as-cut wafer inspection by wafer and cell manufacturers.

Figure 4.6.3: PL images of two multicrystalline silicon wafers. The left hand image shows reduced material quality caused by an enhanced defect concentration near the bottom edge, showing that this wafer originates from an edge brick. The right hand image shows a very high density of structural defects across the wafer area, significantly limiting the cell efficiency entitlement of that wafer.

### 4.6.4 Series resistance imaging

The UNSW PL group established luminescence imaging as a very fast and spatially resolved method for measuring the series resistance in silicon solar cells. The very first experimental luminescence imaging data, which showed the potential to use combinations of luminescence images taken under different operating conditions in order to obtain information about local variations in the series resistance were published in [4.6.2]. Two quantitative PL-based Rs-imaging methods were introduced shortly after by our group [4.6.4-4.6.5] and have since then been adopted and verified by other research groups [4.6.10].

Luminescence baser Rs-imaging rapidly develops into a standard technique used by R&D groups and in production.

An example for an application of the method proposed by Henner Kampwerth [4.6.5] is shown in Fig. 4.6.4. It shows local areas of enhanced series resistance in a pattern that resembles the pattern...
of the belt in the firing furnace, indicating a problem with the firing conditions. The method involves a combination of luminescence images taken under different operating conditions and eliminates the influence of local variations of diode properties on resulting Rs images and is less sensitive to shunts and other defects. The fundamental principle of this method is to find two operating conditions of a solar cell that result in the same local luminescence intensity. In 2009 that concept was expanded with the aim to develop a quantitative method for measuring the emitter sheet resistance on fully processed solar cells [4.6.11].

Figure 4.6.4: Series resistance image obtained using the luminescence imaging based methodology by Kampwerth [4.6.5] indicating unsuitable firing conditions.

4.6.5 Emitter sheet resistance imaging

The emitter sheet resistance is an important electrical parameter of a fully processed solar cell. In solar cell production the value of the emitter resistance typically needs to be maintained within a tight specification window in order to avoid, for example subsequent problems with contact formation such as junction shunting or high contact resistance. Lateral non-homogeneities in the emitter resistance therefore generally have a strong impact on the performance of a solar cell. A fast and spatially resolved method to assess spatial variations of the emitter sheet resistance would therefore be of benefit for R&D in photovoltaics. Fundamental benefits of luminescence imaging include the generally short measurement time and the non-destructive nature. In 2009 the PL group therefore developed a photoluminescence based imaging method to measure the spatially resolved sheet resistance (R_{sheet}) of a fully processed solar cell. The theoretical framework for this technique was developed and preliminary proof of concept experimental results could be achieved [4.6.11].

Figure 4.6.5 shows an example of an application of that new technique. The left hand side shows an open circuit PL image of a multicrystalline silicon solar cell, which displays substantial variations in the diffusion length and a crack in the top right hand corner. The right hand side of Figure 4.6.5 shows the sheet resistance of the same section of that cell in Ω/□, as obtained with the new algorithm. The direct comparison of the open circuit PL image and the emitter sheet resistance images highlights an advantage of the new method, i.e. that the influence of local variations in the diffusion length is strongly reduced from the resulting R_{sheet} image. However, the compensation capability of the algorithm fails, when sections are electrically isolated, as seen at the crack in the upper right hand corner of both images. The changes of the R_{sheet} values toward the edges suggest possible problems in the emitter diffusion process. Testing of the new emitter sheet resistance method on a larger sample set and comparison with existing methods will be used to evaluate the accuracy and reliability of this new method and its limitations.

Figure 4.6.5: The left hand side shows a conventional PL image of a multicrystalline silicon solar cell taken under open circuit conditions. The right hand side shows the emitter sheet resistance as obtained from a new analysis algorithm [4.6.11].

4.6.6 Luminescence based shunt imaging

Shunt detection by luminescence imaging has been demonstrated in the past by various groups including the UNSW PL group [4.6.12-4.6.14]. However, previous work on this topic has been largely qualitative. It has been shown that in both PL and EL images the vicinity of shunted areas appears as a blurred region of reduced luminescence intensity. This blurring is caused by voltage drops associated with lateral current flow through the emitter and the front surface grid. In collaboration with the Max Planck Institute for Microstructure Physics, a luminescence imaging based method for determining quantitative shunt values in silicon solar cells from open circuit photoluminescence images has been demonstrated. The method is based on interpretation of the luminescence intensity around a local shunt in terms of the extracted current density. Results were presented at the 24th EUPVSEC in Hamburg [4.6.15].
Figure 4.6.6 shows two PL images of a specifically prepared test structure, which allowed generating a local shunt with variable and well defined external shunt resistance. It involves physically connecting an external resistor between the full area rear contact of the structure and a local point metal contact on the front surface. Application of our new analysis methodology allowed extracting the shunt value from the luminescence intensity distribution. This method was applied to images taken of the test structure with a range of external resistors connected. Excellent agreement was observed between the nominal shunt resistance of the test structure and shunt values calculated from PL images using our new method [4.6.15]. Good agreement was also observed with shunt values calculated from Lock-in thermography images on industrial multicrystalline cells.

Figure 4.6.6: PL images taken on a test structure. An external resistor is connected in parallel to the structure using a contact probe (visible in the bottom left). The images show the impact of a large resistance (mild shunt, left) and a small resistance (strong shunt, right) on the PL image.

The appearance of shunts in PL images is affected by the proximity of the shunt to the metal grid, an effect which has been previously modelled [4.6.3] and is expected to have a strong impact on the accuracy of our method. Experimental work to quantify these effects is currently under way.

4.6.7 Summary

An exceptional variety of material and cell parameters can be measured on silicon wafers and silicon solar cells with high lateral spatial resolution and short measurement time using luminescence imaging techniques. An increasing number of applications for PL imaging is developed at UNSW, in other research institutes and by companies. In addition, the commercial availability of PL imaging tools results in these applications increasingly being adopted by both research institutes and the PV industry as standard characterisation tools.

4.6.8 References

Summary

The Centre for Advanced Silicon Photovoltaics and Photonics incorporates the activities of the former Key Centre for Photovoltaic Engineering. The former Key Centre started in 1999, after the award of special funding from the Australian Government to promote teaching and research in the area of photovoltaics. The main initiative of this Key Centre was the establishment of the world’s first undergraduate degree in Photovoltaics and Solar Energy. This was one of only eight such Key Centres awarded Australia-wide across all disciplines, demonstrating the Government’s understanding of the importance of the field of renewable energy. In 2003 the Key Centre and its activities were incorporated into this Centre of Excellence, awarded to the same team at the University of New South Wales. On 1 January 2006 UNSW officially formed a new School within the Faculty of Engineering, the School of Photovoltaic and Renewable Energy Engineering, which includes the ARC Photovoltaics Centre of Excellence.

The School offers undergraduate, postgraduate and research programs encompassing a range of aspects relating to the photovoltaic and other renewable energy industries. These programs have been developed in consultation with representatives from industry to ensure graduates are appropriately qualified to enter the field upon completion of their studies. Since 2003, the School has seen a total of 114 students graduate from its undergraduate programs, and 82 students from its postgraduate degrees. These graduates are now taking advantage of a range of opportunities being created in the booming photovoltaics and renewable energy industries. The undergraduate programs have experienced strong growth since 2007.

