4.4 SECOND GENERATION: SILICON, ORGANIC AND OTHER “EARTH ABUNDANT” THIN-FILMS

4.4.1 Silicon Thin Films

4.4.1.1 Summary

The focus of the silicon thin-film group research has been on further improvements in the technology of e-beam evaporated poly-crystalline (poly-Si) thin-film solar cells, which is conducted within an ARC Linkage grant project with CSG Solar.

The UNSW e-beam evaporator, the tool supplying precursor Si films for the project, underwent major refurbishment during 2010, allowing greatly improved reliability and up-time of the tool, to reduce background contamination level and to achieve more accurate control of Si deposition rate and doping, allowing deposition of high quality Si films. After processing the films into solar cells and applying a newly developed etch-back Si texturing process a new UNSW efficiency record for evaporated cells of 7.1% (Voc 458 mV, Jsc 26.6 mA/cm², FF 58%) has been demonstrated.

Outstanding progress has been made in the area of light-trapping in poly-Si thin-film cells. Firstly, a comprehensive study of various back-surface reflectors (BSR) of practical significance has been conducted. It allows choosing the best BSR depending on the cell design and structure. For example, the best BSR for a planar cell is a thick pigmented resin (P150) with a high load of TiO₂, while the best BSR for a textured cell is a highly reflective white paint. Secondly, further development in plasmonic poly-Si thin-film cells led to record-breaking Jsc enhancement of 50%. Thirdly, a simple and effective Si film etch-back texturing process has been introduced to improve light-trapping in the e-beam poly-Si cells on planar glass, which allowed achieving a record current of 26.6 mA/cm², the highest ever reported for evaporated poly-Si solar cells.

The first encouraging results have been obtained for transient heating defect anneal of poly-Si films. The open-circuit voltage improvement of about 58 mV was demonstrated after poly-Si cell structures were exposed to diode laser or flash lamp radiation for only a few milliseconds. The diode laser was also successfully applied to large area boron diffusion to prepare back surface field (BSF) layers.

A large amount of data has been collected about effects of different annealing treatments on solid phase crystallisation (SPC) of Si films and resulting poly-Si film quality and cell performance. A focus was on application of higher temperatures during either the whole SPC process or...
its stages, such as the incubation, to shorten the crystallisation while maintaining or even improving the cell performance. The result is that, regardless of when a higher temperature is used, it always causes poorer poly-Si crystal and electronic quality. However, the degree to which the cell performance deteriorates, depends on the Si film preparation conditions. E-beam cells and hybrid cells, i.e. the cells with PECVD emitter and e-beam absorber and BSF, can be crystallised at 640°C within only two hours (as compared to 20 hrs at 600°C) without a significant loss in their performance. In the area of the SPC emitter seed-layer approach, the factors leading to the best seed crystal quality are being studied.

A comprehensive concept of performance limiting recombination in poly-Si has been developed. According to the concept it is intragrain defects, such as dislocations that are responsible for limiting the minority carrier lifetime in poly-Si material and thus the cell performance. In the practical range of dopant concentrations in the quasi-neutral region of the cell absorber (> ~5E15 cm^-3), the lifetime limiting recombination occurs via shallow levels linked to dislocations. At dopant concentrations lower than ~5E15 cm^-3 the lifetime is limited by recombination via deep levels introduced by charged impurities at dislocations and possibly grain-boundaries. The dislocation density in poly-Si thin-film cells was estimated from the TEM images and found to be of an order of 1E10 cm^-2, which is consistent with experimental voltages of about 500 mV.

4.4.1.2 Introduction

The technology of thin-film poly-Si on glass solar cells is developing steadily and it is expected ultimately to become cost-competitive with other thin-film technologies [4.4.1.1, 4.4.1.2]. The presently best developed poly-Si on glass PV technology has been commercialised by 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 activate dopants, remove and passivate defects, and then processed into metalised modules [4.4.1.3]. The highest achieved efficiency for 94 cm² mini-modules produced by CSG technology is 10.5% [4.4.1.4], and full scale 7-8% efficient modules have been 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 to the key steps of the cell fabrication process, including Al induced glass texturing (AIT) [4.4.1.5] and localised surface plasmons (SP) in metal nanoparticles [4.4.1.6] for enhanced light trapping, silicon deposition by high rate PECVD [4.4.1.7] and e-beam evaporation [4.4.1.8], defect anneal and passivation, and cell metallisation and interconnection [4.4.1.9]. 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 2010 focused 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 Figure 4.4.1.1 and Figure 4.4.1.2 describes the cell fabrication sequence.

Additionally hybrid cells combining a PECVD emitter with an 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.
texture is prepared by the UNSW-developed AIT method (4.4.1.10) described below and 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+/p/p+ precursor diode is then deposited by either e-beam evaporation or PECVD on planar or AIT glass respectively, followed by SPC at 600°C. The resulting as-crystallised poly-Si diodes have Voc of only about 150-180 mV. A high temperature treatment is then performed at ~1000°C for 30-60 s to activate the dopants and to anneal defects, which increases Voc up to 220-250 mV. The final step of the material preparation is hydrogenation in a remote hydrogen plasma to passivate the remaining defects resulting in Voc of 450~500 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 (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 (4.4.1.11, 4.4.1.12). The BSF electrode of the e-beam cells consists of thin Al fingers covering only 4% of the rear surface, thus allowing bifacial (i.e. illumination from both glass and Si side) operation of the cells (4.4.1.13, 4.4.1.14, 4.4.1.15). 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 Solar large area KAI PECVD tool and the absorber and BSF layers in the UNSW e-beam evaporator. The films are processed into either individual 2 cm² large solar cells using the UNSW bifacial metallisation or solar mini-modules of 36 cm² area using the proprietary CSG Solar metallisation technology described elsewhere (4.4.1.4).

