4.5 THIRD GENERATION STRAND – ADVANCED CONCEPTS

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Abstract

There has been approximately equal work on the two major projects in Third Generation in 2010. These are the Group IV nanostructure tandem cells project - the “all-Si” tandem cell - and the Hot Carrier solar cell project, with its continuing funding from GCEP (Global Climate and Energy Project). There has also been further work on Up-conversion and on Plasmonics.

The Si nanostructure work has seen increased understanding of the mechanisms for transport and quantum confinement. More sophisticated modelling of both has been tied more directly to improved interpretation of experimental results. This has led to establishment of a predictive ‘equivalent circuit modeller’ which will allow optimisation of Si QD device parameters to maximise transport and performance in the photovoltaic devices. Improved models for the understanding of doping effects in these materials have also been established. Work on alternate matrices for Si quantum dots, in both silicon nitride and carbide, has seen development of composite structures which have improved transport in the growth direction, whilst maintaining quantum confinement in the plane, but which also increase the uniformity of QD sizes. Work on Ge nanostructures has also improved with high electrical p-type conductivity established for Ge quantum dots and excellent pseudo single crystalline growth quality for Ge quantum wells in a nitride matrix. Heterojunction photovoltaic devices combining the advantages of two of these different material types are now being investigated.

Hot Carrier cells have seen very significant improvement in demonstrated resonance in energy selective contacts using Si nanostructure layers, as well as a development of 2 and 3D modelling of transport in these structures. Modelling of Hot Carrier efficiencies continues to get more sophisticated with application to real material systems such as III-nitrides and inclusion of Auger processes which become significant at high carrier concentrations. Work on absorbers has allowed modelling of the phononic properties of a range of bulk materials, in conjunction with time resolved photoluminescence measurement of carrier cooling in some of these materials. Also modelling of coherent nanoparticle nanostructures, which emulate the phononic properties required, has developed into direct application to structures grown directly. These structures include the
colloidal dispersion of Si nanoparticles, which has seen coherent arrays successfully grown, and growth of III-V quantum dot structures with collaborators, with modelling and characterisation indicating their usefulness as absorbers. The parameters needed for a real hot carrier solar cell are now better defined, and candidates for its structure are now being modelled in more detail. This will feed into fabrication and characterisation of some candidate structures in the near future.

The up-conversion project in 2009 reported the approach of use of porous-Si as a host material for an Erbium upconverter. This has the advantage of much greater versatility in fabrication and electrochemical doping with Er, compared to other host phosphors. Work in 2010 has further demonstrated up-conversion of below band gap photons. The ease of control of porous-Si growth at different refractive indices has also been exploited to create fully integrated multiple Distributed Bragg Reflectors. These allow a tuning of the forbidden photonic band such that regions just outside the bandgap (which have enhanced density of photonic states) lie at the 1500nm absorption window of Er. This effectively concentrates light into this absorbance window and boosts up-conversion quadratically. Enhancements of up to 80 are possible with multiple levels, with a consequent narrowing of the wavelength range enhanced. Enhancements of 40 are very practical. This represents a big potential improvement for up-conversion efficiency.

Plasmonics has previously been applied to both first generation and second generation Si cells with very significant enhancements in absorbance of near band gap photons. Work in 2010 has applied plasmonic silver nanoparticles to nanostructured Si QD layers. Again significant enhancements of photoluminescence (reciprocal with absorption) have been absorbed, up to 16x for wavelengths just shorter than the effective band gap. Also application to the rear of the layer is seen to be better than the front because the reflection of the silver particles themselves is beneficial rather than parasitic. Just as with thin film second generation cells, light trapping by these non-texturing methods is very important for third generation devices, which consist of very thin layers of material.

This progress in all the main Third Generation project areas is improving understanding and allowing optimisation of modelling, structures and devices. Developments to come in the next year will see significant advancement in these areas, with excellent prospects for good demonstration devices.