The revised postgraduate program began operation in semester 1 of 2008. In the number of enrolled students in 2009 was double that in the previous year. The higher media profile of global warming, greenhouse and energy issues in the general Australian community is helping to raise the School’s profile locally and the industry growth in Asia raised the School’s profile internationally.

The granting of a large number of scholarships was finalised in August 2007 for up to $5.2m support from the Australian Government for study at the School, as part on the Asia-Pacific Partnership on Clean Development and Climate. In Semester 1 of 2009, these scholarships attracted 26 new undergraduate and 20 new postgraduate coursework students to the School. The number of formal agreements with Chinese universities established as a result of the Partnership grew to six during 2008.

At the end of 2009, there were 354 undergraduate students (20% growth relative to 2008), 60 postgraduate coursework students (100% growth relative to 2008) and 55 research students (6 Masters by research and 49 PhD) (flat relative to 2008) enrolled in the School’s programs.

5.1 Undergraduate Educational Programs

The School offers two undergraduate coursework engineering programs, each of which can be taken in combination with a Bachelor of Arts, Bachelor of Science, Bachelor of Commerce or a Bachelor of Laws. These degrees aim to develop well-educated graduates with the basic skills, attributes and knowledge required to practise as professional engineers in the booming photovoltaics and other renewable energy industries.

The Photovoltaics and Solar Energy Engineering program draws on the long history of expertise of Centre staff in this field and was the first of its kind internationally. Two new programs were established in 2009 in China, at Nanchang University in Jianxi Province and at North China Electric Power University in Beijing. The UNSW program includes education in technology development, manufacturing, quality control, reliability and life cycle applications, system design, maintenance and fault diagnosis, marketing, policy development and other renewable energy technologies. It has two unique features: a group project in the second year of the program, and a ‘strand’, which is a minor area of specialisation. Since 2003, a total of 99 students have graduated from the program, 10 graduated in 2009 and another 15 are expected to graduate in March 2010 after completing their studies in 2009. At the end of 2009, a total of 248 students were enrolled, showing growth of 55% relative to the previous year.

The second, broader degree program, in Renewable Energy Engineering, was introduced in 2003. In addition to photovoltaic devices, students in this program study solar architectural technologies, wind energy, biomass, solar thermal and renewable energy policy as
energy efficiency is a subject studied as an elective available to students from both programs. At the end of 2009, a total of 106 students were enrolled, growth of 22% from 2008. 2009 saw six new graduates of this program, bringing the total to 15, and seven more are expected to graduate in March 2010.

At the end of 2009, 19% of enrolled undergraduate students were women.

Some of the students attracted to the School by the sponsorship offered by the Australian Commonwealth Department of the Environment, Water, Heritage and the Arts, through the Asia Pacific Partnership for Clean Development and Climate. Also shown in the group photo are the Mr Bai Gang, Consul and Head of the Education Office, and Ms Guo Liang, Education Consul, from the Consulate-General of the Peoples Republic of China in Sydney, Indian Consul General Mr. Amit Dasgupta, and UNSW staff.

Graduates of these programs are gaining employment within a variety of organisations, including in the areas of energy efficiency and sustainable design. Each year a number of graduates start on a research program at the Centre, elsewhere at UNSW or at other institutions while others are employed in industry by solar cell and equipment manufacturers, system design and integration companies, electricity utilities and major end users of products.

5.1.1 The Strand

The strand is unique within UNSW to the Photovoltaics and Solar Energy Engineering program, and is essentially a minor area of specialisation which complements a student’s study of photovoltaics. Students can take strands covering a wide variety of areas including computing, electronics, mathematics, physics, mechanical engineering, civil engineering, and architecture. The aim of the strand is to provide students with broader engineering backgrounds important for the cross-disciplinary nature of photovoltaic applications.

5.1.2 Undergraduate Second-Year Student Group Projects

In the second year of the Photovoltaics and Solar Energy program, students have the opportunity of undertaking a year-long group project. The main emphasis of the second year group project course is hands-on project engineering. The course has a lecture component covering project engineering, report writing and presentation skills and practice and each project has a research component, a planning component, a hands-on component and a presentation/reporting component. This course helps to prepare students for their fourth year thesis, which is undertaken by all students enrolled in both the Photovoltaics and Solar Energy and Renewable Energy Engineering undergraduate programs.

In 2009, second-year project groups worked on the following projects: wind power assessment, solar water pumping, solar electric tricycles for developing countries and biodiesel production from waste cooking oils and fats.

5.1.2.1 Developing Countries

The School has been involved with projects in the developing countries for the last seven years. The application of photovoltaics and other renewable energy technologies can make a great difference to people’s lives and living standards in these places. Students involved with this project in the past have installed and maintained photovoltaic lighting systems in rural locations in Nicaragua, Vanuatu and Nepal and photovoltaics powered water purification in Sri Lanka. Skills that the students had developed throughout the year were put to good use in the field as invaluable lessons were gained regarding project management of activities in developing countries. Students faced and overcame many technical and non-technical issues in project implementation. With the rapidly growing student population the School has ceased to directly supervise international journeys for groups of second year students but, instead, suggests interested students involve themselves in the UNSW Chapter of Engineers Without Borders.

SOLAR ELECTRIC TRICYCLES PROJECT

Developing countries comprise around 80% of the world’s population, with high levels of population growth and rapidly growing rates of private vehicle ownership, especially light vehicles, such as motorcycles and bicycles. Transport needs in developing countries present significant and increasing environmental issues, including high levels of CO₂ and particulate emissions. At the same time, efficient transport systems are critical for improved livelihoods and economic growth.

Second year students were given the assignment of designing a solar powered tricycle for transportation of people and small loads in developing countries throughout 2009. The aims of the project were to gain a practical understanding of engineering project management,
in particular, the technical considerations involved in designing, building and evaluating a solar-electric powered tricycle, as well as a broad understanding of transportation needs and issues in developing countries.

A variety of approaches were taken by four groups, each of four students. Some groups opted for an integrated solar panel, while others chose to implement a ground-mounted charging station system. Some students chose to build their system out of existing bicycles, while others retrofitted commercially available tricycles. The final designs were built and tested for best range, efficiency, manoeuvrability and power. Different wheel sizes, gear ratios designs and the weight and aerodynamics of storage solutions made the difference on testing day.

5.1.2.2 Thin-Film Solar Processing Equipment

This project aims to give students a broad experience in enhancing and maintaining a world-class thin-film solar cell research laboratory. This is achieved through a two-stage process. Firstly, students develop a fundamental understanding of equipment and systems within the Centre's thin-film laboratory, including vacuum systems, gas delivery systems, leak testing equipment, and plasma processing machines. The second stage involves the students integrating what they have learnt, by applying it to a specific project in the thin-film laboratory.

In 2009, six second-year students undertook this project. A group of three students worked on upgrading a vacuum test chamber to reduce the dead volume in the system, reducing pump down times of the system. They also undertook work on a vacuum annealing stage, with the aim of being able to anneal samples at up to 1000°C. This group was successful in both reducing the pumping time of the system and lowering the base pressure of the system.

A second group of three students upgraded a thermal vacuum evaporator with a new lifting mechanism and substrate heating stage. The project required the students to design an effective lifting system, modify the chamber, seek manufacturers and arrange for the construction of the mechanism. The final design met this criteria and the chamber was built, fitted and commissioned on time. Both groups benefited greatly from the course as they learnt to integrate project management and engineering problem solving to successfully complete their projects.