### 4.4.1.4 Glass Texturing

An advanced glass texturing method was developed at UNSW and it is referred to as “aluminium induced texture” (AIT) (4.4.1.5, 4.4.1.10). 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 (Figure 4.4.1.3a). Further improvement in the AIT process conditions led to development of so-called “sub-micron AIT” (SAIT) glass with smaller and steeper feathers (Figure 4.4.1.3b), which ensure even better light absorption in a poly-Si film prepared on such texture (Figure 4.4.1.4) (4.4.1.16).

Typical atomic force microscope (AFM) images of the bare AIT and SAIT glass surfaces with the RMS roughness of 800 and 150 nm respectively and an SEM image of the AIT glass coated with a 2 μm thick poly-Si film are shown in Figure 4.4.1.3.

As shown in Figure 4.4.1.4, the absorption in the 2 μm thick poly-Si films on the best AIT and particularly SAIT 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 attributed to the enhanced parasitic absorption in the glass and/or measurements errors as discussed elsewhere (4.4.1.11).
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. A detailed study of the SPC kinetics was conducted to clarify such effects. Several techniques – optical transmission microscopy (OTM), Raman, UV reflection (UV-R), and X-ray diffraction (XRD) spectroscopes, 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 [4.4.1.17, 4.4.1.18].

Representative SPC kinetics for Si films deposited by different techniques (PECVD, e-beam, and hybrid) at different temperatures based on the UV-R measurements are shown in Figure 4.4.1.5. 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.

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. The Arrhenius plots are shown in Figure 4.4.1.6. The Ea calculated from the plots are 3.0 and 3.3 eV (e-beam), and 2.7 and 3.2 eV (PECVD), and 2.8 and 3.2 eV (hybrid) 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 less than 3.0 eV for the incubation is significantly smaller than ~3.4 eV previously found [4.4.1.20]. 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 Figure 4.4.1.7, where the grain boundaries were enhanced by Secco etching. The SEM images of the fully crystallized and Secco etched e-beam poly-Si films for different SPC temperatures. Performance parameters of the poly-Si thin film solar cells obtained by integration of the EQE curves over the AM1.5G solar spectrum, from Suns-Voc measurements, and C-V analysis. All cells have an area of 2 cm².

<table>
<thead>
<tr>
<th>Films</th>
<th>Method</th>
<th>Incubation Time [min]</th>
<th>Crystallisation Time [min]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>600°C</td>
<td>640°C</td>
</tr>
<tr>
<td>OTM</td>
<td>300</td>
<td>50</td>
<td>16</td>
</tr>
<tr>
<td>Raman</td>
<td>360</td>
<td>50</td>
<td>12</td>
</tr>
<tr>
<td>XRD</td>
<td>270</td>
<td>62</td>
<td>16</td>
</tr>
<tr>
<td>UV-R</td>
<td>270</td>
<td>50</td>
<td>14</td>
</tr>
<tr>
<td>Average</td>
<td>300</td>
<td>53</td>
<td>14</td>
</tr>
<tr>
<td>OTM</td>
<td>300</td>
<td>35</td>
<td>11</td>
</tr>
<tr>
<td>Raman</td>
<td>300</td>
<td>32</td>
<td>10</td>
</tr>
<tr>
<td>XRD</td>
<td>270</td>
<td>31</td>
<td>12</td>
</tr>
<tr>
<td>UV-R</td>
<td>270</td>
<td>31</td>
<td>9</td>
</tr>
<tr>
<td>Average</td>
<td>285</td>
<td>32</td>
<td>10</td>
</tr>
<tr>
<td>OTM</td>
<td>300</td>
<td>45</td>
<td>14</td>
</tr>
<tr>
<td>Raman</td>
<td>360</td>
<td>40</td>
<td>12</td>
</tr>
<tr>
<td>XRD</td>
<td>270</td>
<td>60</td>
<td>15</td>
</tr>
<tr>
<td>UV-R</td>
<td>270</td>
<td>45</td>
<td>12</td>
</tr>
<tr>
<td>Average</td>
<td>300</td>
<td>48</td>
<td>13</td>
</tr>
</tbody>
</table>

Generic equation [4.4.1.19]

\[ 1/\text{time} = \text{constant} \times \exp(-Ea/kT) \]

Performance parameters of the poly-Si thin film solar cells obtained by integration of the EQE curves over the AM1.5G solar spectrum, from Suns-Voc measurements, and C-V analysis. All cells have an area of 2 cm².

<table>
<thead>
<tr>
<th>Films</th>
<th>Method</th>
<th>Incubation Time [min]</th>
<th>Crystallisation Time [min]</th>
</tr>
</thead>
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<td></td>
<td></td>
<td>600°C</td>
<td>640°C</td>
</tr>
<tr>
<td>PECVD</td>
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<td>50</td>
<td>16</td>
</tr>
<tr>
<td>E-beam</td>
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<td>50</td>
<td>12</td>
</tr>
<tr>
<td>UV-R</td>
<td>270</td>
<td>62</td>
<td>16</td>
</tr>
<tr>
<td>Hybrid</td>
<td>270</td>
<td>50</td>
<td>14</td>
</tr>
<tr>
<td>Average</td>
<td>300</td>
<td>53</td>
<td>14</td>
</tr>
</tbody>
</table>

![Image](image-url)
The Raman peak shift and FWHM for emitter seed layers of different thickness and with different P doping. TABLE 4.4.1.3

<table>
<thead>
<tr>
<th>Thickness, nm</th>
<th>Intrinsic P BE18, cm⁻¹</th>
<th>P 1E20, cm⁻¹</th>
<th>P 3E20, cm⁻¹</th>
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<tbody>
<tr>
<td>50</td>
<td>517.7</td>
<td>517.6</td>
<td>517.4</td>
</tr>
<tr>
<td>100</td>
<td>518.4</td>
<td>517.3</td>
<td>517.0</td>
</tr>
<tr>
<td>200</td>
<td>518.5</td>
<td>518.3</td>
<td>518.5</td>
</tr>
</tbody>
</table>