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 well below US$0.50/W, towards US$0.20/W or better, by dramatically increasing efficiencies but maintaining the economic and environmental cost advantages of thin film deposition techniques (see Fig. 4.1.3 showing the three PV generations) [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 device [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 energy threshold
approaches can utilise some of this lost energy. Such approaches do not in fact disprove the validity of the Shockley-Queisser limit, rather they avoid it by the exploitation of more than one energy level for which the limit does not apply. The limit which does apply is the thermodynamic limit shown in Fig. 4.1.3, of 68.2% or 86.8% (again depending on concentration).

In the Third Generation Strand, we aim to introduce multiple energy levels by fabricating a tandem cell based on silicon and its oxides, nitrides and carbides using reduced dimension silicon nanostructures to engineer the band gap of an upper cell material.

We are aiming to collect photo-generated carriers before they thermalise in the “Hot Carrier” solar cell. Also we are investigating absorption of two below bandgap photons to produce an electron-hole pair in the cell by up-conversion in a layer behind the Si cell using erbium doped host materials.

In order to optimise the requisite properties, all these structures are likely to be thin hence maximising absorption of light in thin structures through light trapping is very important. Hence we are also investigating localised surface plasmon enhanced coupling of light into these Third Generation devices.

4.5.2 Si nanostructure solar cells

4.5.2.1 The “all-Si” Tandem cell

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

Previously we have demonstrated the ability to fabricate materials which exhibit a blue shift in the effective band gap as the QD or QW size is reduced, using photoluminescence [4.5.4] and absorption [4.5.5] data [4.5.6]. A thin film deposition of a self-organised QD nanostructure is achieved through a sputtered multi-layer of alternating Si rich material and stoichiometric dielectric [4.5.4]. On annealing the excess Si precipitates into small nanocrystals which are limited in size by the layer thickness, thus giving reasonable size uniformity, as first demonstrated by Zacharias [4.5.7]. Demonstration of doping of these layers with both phosphorus and boron to create a rectifying p-n junction has resulted in devices with a photovoltaic open circuit voltage of 490mV [4.5.6, 4.5.7, 4.5.8].

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

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

For photovoltaic applications, nanocrystal materials may allow the fabrication of higher band gap solar cells that can be used as tandem cell elements on top of normal Si cells [4.5.11, 4.5.12]. For an AM1.5 solar spectrum the optimal band gap of the top cell required to maximize conversion efficiency is ~1.7 to 1.8eV for a 2-cell tandem with a Si bottom cell [4.5.13]. To date, considerable work has been completed on the growth and characterization of Si nanocrystals embedded in oxide [4.5.7, 4.5.14] and nitride [4.5.15, 4.5.16] dielectric matrices. However, little has been reported on the experimental
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.

**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. 4.5.3, followed by an anneal during which Si nanocrystals precipitate limited in size by the Si rich layer thickness [4.5.12, 4.5.7]. 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.

RF magnetron sputtering is used to deposit alternating layers of SiO₂ and SRO of thicknesses down to 2nm. [SRO refers to Si rich oxide, formed by co-sputtering Si and SiO₂.] Deposition of multi-layers, consisting typically of 20 to 50 bi-layers, is followed by an anneal in N₂ 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 SiO₂, the precipitation occurs according to the following:

$$SiO₂ \rightarrow \frac{x}{2} SiO₂ + \left(1 - \frac{x}{2}\right) Si$$

Precipitation of excess Si from Si rich dielectrics in SiₐNₐ and SiC follows a similar crystallisation reaction as Si precipitates from the amorphous matrix. The techniques has also been applied to growth of Sn and Ge QDs in SiₐNₐ in SiO₂. Ge 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. 4.5.4 different matrices produce different transport barriers between the Si dot and the matrix, with tunnelling probability heavily dependent on the height of this barrier. SiₐNₐ and SiC give lower barriers than SiO₂ allowing larger dot spacing for a given tunnelling current.

$$T_e = 16 \exp \left\{ -d \frac{8m_e^*}{h^2} \Delta E \right\}$$

The results suggest that dots in a SiO₂ 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 [4.5.18]. Hence, transport between dots can be significantly increased by using alternative matrices with a lower barrier height, ΔE. For the same tunnelling current the spacing of QDs can increase for oxide to nitride to carbide matrix.
4.5.2.2.2 Modelling of quantum confinement and tunnelling transport