5.1.2.3 Water Pumping Project

A group of students was charged with the task of demonstrating, on a reduced scale, the feasibility of pumping with photovoltaic power excess stormwater on the Kensington campus to the roof of the UNSW Electrical Engineering building for use for toilet flushing in the building. For their demonstration project, they were required to provide sufficient flow and storage to supply only a single toilet. The skills learnt are directly applicable to solar water pumping for a wide range of applications, including in rural villages around the world.

5.1.2.4 Biodiesel Trailer Project

Biodiesel is a substitute for diesel fuel derived from plant oils or animal fats – even waste cooking oil. The CO₂ that results from the combustion of biodiesel was recently drawn from the atmosphere, so, assuming the sources of the raw oil are sustainably produced, low net greenhouse gas emission result. Biodiesel also burns with fewer emissions of particulates that are harmful to health. Since oil-producing plants can be grown in Australia, it also has an energy security pay-off. Second-year students in the Photovoltaics and Solar Energy engineering program are designing and building a mobile, trailer-mounted, biodiesel production unit. The goal is to make biodiesel from waste oil taken from food outlets on campus, and there are plans to
take the trailer to high schools to demonstrate renewable energy and sustainable energy engineering principles.

To make the raw oil suitable for burning in an unmodified diesel engine, the viscosity must be reduced. The students have designed the trailer to achieve this using a process called transesterification.

The students this year were the first to actually produce a usable product, and performed tests using a small electric generator. They also demonstrated the biodiesel production process at a Sydney High School. The team also made a very good effort to produce a complete set of documentation of the equipment and procedures associated with the trailer, including finalizing the occupational health and safety guidelines. The trailer now is poised for completion by the next group of students.

5.1.2.5 UNSW Building Energy Efficiency and PV Projects

A group investigated energy efficiency of the Red Centre building on campus, relating energy used for heating, ventilation, cooling and lighting to solar gain from positioning of external louvres and window shading. An effort was made to assess occupant comfort. Facilities Management provided actual electricity consumption figures.

Another group designed a charging station for electric bicycles incorporated into the UNSW Botany Street car park. Power was generated by grid-connected PV panels on the open top floor of the car park, and electric bikes and scooters were charged in a ground level station adjacent to the car park.

5.1.2.6 UNSW Sunswift Project

The UNSW Racing Team’s solar car, Sunswift IV (Ivy), on the way to winning the silicon class of the 2009 Global Green Challenge (photo courtesy of sunswift).

2009 GLOBAL GREEN CHALLENGE

Over the past year, second year SPREE students have helped to design and build several major components of the UNSW solar car, which placed the first in the silicon class in the 2009 Global Green Challenge (GGC), the premier international solar car race. The result was the best result achieved by the team in its 14 year history.

Students were involved in two solar car related projects – design and construction of the photovoltaic array that powers the car, and construction of the lightweight composite components that reduce the weight, and hence the energy usage of the car.

ARRAY

The solar array is essentially an off-grid solar system, with the added complications of very fragile modules, and the requirement that it must withstand the conditions of driving 3000km of dusty, bumpy road.

The students designed the module and array sizing to conform to the race regulations, and selected the appropriate cabling and bypass diodes. They also performed array calculations and simulations in order to calculate the optimum wiring scheme that allowed for maximum output power, the most efficient battery charging, and maximum robustness against shading.

Two types of cells were used for maximum efficiency, standard industrial cells, and UNSW-produced Topcell cells. The team characterised the Topcells, initially by open-circuit voltage measurements, and later by full IV sweeps. The cells were then encapsulated, with assistance from CSG solar, and assembled into modules.

Finally, the array team and other Sunswift members assembled the array, mounting and soldering the fragile modules onto the solar car. The array performed well, with no issues throughout the entire 3000km.
COMPOSITES
Carbon fibre composites are extremely strong, lightweight materials, which are currently used, e.g. in aeroplanes and wind farms, to increase the energy conversion efficiency of the systems.

The composites team had the substantial job of building the carbon fibre composite components for a car which was almost entirely carbon fibre. These included the top shell, which housed the solar array, the bottom shell, which formed the structural chassis to safely house the driver, and the structural components which held the braking, steering and suspension systems. The team also successfully constructed the first new carbon fibre wheels for the car in 8 years. The wheels are the most complicated composite part to construct, require a great deal more care and attention, and must be thoroughly tested. The new wheels were manufactured extremely well, and performed beautifully over the 3000km of rough terrain.

The construction of all of the components took over six months, and was done at the Boeing Aerospace facilities in Bankstown. Boeing sponsored the team the carbon fibre and other materials, and the students learned how to work with composite materials from the experts.

The carbon work on the car by these students was easily some of the highest quality work in a field of 40 international solar cars, including semi professional teams, and also suffered no issues during the race.

5.1.3 Fourth Year Thesis
The thesis project is usually completed in the last two sessions of an engineering undergraduate student’s studies. Students undertake directed laboratory and/or other research work on an approved subject under guidance of the School’s academic staff. Typically, the thesis involves the design and construction of experimental apparatus together with practical tests. Each student is required to present a seminar, submit a written report, and present a poster as part of an Open Day in the last week of their second semester. It is a chance for students to demonstrate some of what they have learned throughout their studies.

Some students finished and presented their projects at the end of Semester 1, 2009. The Thesis Project Prize was a tie between Adrian Ho (“PV performance and energy efficiency in Kogarah Library”) and Gareth Forwood (“Cost effectiveness of carbon neutral commercial buildings”). Other projects coming to completion at that time were concerned with petrol use reduction policies, rural village electrification and an eco-village display in The Philippines. The Poster Prize selection in November 2009, for students completing at end of Semester 2, resulted in a win for Pei Hsuan Lu for her poster about “Photoplating for ink-jet printed solar cell”. The other topics on which theses were completed at the end of 2009 included: energy analysis of the Narrabeen Coastal Environment Centre, solar airconditioning, energy auditing of commercial buildings, study of the effectiveness of BASIX, building energy efficiency - computer modelling, solar schools, energy audit - Yarramundi YMCA, improving strategies for renewable energy deployment in developing countries: the case for solar powered education, waste heat recovery in automobiles, tandem photoelectrolysis for direct water splitting, assessment of fuel switching opportunities as a means of demand management, operational issues for NEM generators in the context of recent policy changes, characterization of ink jet printed PERC & PERL solar cells, ink jet printed selective emitters for silicon solar cells, ink jet printed etchants for silicon solar cells, investigation of the iJET concept, photovoltaics performance enhancement using chimney ventilation, ground source heat pump feasibility study for UNSW Tyree Energy Technologies Building, hydro power for a Vanuatu village school, feasibility study of renewable energy projects at Randwick Community Centre, photovoltaics integration into a solar thermal chimney, colloidal self-organization of silicon quantum dot dispersions, PECVD silicon oxynitride for high efficiency silicon solar cells, and photoplating for high efficiency solar cells.

The $500 Photovoltaics Thesis Prize for 2009 was won by Brett Hallam (Photovoltaics and Solar Energy) and Chris McGrath was awarded the Renewable Energy Thesis Prize. These prizes are awarded for the highest marks in the final year thesis subjects.