All performance parameters of the poly-Si thin-film solar cells degrade for higher SPC temperatures but to a different extent (Table 4.4.1.2). The PECVD cells are most affected, with the pseudo efficiency decreasing from 4.6% to 3.1% for SPC temperatures of 600°C and 680°C respectively. The e-beam and hybrid cell pseudo-efficiencies decrease more modestly, from 4.9% to 4.2% for the same SPC temperatures. There is hardly any loss in the e-beam and hybrid cell performance after SPC at 640°C but it allows shortening the SPC time from typical 20 hrs to only 2 hrs. It makes 640°C a preferred SPC temperature for such cells, particularly for process development purposes when 0.1-0.2% loss in the efficiency is not 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 3 min, while a similar Voc effect can be achieved at 1050°C for only 50 s. Following this trend, it can be estimated that, at temperatures near the Si melting point (1414°C), the optimum annealing times can be of order of a few milliseconds, because of the very high thermal diffusion length in glass is of an order of tens of microns only after SPC [4.4.1.21]. If it is used as a seed layer followed by solid-phase epitaxy (SPE) of the absorber and BSF layers, it can help to improve the quality of the cell poly-Si material and to lead to better cell performance. To find preparation conditions that result in better seed layer properties a series of films was fabricated with different P concentrations and thickness. The seed layer quality was assessed by Raman (Table 4.4.1.3) and UV-R spectroscopy and the Hall mobility (Table 4.4.1.4). The best quality is found for the thickest seed layer of 200 nm and intermediate P concentration of 1e20 cm⁻³. Using the optimised emitter seed layers high crystal quality poly-Si cell structures were grown by SPE as confirmed by the 98% Quv quality factor (Figure 4.4.1.9).

### 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 smearing 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 3 min, while a similar Voc effect can be achieved at 1050°C for only 50 s. Following this trend, it can be estimated that, at temperatures near the Si melting point (1414°C), the optimum annealing times can be of order of a few milliseconds, because of which this type of processes are generally called “millisecond annealing” [4.4.1.22]. Very importantly, for such short times the thermal diffusion length in glass is of an order of tens of microns only [4.4.1.23], which means the bulk of the glass stays
cold resulting in less distortion and lower thermal budget for the annealing process.

Two recently available techniques, which allow heating a few micrometers thick Si film up to its melting point within a few millisecond long time are diode lasers and flash lamps [4.4.1.22, 4.4.1.24]. 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.

Initial experiments on effects of millisecond annealing of poly-Si cell structures have been conducted using either the UNSW diode laser (LIMO450-12x0.3) or the flash lamp system provided by external collaborators (Research Center Forschungszentrum Dresden-Rossendorf, Dresden, FZD). In the very first tests the Si film samples developed severe cracking and even delamination after diode laser treatments at room temperature, so all following experiments were performed at elevated glass temperatures from 550°C to 700°C. A Voc increase up to about 60 mV has been observed for poly-Si film samples on both planar and textured BSG as well as SLG for the exposures between 3 and 20 ms (Tables 4.4.1.5 and 4.4.1.6). It is only slightly lower than the Voc increase of about 75 mV typical for the standard RTA treatment at 950-1000°C for tens of seconds.

### 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 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 Figure 4.4.1.10 and described elsewhere [4.4.1.11].

One of 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 BSF layer through small vias photolithographically defined in the silica film (Figure 4.4.1.11). When the PECVD cells are fabricated on the AIT glass and metallised using such a point contacted rear-surface structure they possess enhanced light-trapping and achieve both high Jsc of 29 mA/cm² and record efficiency of 9.3% [4.4.1.7].

The measured I-V curve of the record cell together with the other important cell parameters is illustrated in Figure 4.4.1.12. The measurements were apertured to 4.0 cm² area and a NREL calibrated cell was used as a reference.

---

**TABLE 4.4.1.5**

<table>
<thead>
<tr>
<th>Power density, kW/cm²</th>
<th>Exposure, ms</th>
<th>Temperature, °C</th>
<th>Voc, mV</th>
<th>Voc change, mV</th>
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<tbody>
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<td>10.3</td>
<td>3</td>
<td>550</td>
<td>354</td>
<td>433</td>
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<tr>
<td>10.0</td>
<td>3</td>
<td>600</td>
<td>336</td>
<td>418</td>
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<tr>
<td>1.1</td>
<td>150</td>
<td>550</td>
<td>261</td>
<td>347</td>
</tr>
<tr>
<td>1.1</td>
<td>150</td>
<td>600</td>
<td>257</td>
<td>344</td>
</tr>
<tr>
<td>0.8</td>
<td>360</td>
<td>550</td>
<td>283</td>
<td>364</td>
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<tr>
<td>0.8</td>
<td>360</td>
<td>600</td>
<td>283</td>
<td>365</td>
</tr>
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</table>

**TABLE 4.4.1.6**

<table>
<thead>
<tr>
<th>Glass</th>
<th>Power density, kW/cm²</th>
<th>Exposure, ms</th>
<th>Pulse shape</th>
<th>Temperature, °C</th>
<th>Voc, mV</th>
<th>Voc gain, mV</th>
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<td>SLG planar</td>
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<td>20</td>
<td>Gaussian</td>
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<tr>
<td>BSG planar</td>
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<td>3</td>
<td>Gaussian</td>
<td>700</td>
<td>407</td>
<td>40</td>
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<tr>
<td>BSG textured</td>
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<td>20</td>
<td>Structured</td>
<td>700</td>
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<tr>
<td>BSG textured</td>
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<td>20</td>
<td>Gaussian</td>
<td>700</td>
<td>425</td>
<td>54</td>
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</table>
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 [4.4.1.1]. However, the deposition of the precursor a-Si films by currently conventional PECVD has been identified as having high cost and a low throughput due to its low deposition rate (25-35 nm/min) and the high equipment cost [4.4.1.3]. Si evaporation by electron beam (e-beam) 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 and the poor textured cell performance [4.4.1.25, 4.4.1.26]. 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-Si:H 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, 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 films. Using a conventional 13.56 MHz PECVD system and a process optimised for the SPC application, much higher deposition rates up to 265 nm/min have been demonstrated as shown in Figure 4.4.1.13 [4.4.1.7].

Raman microprobe characterisation of the poly-Si films obtained after SPC from the high rate PECVD a-Si:H material confirms an identical crystal quality to that of the standard rate poly-Si as shown in Figure 4.4.1.14.

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 4.4.1.7.

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 [4.4.1.9]. Figure 4.4.1.15 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 Figure 4.4.4.16. 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.
PECVD thin-film cell (prior to interconnection, encapsulation) and module (after interconnection, encapsulation) electrical properties.

**Table 4.4.1.8**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Details</th>
</tr>
</thead>
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<tr>
<td>Glass</td>
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</tr>
<tr>
<td>AR coating</td>
<td>SiN (<del>75 nm, n</del>2.1)</td>
</tr>
<tr>
<td>Emitter</td>
<td>n+ (<del>100 nm, P, 5e19</del>1e20 cm⁻³, 400~500 W/sq)</td>
</tr>
<tr>
<td>Base</td>
<td>p (<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>Diffuse white paint</td>
</tr>
</tbody>
</table>

**Typical design parameters of the UNSW E-beam Si cells.**

---

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 > 1x10⁻⁴ Torr, pressure during Si evaporation > 1x10⁻³ Torr), e-beam evaporation is a cost effective Si deposition method for the thin-film PV applications (Figure 4.4.1.18).

The thin-film group at UNSW has been researching e-beam Si thin-film cells since 2004, 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 2 cm² area 6% efficient cells. Figure 4.4.1.19 illustrates the progress with the efficiencies of the e-beam cells and Table 4.4.1.9 summarises the design features of the cells typically fabricated at UNSW. The cells are also made with the reverse polarity structure, i.e. the p-type glass side emitter, and the n-type absorber and air-side BSF layers.

During 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 up to 500 mV were measured by the Suns-Voc technique on the non-metallised cells. More recently the focus has 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.
Performance parameters of e-beam cells with different absorber doping densities.

TABLE 4.4.1.11

<table>
<thead>
<tr>
<th>Doping (cm⁻³)</th>
<th>Vₜ (mV)</th>
<th>FF (%)</th>
<th>Jₛ (mA/cm²)</th>
<th>Rₛ (Ωcm²)</th>
<th>Eff (%)</th>
<th>pEff (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.7×10¹⁴</td>
<td>413</td>
<td>64.1</td>
<td>19.2</td>
<td>2.0</td>
<td>5.09</td>
<td>5.5</td>
</tr>
<tr>
<td>5.7×10¹⁴</td>
<td>418</td>
<td>61.9</td>
<td>17.6</td>
<td>3.4</td>
<td>4.67</td>
<td>5.3</td>
</tr>
<tr>
<td>1.0×10¹⁵</td>
<td>449</td>
<td>62.5</td>
<td>6.5</td>
<td>7.9</td>
<td>2.16</td>
<td>2.5</td>
</tr>
<tr>
<td>5.3×10¹⁵</td>
<td>403</td>
<td>54.4</td>
<td>4.0</td>
<td>19</td>
<td>1.04</td>
<td>1.3</td>
</tr>
</tbody>
</table>

The dopant concentration was determined using the Z-analysis technique described elsewhere [4.4.1.27]. 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 4.4.1.11. 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.

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 Vₜ 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 1e15/cm³ and 5e15/cm³. Figure 4.4.1.21 shows the effect of the doping densities on the key cell parameters.

Role of back surface filed

The BSF is very important for the poly-Si solar cell. Besides transporting the holes to the metallic contacts, it also repels the electrons from the rear cell surface thus reducing recombination at this interface. In fact, this effect is crucial for the poly-Si thin-film device as shown in Figure 4.4.1.15. Without the BSF the Vₜ of the cell is reduced from 435 mV to only 270 mV. Increasing the BSF thickness from 30 to 90 nm decreases the sheet resistance by a factor 3 (as expected) but does not impact the Voc of the device as presented in Figure 4.4.1.22. Increasing the deposition rate of the BSF has a positive effect on the Voc. The Voc increases by 40 mV when the deposition rate increases from 5 A/s to 10 A/s.

The best efficiency reported previously for the poly-Si cell with the identical metallisation was 5.2% with a voltage of 435 mV [4.4.1.13]. The development of the high rate BSF clearly improved...
the voltage. The I-V curves data of the solar cells with and without a BSR are presented in Figure 4.4.1.23. The poly-Si solar cells with a white paint BSR has a conversion efficiency of 6.3% with Voc=479 mV, FF=66% and Jsc=20.1 mA/cm². The BSR increases the Jsc by 5.3 mA/cm² and decreases the FF by 2% due to the increase of Jsc and (increase of ohmic losses in the metallization).

Light-trapping in e-beam poly-Si thin-film cells
Poly-Si thin-film solar cells need effective light-trapping to compensate for the moderate absorption. This is typically achieved by glass substrate texturing for PECVD cells. However, evaporated poly-Si cells are not compatible with textured glass due to low density material grown on textured substrates as shown in Figure 4.4.1.24. A cross-sectional FIB investigation of the evaporated Si films on the textured glass reveals noticeable morphological differences from the films on the planar glass. 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, 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. Clear experimental evidence for the columnar microstructure and the low density void network present in the SPC poly-Si films was recently reported [4.4.1.26]. 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 Figure 4.4.1.25. 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 an 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 or a completely different approach, the localized surface plasmon (LSP) enhanced light-trapping. The different structures are presented in Figure 4.4.1.26.
The plasmonic light-trapping relies on scattering by Ag nanoparticles as shown in Figure 4.4.1.27 [4.4.1.28]. Such nanoparticles can be relatively simply formed by depositing a 5–30 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 irregularly shaped particles. The AFM profile and SEM image of the Ag nanoparticles on a poly-Si film are presented in Figure 4.4.1.27.