VANUATU
A fourth year thesis student, Chris McGrath, travelled twice in 2009 to the island of Tanna, Vanuatu to plan and implement a new project in the village of Imaki and to check on and maintain the previous year’s project in Lowun village. The 2009 project was again supported financially by Cundall and the Darcy and Patricia Wentworth Fund. This project involved the installation of a small hydro turbine on the village’s existing water supply pipeline, providing electricity to the primary school that services the region and incidentally improving the reliability of the water supply. Chris faced and overcame many difficult challenges with weather and equipment deliveries, including two boat breakdowns, one plane breakdown and equipment impoundment.
5.1.4 Dean’s Awards

Each year the Dean of Engineering presents awards for outstanding students in each non-final year of study in each Engineering School. Prizes were awarded during 2009 for academic performance in the previous year and went to Vincent Allen and John Durrant (first year), Patrick Wong (second year), Shen-Long Ooi (third year) and Brett Hallam (fourth/fifth year).

5.1.5 N&M Radiant Design Prize

The N&M prize is awarded to one student group undertaking the School’s project in the first-year Faculty of Engineering course, ENGG1000, Engineering Design. The project is to design, build and demonstrate a solar powered “space elevator” to climb a suspended tether in the final weeks of the semester. The Prize is awarded to the fastest team. The winners in 2009 were “The Flaming Monkeys, team members being Jiahao Chen, Dongchen Lan, Vicki Mo, Joanna Murphy, David Nguyen, and Oliver.

5.1.6 N&M Suntastic Project Prize

This prize, donated by the same sponsors as the N&M Prize, was offered again in 2008. It recognises best performance in SOLA2052 second year project course. It was won by John Durrant.

5.1.7 Photovoltaics Prize

This prize honours best performance in SOLA3540, Applied Photovoltaics, and was awarded in 2009 to Xue Bai.

5.1.8 Steve Robinson Memorial Prize

This prize is in memory of a former PhD student, Steve Robinson, and recognises the best postgraduate performance in SOLA9002, Solar Cells and Systems. It was awarded in 2009 to Amir Nashed.
5.2 Postgraduate Programs

The School offers three postgraduate coursework programs, a Graduate Certificate of Engineering Science, a Graduate Diploma of Engineering Science and a Master of Engineering Science, and two research programs, Masters by Research and a Doctor of Philosophy. These degrees are intended to provide students with an exceptional education in advanced concepts and research in the photovoltaics or other renewable energy areas.

The 1.5-year Master of Engineering Science coursework program was developed to build on the prior education of engineers from other engineering disciplines who are attracted to the photovoltaics and renewable energy industries. Students study courses chosen from the areas of photovoltaic devices, photovoltaic systems and applications, and renewable energy technologies. Enrolments in the program have grown significantly from the previous small numbers, with total enrolments of 60 at the end of 2009, doubled from 2008. There were 20 graduates in 2009 and 18 more are expected in early 2010.

At the end of 2009, the School had 55 students enrolled in postgraduate research degrees, 49 in a Doctor of Philosophy and 6 in Masters by Research. Research topics available to these students cover the entire photovoltaic sector and building energy efficiency, but with greatest emphasis on device theory, device and module design, balance of system components, and photovoltaic systems and applications. Research students play a pivotal role throughout all the Centre's activities. In 2009 the Centre produced five PhDs and two Masters by Research graduates, and one new PhD is expected to graduate in early 2010.

All the Faculty’s postgraduate coursework programs include an emphasis on engineering management and all students will be required to take some faculty-based courses of general engineering importance. The School will have its Energy Efficiency course included in the set of generally available courses in 2010.

5.3 Scholarships

The undergraduate programs at the Centre attract very bright students from across the world. The UAI cut off for local students for these programs was lifted at 88.65 for the 2009 intake. The Co-Op Scholarship Program and the Faculty of Engineering's Rural Scholarship Program have helped to attract these high-achieving students, while the Taste of Research Summer Scholarship Program and occasional casual employment opportunities provide experience in the School's laboratories with research leaders and encourage them to pursue research careers. The Centre's very high international profile also allows it to attract high quality research students, evidenced by the number doctoral students undertaking research programs at the Centre who have been awarded either of an APA (local students) or IPRS (international students) scholarships.

5.3.1 Asia-Pacific Partnership on Clean Development and Climate (APP)

The School applied during 2006 for sponsorship funding from the Australian Government under the Asia-Pacific Partnership on Clean Development and Climate programme to bring students from the Asia-Pacific region, specifically China, India and South Korea, to study photovoltaics engineering at UNSW. In January 2007, APP Programme investment of $5.2m was approved by the APP Ministers. This significant grant supports study at UNSW by international PhD students (full fees), MEngSc coursework students (50% fees), and third and fourth year undergraduate students (100% fees). The undergraduate arrangement of shared education requires detailed agreements between UNSW and the selected source universities, which are restricted to China. These scholarships will address a key need for additional expertise and knowledge in the rapid expansion of the photovoltaics industry in the region and their award acknowledges UNSW's importance in the field. In Semester 1 of 2008, these scholarships attracted five undergraduate, one postgraduate coursework and three PhD research students to the School. In Semester 2 of 2008, these scholarships brought in a further eight undergraduate, eleven postgraduate coursework and two PhD research students. Enrolments for 2009 are much stronger and the APP students comprise a significant proportion of the year’s intake. Twenty-six undergraduate and twenty MEngSc APP students commenced their study in Semester 1 of 2009.

Agreements, known as “2+2” agreements, have been signed with six leading Chinese universities: Sun-Yat-Sen University in Guangzhou; Nankai University and Tianjin Universities in Tianjin; Zhejiang University in Hangzhou; Nanchang University in Nanchang and Beijing Jiaotong University in Beijing.

Six MEngSc students completed the APP program at end of Semester 1 2009. A further ten MEngSc and five undergraduate are expected to complete the APP program at end of Semester 2 2009.
Four School of Photovoltaic and Renewable Energy Engineering students have received 2009 Certificate of Excellence awards for outstanding academic performance in the Asia-Pacific Undergraduate Partnership Program. Yu Yao, Yu Feng, Xue Bai (pictured above) & Dong Lin (not pictured) were awarded their certificates by the Head of School, on the 22nd of July, 2009.

5.3.2 Co-Op Scholarship Program
The Co-Op Program is an industry-linked scholarship program where students obtain a year of work experience with industry sponsors as part of their undergraduate studies. In addition to their outstanding academic achievements, students are selected based on their involvement in school and community activities, their demonstrated leadership and teamwork skills and their ability to communicate. Participation in this program enables students to apply the knowledge they have gained during their studies in industry, as well as opportunities for networking, recruitment and professional development through leadership camps. This program is also beneficial to industry sponsors, who have access to excellent students, can observe these students in their workplace, and have the first opportunity of recruiting the best new graduates.

Co-Op sponsors currently include, BP Solar, a global company that has been supplying PV systems to Australian markets for 30 years, CSG Solar, a new technology startup with an innovative crystalline silicon on glass PV product, Suntech Power Co. Ltd., the leading Chinese photovoltaics manufacturer and Renewable Energy Corp. (REC), a Norwegian based silicon and photovoltaics company that is establishing photovoltaics manufacturing in Singapore.