The silicon back texture can be simply made by etching the silicon film in a KOH solution. After a few seconds, pyramids formation appears as presented in Figure 4.4.1.28. The roughness is typically around 100 nm whereas the roughness of the nanoparticles is around 15 nm. This demonstrates the different mechanism of light scattering involved into the two methods.

The optimisation of the two approaches is currently ongoing at UNSW. The best developed process for plasmonic light-trapping uses a Ag nanoparticle array formed from 16 nm thick precursor Ag film directly on the poly-Si cell coated with a 350 nm thick MgF₂ layer, with a white paint BSR on the top, a spacing layer between the nanoparticles and the back reflector, typically 350 nm of MgF₂ (Figure 4.4.1.29) [4.4.1.6]. The Jsc enhancement due to the plasmonic light-trapping is 44%.

The Si-back texture can be made by wet chemical etching, plasma etching, or a combination of both. The current gain achieved due to the Si-back texture is about 66%, significantly higher than the gain due to the plasmonic light-trapping (Figure 4.4.1.30).

For the planar cells the Ag nanoparticles provide the best Jsc enhancement of about 48% on average (Jsc ~21 mA/cm²) (the best cell enhancement is 50%) followed by the double P150DW and the white paint. For the textured cell one has to note a lot higher Jsc (~24 mA/cm²) compared to the planar cells even without any BSR due to excellent light trapping providing by the random glass texture. The enhancement due to BSRs are very modest with the white paint performing the best. The Ag nanoparticle BSR is not tested for the textured cells because nanoparticles cannot be formed on the textured surface.
4.4.1.10 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 Voc 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 merit 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]. While the grain boundary recombination can be 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 research at UNSW 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.

As a result of a comprehensive study of the poly-Si on glass solar cell characteristics (Suns-Voc, EQE) and film properties over a range of temperatures and absorber dopant concentrations, a concept consistent with experimental observations, which describes the dominant recombination in poly-Si has emerged [4.4.1.31, 4.4.1.32, 4.4.1.33, 4.4.1.34]. According to the concept, the carrier recombination in poly-Si on glass solar cells can be modelled as a superposition of two processes. The first one involves the electronic transition between shallow states which are 0.05-0.07 eV below the conduction band and 0.06-0.09 eV above the valence band, respectively, which are consistent with the shallow bands at silicon dislocations (Figure 4.4.1.32a). The second process occurs via deep levels at charged defects. The shallow band recombination dictates the solar cell properties over the entire practical absorber doping range of 5E15~1E17 cm⁻³; the deep level recombination originates from either charged dislocations or grain boundaries and only becomes influential at dopant concentration lower than ~5E15 cm⁻³ (Figure 4.4.1.32b).
In the ideal sc-Si the diode saturation current \( J_0 \) follows the Arrhenius law with the activation energy \( E_a \) equal to the Si bandgap when extrapolated to 0K. The short-circuit current density, \( J_{sc} \), in sc-Si is only very weakly dependent on the temperature (due to the effect of band-gap variation). However, poly-Si solar cells exhibit different characteristics [4.4.1.31]. The Arrhenius plots for \( J_0 \) of poly-Si solar cells have distinctively a smaller slope, which reflects a lower \( E_a \) associated with \( J_0 \) by 0.15-0.18 eV. As a consequence, the \( V_{oc} \) plots versus \( T \) extrapolated to 0K have a lower intercept in the range 1.0~1.1 eV as compared to sc-Si solar cells (Figure 4.4.1.33a, b). The Arrhenius plots for \( J_{sc} \) of poly-Si solar cells have distinctively a smaller slope, which reflects a lower \( E_a \) associated with \( J_{sc} \) by 0.15-0.18 eV. As a consequence, the Voc plots versus \( T \) extrapolated to 0K have a lower intercept in the range 1.0~1.1 eV as compared to sc-Si solar cells (Figure 4.4.1.33a, b). The Arrhenius plots for \( J_{sc} \) of poly-Si solar cells whose absorber diffusion length is shorter than the absorber thickness have steeper slopes indicating stronger temperature dependence of the poly-Si cell current (Figure 4.4.1.33c).

Although the smaller \( E_a \) and the intercept could in principle be due to the narrower band gap in poly-Si material as compared to c-Si, it cannot explain the temperature sensitivity of \( J_{sc} \). On the other hand, both effects are consistent with existence of shallow sub-bandgap states acting as either minority carrier traps or recombination centres.

Further confirmation of the shallow-level related recombination in poly-Si solar cells comes from the study of the bulk lifetimes as a function of temperature which allows 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). The EQE measurement and fitting procedure were repeated for each sample at different temperatures ranging from 120K to 320K. Figure 4.4.1.34 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.

Figures 4.4.1.35 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 (\( E_a \)) of 0.17-0.21 eV near room temperature [4.4.1.32]. These activation energies...
are much larger than those reported for plastically deformed Si and multicrystalline Si [4.4.1.35], where the dominant recombination is thought to be via transitions between the shallow and deep levels. Assuming direct transitions between shallow levels, the Ea is expected to be \((E_c - E_{nv}) + (E_{nv} - E_v) + 2.5kT = 180\sim 120\) meV (where \(E_{nv}\) and \(E_v\) are shallow band energies near the conduction and the valence bands respectively), which is in remarkable agreement with the experimental values.

Furthermore, as a consequence of electron transitions between the shallow bands, the recombination rate becomes proportional to the concentrations of both minority and majority carriers, as in the case of radiative recombination, in contrast to recombination via deep levels, where the rate is proportional to the minority carrier concentration only. This leads to minority carrier lifetime inversely proportional to the majority carrier concentration, or roughly to the dopant concentration [4.4.1.32]. The experimental confirmation of this effect is shown in Figure 4.4.1.36 which plots the minority carrier lifetimes in a number of poly-Si solar cells versus the dopant density. There is a clear inverse relationship between the lifetime and dopant density.