BP Solar closed its Sydney cell and module factory in March 2009, and has subsequently provided industrial training placements for sponsored students within its systems integration operations, but has not yet made any commitment to sponsor new students. Suntech Power is also not currently sponsoring new students although the company has been active in its support of other Centre initiatives. The School is actively seeking new sponsors to further extend the Co-Op program.

5.3.3 Rural Scholarship Program
The Faculty of Engineering established the Rural Scholarship Program in 2001 to encourage high-achieving students living in rural and isolated areas to study engineering. The scholarships are valued at approximately $9,500 per annum for four years of full-time study which eases the financial hardship of relocating to and living in Sydney. Three new rural scholars began their studies in the School in 2009. In 2009, the School again funded an extra scholarship in addition to the Faculty-funded scholarship. These students will commence studying with the School in 2010.

5.3.4 Thyne Reid Foundation Scholarships
During 2008 two new undergraduate four-year scholarships were awarded to the School by The Thyne Reid Foundation, one for Photovoltaics and Solar Energy Engineering and one for Renewable Energy Engineering. The two students began studies in Semester 1 of 2009 and will proceed into their second year in 2010.

5.3.5 Taste of Research Summer Scholarship Program
The Taste of Research Summer Scholarship Program is primarily for high achieving 3rd year students and, in exceptional cases, 2nd year students may be considered. As part of the program, engineering schools offer 10 week projects for students to complete during their summer break. These projects provide students with scholarship support to gain experience working as part of a research team, for example in the world class laboratories at the Centre.

In addition to providing an opportunity for checking whether research is their ideal career path, participation in these projects helps students further develop their technical skills and their written and oral communication through written reports and poster presentation.

From December 2008 to February 2009, the Centre hosted an unusually large number of eight students, taking advantage of the growing interest in the Centre's research programs among outstanding undergraduates, particularly from those in this School. Again, in the 2009/2010 summer the Centre was keen to retain for research training as many as possible of the outstanding senior undergraduate students and took on an unprecedented 12 students through the Taste of Research program.

5.3.6 Research Scholarships
Through thesis projects, and scholarships, including the Taste of Research Scholarship program, the Centre encourages some of the best undergraduate students, particularly those from the School, into research. Being an internationally recognised research organisation, the Centre attracts very high quality students to its research programs where students have the opportunity to work with leaders in this field. The fact that 21 of our doctoral students are currently in receipt of the very competitive Australian Postgraduate Award (APA) for local students or the Australian Government’s International Postgraduate Research Scholarship (IPRS) for international students is testament to the quality of these students. To be awarded an APA, the student must be a local student with first class honours graduate at Bachelor degree level, while the IPRS is available to international students and are even more competitive. Suntech Power also sponsors a PhD scholarship in the Centre. Interest in and applications for postgraduate research in the School boomed during 2009 and the School expects to have six new APA recipients and four new IPRS recipients begin their research
programs in 2010. The Centre also has five PhD scholars sponsored by the Australian Government through the Asia-Pacific Partnership on Clean Development and Climate scheme.

5.4 Educational Resources

5.4.1 New Book Translation

A revised second edition of the Centre’s book, entitled “Applied Photovoltaics” was published by London publication house, Earthscan, in 2006. This book was originally published by Stuart Wenham, Martin Green, and Muriel Watt in 1995, and the revisions were the result of experience teaching a course on applied photovoltaics as part of the Centre’s undergraduate and postgraduate programs and of the changes in the industry and technologies in the intervening decade. This book was, in 2008, the Centre’s first recent foray into publication in translation when a simplified Chinese version was released onto the market by Shanghai Jiao Tong University Press. New traditional Chinese versions of the second edition of “Applied Photovoltaics” and of “Solar Cells. Operating Principles, Technology and Applications”.

This book has now also been converted into traditional Chinese script for the Taiwan, Hong Kong and Macau market and publication by Wu-Nan Book Inc., Taipei, occurred in 2009. Additionally, work began in 2009 on a new English language edition for publication by Earthscan, London.

Another of the Centre’s English language textbooks, the popular and important, “Solar Cells” by Prof. Martin Green (1995), has also been published in traditional Chinese form by Wu-Nan Book Inc. in 2009. This book is expected to appear in simplified Chinese translation in 2010. Another of Prof. Green’s books, “Advanced Silicon Solar Cells” is currently being translated into both Chinese forms by the Centre.

5.5 PVSOC

One characteristic of the Centre which has led to the success of the educational programs is the friendly atmosphere that is engendered by being a small (but strongly growing!) school with highly motivated students and academic and general staff. Students appreciate being able to form friendships and support networks with fellows, as well as feeling comfortable and familiar with academic, technical and administrative staff. PVSOC (Photovoltaics Society) is a social committee established by the students which fosters this atmosphere with organised social events and activities to encourage student interaction. In 2009, the committee organised several events, including barbeques, student participation in Sustainable House Day (organised by ANZSES and held in September) and the PVSOC Annual Dinner. Students and staff enjoyed this party at Waverton in September 2008 (held earlier in the year than previously to avoid distraction from final week assignments and exam preparations) where final year students were farewelled, staff thanked, and the 2010 PVSOC committee was elected.

5.6 Promotional Activities

The Centre regularly participates in promotional activities organised by the Faculty of Engineering and Student Recruitment at UNSW and in the 60/60 Anniversary event in Beijing. These events are important for increasing awareness and interest in the Centre’s educational and research programs.

5.6.1 The Shi’s Family Charitable Foundation and The Sydney Theatre Company

Artistic impression of the Wharf Theatre with the rooftop photovoltaics system installed (Image produced by and used with permission of NSW Government Architect’s Office).
The School is a major participant in the Sydney Theatre Company's high-profile "Greening the Wharf" project that is improving the water efficiency and greenhouse gas impact of the Wharf Theatre, at Walsh Bay. UNSW, in consultation with the Shi’s Family Charitable Foundation has agreed that the STC’s ‘Greening the Wharf’ project is a project suitable to showcase the Pluto technology as an example of UNSW and Suntech’s research excellence. The School will contribute $2m, donated by the Shi’s Family Charitable Foundation, towards the establishment of a 380kWp grid-connected photovoltaic array on the Wharf’s roof, to be constructed in 2010. The balance of funding for the $4 million project has been raised by Sydney Theatre Company from The Commonwealth Government’s Green Precincts Fund, NSW Government’s Public Facilities Program, corporate sponsor Energy Australia and leading philanthropists.

The project grew from two sources. Firstly, Dr Shi Zhengrong, CEO of Suntech Power, expressed a wish to make a gift to UNSW and to Sydney for helping him start his successful career in photovoltaics and to use it as a promotional tool. This led to a study of several prominent sites in Sydney and a pre-feasibility study, carried out as a final year thesis project by Samantha Wong. In parallel, Cate Blanchett and Andrew Upton, the Artistic Directors of the Sydney Theatre Company, were seeking opportunities to generate a significant part of the Company’s energy from renewable sources. Bringing the two ideas together led to the official launch in July 2009 of the project at a ceremony with Federal Minister for Climate Change and Water Penny Wong and Federal Environment Minister Peter Garrett, Mrs Vivienne Shi, UNSW Chancellor David Gonski, Scientia Professor Martin Green and Dr Richard Corkish. The project will be installed during 2010.