Amongst the n-type cells in Figure 4.4.1.35b, 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 an 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 Figure 4.4.1.36 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 in fact, of the two rightmost triangle data points representing AIC cells at about 5E16 cm\(^{-3}\) doping in Figure 4.1.1.36, the higher lifetime point originates from (100) preferentially oriented material and the lower lifetime point comes from (111) preferentially oriented material.

All the above evidence points at intragrain defects, as a likely limit on poly-Si thin-film cell lifetimes. In particular, dislocations are the most likely candidates because they provide the strain fields necessary to create split-off states from the band edges that can act as shallow levels [4.4.1.36]. To estimate dislocation density in poly-Si solar cells a TEM study was conducted using the Weak-Beam-Dark-Field (DFWB) technique. An example image is shown in Figure 4.4.1.37 and the dislocation density deduced by the image analysis is in the order of 1E10 cm\(^{-2}\). There is very rough correlation between the dislocation density found in poly-Si solar cells and the cell Voc. The best cells with Voc > 500 mV have dislocation density of 6~8x10\(^9\) cm\(^{-2}\), while for the cell with very poor Voc < 450 mV the dislocation density is about 1.5x10\(^10\) cm\(^{-2}\) [4.4.1.37].

As the dopant density decreases, the shallow band recombination gradually becomes less and less significant and eventually, at sufficiently low dopant densities, less than about 5x10\(^15\) cm\(^{-3}\) the recombination involving deep levels starts to dominate (process 2 in Figure 4.4.1.32a). Such deep levels are associated with defects concentrating in dislocations and grain boundaries. The defects are usually charged to the same polarity as the majority carriers thus creating potential barriers which attract the minority carriers. The lifetime in this case depends on the potential barrier heights, which become greater with lowering dopant density.
The effect of recombination via deep levels at charged defects is to place an upper limit on the minority carrier lifetime (thus the cell Voc). Figure 4.4.1.38 shows Voc simulation results of poly-Si solar cells where two recombination processes in the absorber, both via shallow bands and via deep levels, taking place in parallel. Above $1 \times 10^{10}$ cm$^{-2}$ doping, the Voc is fairly constant and approaches the 485 mV limit corresponding to the case where only shallow band recombination occurs. Below $1 \times 10^{10}$ cm$^{-2}$ doping, deep level recombination becomes influential to the device performance eroding the Voc by about 21 mV when the doping reaches $1 \times 10^{11}$ cm$^{-3}$. Thus, in the practically significant dopant concentration range of $5 \times 10^{15}$ to $5 \times 10^{16}$ cm$^{-3}$, an immediate challenge to consistently raising the Voc above 500 mV is to reduce the dislocation density to below the $1 \times 10^{7}$ cm$^{-2}$ level. If and when this is achieved the next step to even higher Voc is minimisation of charged defects likely associated with impurities.

4.4.1.11 References


4.4.1.30 J. Wong, J. Huang, S. Varlamov, M. Green, R. Evans, M. Keevers, R. Egan, “Structural inhomogeneities in polycrystalline silicon on glass solar cells and their effects on device characteristics”, Progress in Photovoltaics, 2011, DOI: 10.1002/pip.1089.


4.4.1.34 J. Wong, J. Huang, S. Varlamov, M. Green, “The roles of shallow and deep levels in the recombination behaviours of polycrystalline silicon solar cells”, Progress in Photovoltaics, 2011, in press.
4.4.2 Organic Thin Films

4.4.2.1 Introduction

A new organic photovoltaic (OPV) research lab has been established at Level-10 in the UNSW Chemical Science Building to accommodate work on organic semiconductor materials and OPV devices. Today this lab is equipped with basic facilities organised with support from an ARC Discovery Grant, UNSW equipment grant, a family grant from the Green family, a Faculty grant and with the support of the ARC Photovoltaic Centre of Excellence. Currently, the research team consists of three academics, two research fellows, one research assistant, 6 PhD, one M.Eng. and 8 honours students.

We have already produced some meaningful data from our research work. Two journal papers, three conference proceeding papers and one patent are already in preparation. The nanoscale texture or thin film morphology of the donor/acceptor blends used in most OPV devices is a critical variable that can dominate both the performance of new materials being optimized in the lab and efforts to move from laboratory-scale to factory-scale production. Although OPV conversion efficiencies (up to 8.3%) have improved significantly in recent years, progress in morphology optimization still occurs largely by trial and error, in part because much of our basic understanding of how nanoscale morphology affects the optoelectronic properties of these heterogeneous organic semiconductor films has to be inferred indirectly from macroscopic measurements. The morphology of the active film is a very important factor in producing high efficiency devices.

Films spin-coated from blend solutions undergo separation of the donor/acceptor phases. The scale of the phase separation depends on the solvent, solubility of the materials and parameters of the spin-coating process such as the spin speed and temperature. If the morphology could be controlled on a molecular scale the efficiency of charge separation and transport could be expected to be substantially higher. Now we are working for the morphology optimization of organic films for OPV devices in respect to fundamental issues such as light trapping, control of electronic structure at films interfaces, exciton dissociation and carrier transport for photovoltaic operation to achieve our goals.

The detailed physical understanding of OPV devices still lags behind their application, on account of fundamental differences in the optoelectronic properties of organic materials compared to conventional semiconductors. This lack of understanding limits the scope of material and device design. Among those features that distinguish OPV devices from inorganic semiconductor based devices are: (i) the charges and excited states are localized on individual molecules or molecular segments, with the result that charge and energy transport processes are relatively slow; (ii) the dielectric permittivity is low, leading to stronger space charge effects; (iii) the organic semiconductor materials are electronically disordered, dispersing the rates of charge transfer and transport processes; (iv) the active layers are often heterogeneous, either as multi-component films or because of nonuniform molecular ordering; and (v) the organic semiconductor is usually not doped, thus precluding the conditions that allow charge dynamics to be linearized in the description of device physics. The need for appropriate device
physics for organic semiconductor materials is of particular relevance to the organic bulk heterojunction solar cell.