5.6.2 Print and Broadcast Media

Student recruitment advertisements were also placed in the HSC Survival Magazine, the HSC Change of Preference Guide, and the HSC Universities Advisory and Information Day Guide. Media mentions of the School and the Centre became more frequent in 2009 as community interest in climate change and renewable energy issues grew. This included a front-page article in the major daily newspaper of the Chinese city of Foshan (Guangdong province), a city of 6 million population.

5.6.3 UNSW Information Day

Local undergraduate students must apply for admission to UNSW programs through the Universities Admissions Centre (UAC), and the first week of January is the final opportunity for students to change their preferences for entry to university programs. Therefore, the university hosted an information day in January 2009 to assist students obtain information to finalise their preferences. School administrative and academic staff attended this event and talked to many prospective students who were unsure of their career direction. Students received information on our programs and had the opportunity to ask questions of staff.

5.6.4 UNSW Courses and Careers Day

UNSW Courses and Careers Day is the annual information day, held in the first week of September, for prospective students to obtain information about programs and student life at the university. As part of this day students and academic and administrative staff from the School provided advice and information to prospective students from information desks in the Roundhouse and in a marquee in the UNSW Quad, nearby the Sunsprint model solar car race finals. This year, the weather was ideal for the 2009 event. During the day Dr Alistair Sproul presented two public lectures about the School’s and Centre’s programs as part of the lecture series organised centrally by the university.

5.6.5 Faculty of Engineering Information Day for High School Students

Each year the Faculty of Engineering organises an information day to give high school students and their teachers an opportunity to learn about engineering and the programs offered at UNSW. As part of the day students visit three engineering schools of their choice and engage in interactive activities aimed at demonstrating the relevant engineering area. Once again in 2008 the demand to attend this event was so great that two High Schools Days were required, with the School running several tours.

5.6.6 Honeywell Engineering Summer School

The Honeywell Engineering Summer School is an event held in December and is conducted by Engineers Australia. As part of the summer school high school students from across NSW and the ACT about to enter their final year take part in a week of activities which involves industry visits and lectures / demonstrations at a number of universities. In 2009 approximately 30 students visited the Centre to participate in hands-on activities and information provision.

5.6.7 Promotion of Sponsorships by Asia Pacific Partnership for Clean Development and Climate

Sustained efforts were made during 2008 to continue to promote the availability of sponsored education opportunities for Chinese, Indian and Korean students at the School. This was done through the School’s and other UNSW web sites, particularly the International Office and the Scholarships Office, interviews, education fairs and exhibitions in target countries and technical conferences in Asia. In addition, Dr Corkish travelled to India, Korea and China, including Hong Kong, partly to alert universities, photovoltaics companies and prospective applicants about the opportunities provided by the Australian Government thorough the Partnership.
5.6.8 Model Solar Car Vehicle Challenges

Over 200 high school students participated in the UNSW SunSprint Model Solar Car Challenge.

The Centre has been running the annual UNSW SunSprint Model Solar Car Challenge since 1999. This is a New South Wales statewide competition designed to involve high school students in project-based learning but brings with it a spirit of fun and competition. Many schools throughout NSW have allowed final year design and technology students to adopt SunSprint as their year-long major project. High school physics and science teachers have also used SunSprint as a class-based teaching project as SunSprint addresses several aspects of the curriculum.

The individual solar cars are designed and built according to specifications provided by the Australian-International Model Solar Challenge (AIMSC), a national organization overseeing and linking all of the state events. These specifications provide design criteria that, when followed, allow students all over Australia to build model solar cars that are uniformly competitive with respect to cost and use of materials. The students contribute ideas, inspiration, time and money with the average vehicle costing over $600 and taking over four months to design and build.

With the success of the UNSW SunSprint events, in 2005, the UNSW Faculty of Science undertook to co-sponsor the UNSW SunSprint event with the Photovoltaics Centre of Excellence with each party committing an equal financial contributions and each supplying similar organizational infrastructure.

Preparations underway for the UNSW Model Solar Challenges.

The Minisprint Model Solar Car Challenge and the Model Solar Boat Challenge were run simultaneously with SunSprint. Both of these events allow primary school students to design and build solar vehicles and then experience the thrill of competition. Twenty primary schools were represented in the two competitions with approximately fifty primary students being involved directly in the challenges.

Place holding students from Clovelly Public School showing their solar powered boat.
Regional students participate at St. Matthew Central School in Mudgee, NSW.

The Regional Minisprint Model Solar Challenge was held at St. Matthews Central School in Mudgee, NSW and involved over 200 primary school students. Preparations are underway to have over 600 students involved in Mudgee in 2010.

5.6.9 60th Anniversary Event in Beijing

The Centre’s Martin Green and Richard Corkish both participated in the celebration of UNSW’s 60th anniversary in Beijing in October 2009, at which alumnus and founding CEO of Suntech Power, Dr Zhengrong Shi, was a guest of honour. They were joined by about 400 alumni and the event allowed strong connections to be formed and reformed.

5.7 Educational Collaborations

A range of educational collaborations have been established between the Centre and other educational institutions and organisations. These collaborations involve the development and implementation of educational programs and courses, the provision of support for student projects and theses, and the exchange of students and staff.

5.7.1 UNSW Ecoliving Centre

The UNSW Ecoliving Centre, under the leadership of Cameron Little, continued development of the Renewable Energy Display Trailer with the support of a team of UNSW students and external volunteers. This work began in 2007 and continued into 2009, creating an excellent promotional resource for both UNSW student recruitment and public promotion of sustainability. Additionally, the Ecoliving Centre provided strong support and collaboration for the School’s practical projects.

5.7.2 Chinese Universities

In 2008 the School continued collaborations with four Chinese Universities for third and fourth year students from those universities to study Photovoltaics and Solar Energy Engineering at UNSW and for Masters by coursework study with Asia Pacific Partnership sponsorship. “2+2” agreements were signed in 2007 with two prestigious Chinese universities, Nankai University in Tianjin and Sun Yat-Sen (Zhongshan) University in Guangzhou. The first students under this scheme started at UNSW in Semester 1 of 2008. During 2008 similar agreements were signed with additional two Chinese universities. The two new partner universities are Tianjin University (two agreements, each with a different school) and Zhejiang University, Hangzhou.

A new agreement has now been made with Nanchang University, in Nanchang, Jiangxi Province, which has formed a new School of Photovoltaic Engineering and an agreement was signed in early 2010 with South China University of Technology, in Guangzhou.

5.7.3 Mirvac

Mirvac has continued its sponsorship of a Faculty of Engineering Linkage Scholarship for a student of Renewable Energy Engineering. The sponsored student, Sarah Eager, completed her fourth year in 2009.

5.7.4 Thyne Reid Foundation

The Thyne Reid Foundation concluded in 2008 an agreement to sponsor the studies of two undergraduate students for four years of their studies, one in Photovoltaics and Solar Energy Engineering and one in Renewable Energy Engineering. The students began their studies in the first semester of 2009.

5.7.5 Cundall and the Darcy and Patricia Wentworth Fund

Cundall, a sustainable design consulting company, and the Darcy and Patricia Wentworth Fund joined forces to financially support a final year thesis project to bring hydro power to a remote village school in Vanuatu, mentioned above in Section 5.1.3.

5.7.6 Suntech Power Corporation

Suntech, a partly Australian-owned company operating in China, has been actively involved in assisting UNSW with the development, testing and evaluation of educational material in the PV area such as in the development, testing and evaluation of a teaching software package called the Virtual Production Line. Significant numbers of UNSW undergraduate students participate in industrial training or in “Taste of Research” projects at Suntech and postgraduate students often travel there to use vital research equipment. Additionally, Suntech sponsored an undergraduate Cooperative Scholarship and a PhD scholarship and has made significant contributions to UNSW to support photovoltaics research.
5.7.7  Singapore Polytechnic, Ngee Ann Polytechnic and Temasek Polytechnic

The Polytechnics in Singapore offer three-year diploma programs, including in engineering. During 2007 the School arranged for future articulation of graduates from the new clean energy diploma of Clean Energy program at Singapore Polytechnic into either of the School’s Bachelor of Engineering programs. In 2008 the School set up a similar articulation arrangement with Ngee Ann Polytechnic and Temasek Polytechnic was included in 2009. Significant numbers of students may flow in future years from these institutions, fuelling Singapore’s drive to become a major photovoltaics manufacturer.

5.7.8  The Darcy and Patricia Wentworth Beneficial Fund

The School gratefully acknowledges the financial gift of the Darcy and Patricia Wentworth Fund, which is to support final year thesis projects, especially those related to sustainable transport. Darcy Wentworth also donates his services as a visiting academic, supervising undergraduate student projects and other tasks.

Mr Darcy Wentworth delivers a cheque on behalf of the Darcy and Patricia Wentworth Fund. The donation was used to partially support the Vanuatu project described above.

5.7.9  Parsons Brinkerhoff

Dr Hanzheng Duo, a practicing Engineer at Parsons Brinkerhoff, in his role as visiting academic, donated his time and industrial project experience to supervise and assess an undergraduate thesis project through 2010.
When the Key Centre for Photovoltaic Engineering was awarded in 1999, it was established as an autonomous Centre within the Faculty of Engineering of UNSW, becoming independent from the School of Electrical Engineering where UNSW photovoltaic activities had been previously located. At that time, the Key Centre was given the same operational independence and rights as the other Engineering schools, with the Director Stuart Wenham being given the same status and authority as other Heads of Schools. With the awarding of the Centre of Excellence in 2003, the University committed to the Key Centre for Photovoltaic Engineering becoming the School of Photovoltaic Engineering, within which the ARC Photovoltaics Centre of Excellence would be located. This transition occurred in January 2006. The corresponding organisational relationships are shown in the upper part of Fig. 6.1.

Within the Centre of Excellence, Deputy Directors have been appointed for the major strands of research as shown. The Management Committee of the Centre comprises the six Directors and Deputy Directors, along with the Head of School and the Business and Operations Manager. This committee meets fortnightly on the 1st and 3rd Fridays of each month, with each Deputy Director giving a report on the activities in his or her area over the preceding fortnight. This committee takes responsibility for decision making within the Centre that affects the Centre as a whole, while the individual Deputy Directors receive their own annual budgets to allow them to make and implement decisions that impact only their own laboratory areas and research activities.

The Advisory Committee for the Centre comprises the Centre Directors, the Head of School for Photovoltaic Engineering, leading academics from other institutions, industry leaders such as CEO’s of various companies involved in the field, and research leaders. This committee provides high level advice, feedback and recommendations in relation to the Centre’s activities and their relevance. The Advisory committee meets annually, taking into account the geographical separation of its members (Australia, USA, China, Germany, Italy, Spain), although more frequent correspondence takes place when necessary with individual committee members either by email or telephone. The membership of
the Advisory Committee during 2009 has included:

- Professor Stuart Wenham, Centre Director
- Professor Martin Green, Centre Executive Research Director
- Dr Gavin Conibeer, Deputy Director (3rd Generation PV Research)
- Associate Professor Thorsten Trupke, Deputy Director (Silicon Photonics)
- Dr Sergey Varlamov, Acting Deputy Director (2nd Generation PV research)
- Professor Allen Barnett: world leading academic in the field; recipient of many prestigious international prizes such as the William Cherry Award; former President of AstroPower, one of the world’s largest solar cell manufacturers, before being purchased by GE.
- Prof. Andres Cuevas, ANU;
- Dr Francesca Ferrazza, Chief Scientific Officer, Enitechnologie;
- David Hogg: CEO of CSG Solar AC, Germany until recently; former CEO of Pacific Solar, Australia;
- Mr. David Jordan, until recently, Manager of New Technology, BP Solar International;
- Dr Larry Kazmerski, Head, Photovoltaic Division, US National Renewable Energy Laboratory;
- Prof. Antonio Luque, Head, ESTI, Polytechnical University of Madrid; Leading European academic in the photovoltaic field; founder of Isofoton, one of Europe’s most established manufacturers;
- Dr Zhengrong Shi, CEO of Suntech-Power, the world’s largest silicon cell manufacturer; recipient of various industry prizes; former Deputy Research Director of Pacific Solar; major collaborator of the Centre;
- Prof. Peter Würfel, Institut für Angewandte Physik der Universität Karlsruhe.

Other distinguished researchers and industrialists have been co-opted to the Committee as required.

Also within the Management structure and a member of the Centre’s Management Committee is the Centre’s Business, Technology and Operations Manager Mark Silver, given the extensive involvement of Centre staff with industry, large number of collaborative research projects, and the high level of success of the Centre in generating, marketing and commercialising technology. The Head of Administrative Support for the Centre during 2009 was Joyce Ho. Not shown in the Management Structure is the Financial Officer Julie Kwan who looks after the Centre Accounts, interfaces with the University Financial System, advises the Centre Directors and Deputy Directors on budgeting and financial matters, and generally assists with sourcing of funding, purchasing, reporting, writing grant applications, and advising on business opportunities.

A primary responsibility of the Director in the Centre is to ensure the Management structure as shown functions efficiently and effectively, with appropriate support and resources to facilitate the Centre’s achievement of its milestones and performance targets. An important aspect of this is managing the Centre’s finances to ensure suitable levels of funding are made available for supporting the major research strands, while simultaneously ensuring adequate funding is available for repair and maintenance of existing facilities and the purchasing of appropriate new infrastructure and equipment.

The Director works closely with the Centre’s Executive Research Director to assist in setting high level research direction and priorities for the Centre’s programs. In the teaching area, with the Key Centre for Photovoltaic Engineering and its activities being incorporated into the Centre of Excellence, the Director also takes significant responsibility in ensuring the successful development and implementation of the Centre’s educational programs, both at undergraduate and postgraduate levels. In this area, the Director works closely with Dr Richard Corkish, the Head of School.
Despite the $0.5 million tapering of the Centre of Excellence Funding from the ARC in 2009 compared to 2008, the total income for 2009 for the ARC Photovoltaics Centre of Excellence was $6.36 million. This does not include $0.5 million delayed funding income from Suntech Power or $2.2 million in funding for scholarships provided by the Dept of Resources, Energy and Tourism, or $2.1 million from the Host Institution based on EFTSU and related income. This latter income has been generated by the Centre through its educational activities that have formed the basis of a School within the Faculty of Engineering. This income has been used for the development of new courses and teaching materials and to fund the salaries of most of the academic staff associated with the Centre.