4.4.2.2 OPV Conversion Efficiency

Interest in OPV with increasing conversion efficiency has grown exponentially over recent years. The key development in the OPV device is the bulk heterojunction cell [4.4.2.1] 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), then 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, after review by a team that includes one of the present team members [4.4.2.2].

Using the above structure, Konarka, USA established 4.8% efficiency for a tiny 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 achieved 7.9% efficiency in December 2009 [4.4.2.3]. In November 2010, Konarka achieved their highest OPV efficiency 8.3%.

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 [4.4.2.4]. The transport of excitons to the interface also limits the conversion efficiency of OPV. The details of the exciton transport mechanism in OPV are still not well understood. There is a need for more systematic study to gain in-depth understanding of the mechanisms of light absorption, exciton 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. Figure 4.4.2.2(b) shows the two examples of donor/acceptor blending design (left) and systematic alignment of donor and acceptor layers for bulk-heterojunction organic solar cells.

We believe that the conversion efficiency of OPV can be increased to over 10% for possible commercial applications through in-depth understanding of the light harvesting behaviour of organic materials and by selecting suitable materials and new device architectures.

4.4.2.4 Active Layer Annealing

Thermal annealing is an effective method that increases the polymer crystallinity and improves the phase segregation of donor and acceptor domains. The surface morphology is also affected by annealing as shown in Fig. 4.4.2.3. Usually, as-cast P3HT:PCBM films have a featureless and
homogeneous surface, while annealing produces a coarser textured surface with obvious phase segregation. The majority of device studies on P3HT:PCBM blends utilize annealing to increase device efficiency. This is believed to be due to changes in both the morphology of the active layer whereby P3HT and PCBM self-organize into nanoscale domains as well as the better intermolecular alignment of the P3HT giving higher hole mobilities.

In our studies, we have found that annealing the device after the application of the cathode improves the efficiency of the device much more significantly that annealing before the cathode deposition. The reason for this is believed to be reduced mobility of the PCBM molecules under the increased confinement of the cathode. In our studies we have explored a range of anneal temperatures and find that the optimum annealing temperature depends upon the blend ratio, and in general lies in the range of 120°C to 150°C. The optimum anneal temperature for our blend appears to be ~125°C (for 15 minutes) – a value subsequently used in the remainder of the optimization experiments detailed below. An improved transport property of the active layer is also observed which leads to a reduced series resistance and in turn a better device performance. Recently, microwave annealing has been proposed as an alternative thermal treatment method [4.4.2.5].

Figure 4.4.2.4 shows the absorbance spectra of the blended active layer of P3HT/PCBM, annealed at different temperature and for different durations. The absorbance spectra almost remain the same under all annealing temperatures and times. However, the intensity of the spectra changes. As mentioned, the optimum annealing temperature was found as 125°C for 15 minutes for the best quality layer.

We have started to fabricate our OPV cells with average Voc = 0.6 V, FF = 70 % and Jsc = 10 mA/cm². The average conversion efficiency is around 3 - 4%. The measured Voc of our OPV devices as a function of light intensity is shown in Figure 4.4.2.5.

We have used different types of P3HT to fabricate our OPV cells. Their corresponding Voc and FF are recorded in Table 4.4.2.1.

4.4.2.5 Light Trapping in OPV
Given the high absorption coefficient of organic materials, 100 nm thick organic layers are typically sufficient to absorb most of sunlight. The diffusion length of excitons in the organic materials is typically in the range of 5–10 nm. A partial solution to the problem of low charge carrier and exciton mobility is the reduction of the active layer thickness, that also implies the loss of a large fraction of the impinging light. The use of a light trapping system has been actively investigated to increase the total path length of light into the active material without needing to increase its physical thickness. The concept is to induce sunlight to travel a longer distance in the active layer by a multi-pass path in order to exploit most of the radiation.

Many different light trapping schemes have been proposed to enhance the quantity of light absorbed in OPV cells such as metal gratings [4.4.2.6], buried nanoelectrodes [4.4.2.7] and multireflection structures [4.4.2.8]. However, the requirement that the feature sizes of the scattering structures be comparable to the film thickness of the OPV cells, i.e., 50–300 nm, and at the same time larger than the wavelength of light to effectively alter the photon propagation direction is intrinsically contradictory. The electrical properties can be negatively affected by the introduction of light scattering elements in direct contact with such thin active layers: defects and shorts may easily occur. Alternate approaches
in improving absorption efficiency have exploited the properties of surface plasmons (SPs). SPs are electromagnetic surface waves confined to a metal-dielectric interface by coupling to the free electron plasma in metals [4.4.2.9]. The evanescent nature of SPs permits the manipulation and enhancement of optical fields below the diffraction limit, allowing the use of thin OPV layers without sacrificing their absorption potential. The integration of plasmonic structures with OPVs has been previously examined in the context of metallic nanoparticles, which can be used to increase optical absorption. We have also started working on the plasmonic light trapping system to increase the efficiency of our OPV cells.

4.4.2.6 Simulation Work

The Centre has purchased an upgrade of the Gaussian Density Functional Theory (DFT) program package to Gaussian09. We 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 include 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. 4.4.2.7) presently rated at 1080 gigaflops. We 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 include 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. 4.4.2.7) presently rated at 1080 gigaflops.

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 becoming attractively interesting in recent years. The solubility of the n-type and p-type components is an important parameter in the construction of hybrid solar cells processed from solutions.

4.4.2.7 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. 4.4.2.8. 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. 4.4.2.9.

Progress to date is reported elsewhere [4.4.2.11]. 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.