The largest three components of Centre income in terms of cash contributions were $2.55 million for the ARC Centre Grant, $1.70 million from industry and $1.25 million from the Host Institution. As mentioned above, the figure for industry support does not include the $0.50 million from Suntech for its 2009 commitment due to delays in sending Suntech the invoice, nor the in-kind contributions for the collaborative research which add a further component in excess of $1 million, effectively making industry funds again the largest income source for the Centre. With the booming photovoltaic industry and the high demand for companies wishing to work with the Centre, this strong industry support is expected to continue and increase. A further $0.48 million was also received from the ARC in the form of other National Competitive Grants such as the Linkage Grant with CSG Solar.

The largest industry contributor for 2009 was the consortium of Toyota, General Electric, Schlumberger and ExxonMobil for the Global Climate & Energy Project, administered by the Stanford University, who contributed $0.69 million. The largest single company contributor for the sixth successive year was Suntech-Power with $0.55 million cash commitment while also generously supporting the collaborative research at their own facilities. The single company contributors from industry, including funding for collaborative research, scholarships, consulting and facility rental, are summarised as follows: Suntech-Power with $546K, E-Ton Solar with $282K, CSG Solar with $274K, Toyota Motor Group with $149K, Corum Solar with $127K, JA Solar with $49K, BP Solar with $61K and REC with $15K. Other cash and in-kind contributions have been made by a large number of collaborators who contribute to the Centre through the expertise and experience they offer in collaborative research areas and the in-kind support provided through access to equipment, facilities and personnel not available at UNSW.

The next largest cash component of income was $197K from the State Government, through the Department of State and Regional Development (DSRD). This funding has been particularly important for the purchase of new equipment and the development of facilities.
A further $131K of income was provided by the Federal Government through the Dept of Resources, Energy and Tourism.

Other Centre contracts, consulting work and technology transfers are conducted through NewSouth Innovations, the commercial arm of the university. These are handled on behalf of the Centre of Excellence and its staff through the NewSouth Innovations accounts and are not included in this financial report.

The Centre also earns income through the sale of educational CDs, books and computer software, with a combined income for 2009 of $62K.

Centre 2009 Expenditure of ARC Grant was $2.13 million in comparison to the $2.55 million received as income. By far the largest component of expenditure was for salaries and scholarships with $1.21 million, including expenditure for research appointments, technical support, administrative staff, financial management, specialised consultants and facility cleaning. Appointments include full-time, part-time and casual.

Equipment expenditure from the ARC Grant can in general be kept relatively small due to the support from the State government through DSRD, Host Institutional support through the provision of equipment and industry donations. During 2009 $85K was spent from the ARC Grant on small laboratory equipment items in direct support of the research. However the intended $0.5 million purchase of a state-of-the-art belt furnace during 2009 has been delayed to 2010 due to the need to modify furnace specifications to fit the available laboratory space.

Another major component of Centre expenditure from the ARC grant is on consumables and maintenance with $685K. These costs are strongly dominated by laboratory consumables to support the device research such as high purity gases, chemicals and general laboratory supplies.

The expenditure on travel during 2009 from the ARC grant was $150K. This is relatively small due to significant amounts of the Centre staff travel being funded by industry collaborators. The primary purposes for Centre staff and student travel were for participation in collaborative research projects with overseas industry partners and for attendance and paper presentation at international conferences.
8. Publications

8.1 Books

8.2 Book chapters

8.3 Patent applications
Ian Brazil and Alison J. Lennon, “Glass texturing”; Provisional Patent Filed September 2009, NewSouth Innovations Pty Limited, Australia, 2009090537.
I. Brazil and A. Lennon, “Method for texturing a surface of selected material”, AU Provisional filed August 2009.
G. Conibeer, M. Green, D. König, S. Shrestha, “Quantum Well Contacts”; Provisional Patent Application NSi Ref NSi 08_2295, filed on 1 Sept. 2009.
D. König, “Acceptor Doping of Si and Ge Nano Crystals”; Provisional Patent Application NSi Ref NSi 08_2315, filed on 14 August 2009.
D. König, “Donor Doping of C, Si, Ge and Sn Nano Crystals”; Provisional Patent Application NSi Ref NSi 08_2316, filed on 14 August 2009.
A. Lennon and S. Wenham, “Method for selective delivery of material to a substrate”; AU Provisional Filed August 2009.
A. Lennon, B. Tjahjono, Y. Yao and S. Wenham, “Method and apparatus for light induced plating of solar cells”; AU Provisional Filed November 2009.
S. Wenham, L. Mai, B. Tjahjono, Z. Shi, J. Ji, “Multilayer Anti-Reflection Coatings that provide thermal expansion mismatch correction”; Patent Application NSi Ref NSi 08_2281
A. Wenham, S. Wenham, M. A. Green, “Improved Metal Adhesion for Plated Metal Contacts for Photovoltaic Devices”; Patent Application NSi Ref NSi 08_2290
A. Wenham, Z. Hameiri, “Improved Laser Operation for Localised Doping of Silicon”; Patent Application NSi Ref NSi 08_2291
S. Wenham, A. Wenham, L. Mai, and A. Lennon, “Photoplotting of metal electrodes for solar cells”; AU Provisional Filed November 2009.

8.4 Papers in refereed scientific and technical journals
Ian Brazil and Martin A. Green, “Investigating polysilicon thin film structural changes during rapid thermal annealing of a thin film crystalline silicon on glass solar cell”, Journal of Materials Science: Materials in Electronics, DOI: 10.1007/s10854-010-0062-6 (accepted 13 Jan 2010).


8.5 Non-refereed journal publications


C. Tsao; J. W. Weber; P. Campbell; G. Conibeer; D. Song and M.A. Green, “In situ low temperature growth of poly-crystalline germanium thin film on glass by RF magnetron sputtering”, Solar Energy Materials and Solar Cells (accepted February 2010).


8.6 Conference papers and other presentations


Richard Corkish, “Education and Research at UNSW”, presentation to 18 students of National Defence University Industrial College of the Armed Forces (USA), 12 May 2009 (invited).


Richard Corkish, presentation to Skull Session of Capacity Development for Sustainable Society, Tokyo, 26 May 2009 (invited).

Richard Corkish, “Photovoltaic array for the Wharf Theatre”, presentation at Walsh Bay Precinct Information Session, 2 June 2009 (invited).


Richard Corkish, “Education and Research Supporting Photovoltaics Industry Expansion in Asia-Pacific Region”, presentation to Pingxiang College, PingXiang, Jiangxi, China, 16 December 2009 (invited).


M.A. Green, “Activities at the UNSW Photovoltaics Centre of Excellence”, Workshop at National Taiwan University, Taipei, 11 November 2009 (invited).


S. Pillai, K. Catchpole, M.A. Green, “Plasmonics for Photovoltaic Applications”, 18th International Photovoltaic Science and Engineering Conference (PVSEC-18), Kolkata, India, 19-23 January 2009.


D. Song, E-C. Cho, G. Conibeer and M.A. Green, “Solar Cells Based on Si-NCs Embedded in a SiC Matrix”, 18th International Photovoltaic Science and Engineering Conference (PVSEC-18), Kolkata, India, 19-23 January, 2009 (oral).


Z. Wan, D. Song, G. Conibeer and M.A. Green, “Structural characterization of solid phase crystallized Si0.5Ge0.5 films for photovoltaic applications,” 34th IEEE Photovoltaic Specialists Conference (PVSC), Philadelphia, USA, 7-12 June 2009 (10.1109/PVSC.2009.5411613), pp 000597 – 000599.


8.7 OTHER REPORTS


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