4.4.2.8 Poly-Si/Organic Hetero-Junction Cell

Recently organic/inorganic hetero-junction thin films solar cells have gained importance for their cost-effective potential applications [4.4.2.12]. The combination of hydrogenated amorphous (a-Si:H) and/or poly-silicon (poly-Si:H) and organic materials is very attractive for organic and inorganic hybrid device applications. Organic/inorganic hetero-junctions have generated a great interest for their potential in developing hybrid devices as well as to understand organic semiconductors and their interfacial properties. We are also investigating the possibility of poly-Si/organic hybrid solar cells. Figure 4.4.2.10 shows the absorption spectra of poly-Si/PEDOT:PSS/P3HT on glass substrate compared with the absorption spectra of c-Si/PEDOT:PSS/P3HT structure.

4.4.2.9 References


4.4.2.3 http://www.solarmer.com


Absorption spectra of poly-Si/PEDOT:PSS/P3HT on glass substrate compared with absorption spectra of c-Si/PEDOT:PSS/P3HT structure. FIGURE 4.4.2.10

Schematic of the LB apparatus used to fabricate a monolayer of encapsulated nanoparticles. FIGURE 4.4.2.8

Si nanoparticle encapsulated with organosilanes. FIGURE 4.4.2.9
4.4.3 Earth-Abundant Photovoltaic Devices (CZTS)

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4.4.3.1 Strand Outline
All successfully commercialised non-concentrating photovoltaic technologies to date are based on silicon or the chalcogenides (semiconductors containing Group VI elements, specifically Te, Se and S). As indicated by Figure 4.4.3.1, the successful chalcogenide materials, CdTe and CuInSe2, can be regarded as “synthetic silicon” where the balance between atoms in these materials provides the same average number of valence band electrons as in silicon.

Unfortunately Cd and Se are toxic “heavy metals” while Te and In are amongst the 12 most rare elements in the Earth’s crust, factors that would seem to limit the long-term potential of the established chalcogenide technologies. However, as indicated in Figure 4.4.3.1, by investigating more deeply into the Periodic Table, the compound Cu2ZnSnS4 is uncovered with the same number of valence band electrons as in silicon.

Although the potential of this material is relatively unexplored for photovoltaics, initial results have been promising with a group at IBM reporting 9.7% efficiency for small cells based on related materials (alloy of the above sulphide and the corresponding selenide). The appearance of the cells involved (Fig. 4.4.3.2) is quite close to the appearance of cells made using CIGS technology (CulnSe2, plus CuGaSe2, alloy).

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

4.4.3.2 Simplified fabrication of CZTS thin film cells
Though various approaches have been applied to fabricate CIGS solar cell, CIGS with the highest efficiency (up to 20.3% so far) have been achieved by the physical vapour deposition (PVD) approach, with the first 10% efficient cell demonstrated in 1980, the first 15% cell in 1993 and the first 20% cell in 2008. As a substitute for CIGS thin film solar cells, CZTS has many similarities to CIGS as mentioned above. As such, it is logical that the full potential of high efficiency CZTS thin film solar cells will be extracted using the PVD approach.

Though a major milestone was reached at the end of 2009 with the demonstration of 9.7% CZTS efficiency (some Se also in device) by a research team at IBM by a “hydrazine-based solution” approach [4.4.3.2], solution growth is believed inherently incapable of giving the material control required for best-possible performance. Evidence for this arises in the similar case of CIGS where the same IBM team holds the record of 12.2% efficiency for solution-deposited CIGS (again hydrazine–based) [4.4.3.2], while in contrast the PVD approach gives 20.3% efficiency.

Evaporation and sputtering are the two most important PVD techniques. The disadvantage of evaporation is that it is very difficult to control the Cu evaporation source; and the lack of commercially available equipment for large area thermal evaporation. In contrast, magnetron sputtering is
a more attractive process because large area/high rate sputtering is a better developed technique than evaporation. In addition, sputtering has commercially available equipment that gives good uniformity over large areas. UNSW has considerable experience in PVD techniques, such as the achievement of the first silicon quantum dot solar cell on quartz [4.4.3.3], a recent patent relating to crystal Ge on Si wafer by a sputtering technique and the polycrystalline silicon thin film solar cell on glass by an evaporation technique [4.4.3.4].

Almost all of the methods that have been attempted for CZTS fabrication involve two steps; deposition of a metal/metal-sulfide precursor and a subsequent anneal at high temperature in a hydrogen sulphide or elemental sulphur environment to incorporate more sulfur into the film and evolve the correct phase [4.4.3.5-4.4.3.7]. It is reported that the H2S/sulphur anneal is a destructive process that can potentially introduce defects into the film due to the out-diffusion of metals. In addition, for large scale production of solar cells, a direct one-step, large area deposition process is preferred.

Fortunately, reactive sputtering is a well suited technique because of the above-addressed feature of precise control on the stoichiometry of deposited films over a large area with high uniformity at a relatively low cost. The experience documented in our patent of “A Method of Forming A Germanium Layer On A Silicon Substrate And A Photovoltaic Device Including A Germanium Layer”, where the introduction of H2 gas into the in-situ deposited germanium thin film by magnetron sputtering results in the significant improvement of the performance of germanium thin film, appears highly relevant.

As such, the idea of one-step reactive sputtering by in-situ introducing H2S gas into the deposited CZT (Cu2ZnSn) film is a logical step to attempt a better CZTS film quality. However, there have been few attempts to date at such a simplified one-step process by introducing the sulphide into the CZTS film during in-situ deposition. In addition, this process is not well understood and significantly more effort is required in order to understand growth mechanisms involved in the reactive sputtering process. Comparison of reactively sputtered films with 2-step sulphidisation processes will provide the early emphasis of the Centre’s work.

4.4.3.3 References
4.4.3.5 J.J. Scragg et al., Thin Solid Films, 517 (2009), pp. 2481-2484.
4.4.3.7 Hirorini Katagiri et al., Thin Solid Films, 480-481 (2005), pp. 426-432.