Researchers: Binesh Puthen-Veetil, Robert Patterson, Dirk König

Band gap engineering for these Si nanostructure materials requires a large number of almost identical quantum dots (QDs), evenly distributed in a dielectric layer. As the proximity of dots increases, confined wavefunctions in the QDs interact with one another to form mini-bands. It is also seen that higher Si content in the Si rich layer gives rise to bigger QDs, due to the tendency of QDs to merge together and form bigger dots during annealing [4.5.12, 4.5.20]. If the dielectric layer is a good diffusion barrier for Si (such as the nitride layer in Si/Si₃N₄ or Si₃N₄ interlayer samples, see sections 4.5.2.3.1 and 4.5.2.3.2), this effect is strongly reduced. For relatively thick layers in which diffusion is not constrained, the shapes of these QDs can differ greatly from an ideal spherical shape. Calculation of confined energy in QD structures is of interest since their electronic and optical properties can be determined by determining the confined energy levels in the structure.

Since these calculations are extremely difficult to perform using ab-initio methods due to the large memory and computation time requirements, we have developed a model to quantitatively analyse electronic states and their interactions in a QD array, in the framework of the effective mass approximation (EMA) calibrated by ab-initio DFT calculations. This model is realized by solving the three dimensional time independent discretized Schrödinger’s equation in the EMA, employing a modified Full Multi Grid method (FMG) [4.5.2.1] to overcome the difficulty of computational intensity.

By using exact solution methods to solve the Eigen equation for the coarsest grid, the non convergence problems [4.5.22] arising from oscillatory eigenvalues are eliminated. Since initial guesses of the solution are very close to the approximate solution, this method proves to be much faster than other iterative methods. The flow diagram for this process is shown in Fig. 4.5.5.

In order to demonstrate the conformity of results from this model with experimental results, we compared it with experimental results for Silicon QDs in SiO₂ dielectric grown using sputtering methods and characterized using photoluminescence (PL) [4.5.20]. Figure 4.5.6 shows the dependency of confined energy on the size of QDs for Si/SiO₂ QD structures. Confined energy increases exponentially as QD size decreases. Comparison shows that for larger QDs experimental and theoretical values are similar, but for smaller dots the experimental results for the confined energy shows a lower degree of confinement than the theoretical result. This difference can be attributed to interface defects between Si and SiO₂ and to defects within the SiO₂ matrix but near the interface. For QDs below a diameter of about 4 nm these interface effects have a larger influence on the confined energy level. This is because the ground state electron density, which is concentrated at the centre of the QD, is closer to these interface defects for the smaller QDs and hence more strongly influenced.

As an extreme example of irregularly shaped QD, we have investigated electronic states in arbitrarily shaped QDs. Here we have used the “horseshoe” morphology [4.5.24], formed by lateral growth of Si QD inside SiO₂ dielectric shown in Figure 4.5.7 (left). These states are found to be very different from the expected electronic energy levels that are associated with spherical QDs as shown in Fig. 4.5.7 (right). The degeneracy in spherical QDs (3 in first excited level and 5 in second excited level) is lost due to the asymmetric shape. The deviation from the expected confinement level becomes significant at higher confined levels.

This thus indicates the importance of knowing the regime of QD growth relevant for the material conditions. As shown in the TEM tomography of Figure 4.5.7 (left), under appropriate conditions of Si density and annealing, a spherical morphology can be maintained and QD merging avoided, thus giving greater control over the confined energy levels.

![Figure 4.5.6](image1)

Simulation results – multigrid method and Density Functional Theory (DFT) calculations [4.5.23] compared with the experimental results for Silicon QDs in SiO₂ dielectric.

**FIGURE 4.5.6**

![Figure 4.5.7](image2)

First three modes of electronic wave-functions in a “horseshoe” shaped QD with high surface to volume ratio (far left). The ground state is located near the centre of the dot and is approximately in a spherical shape with zero nodes. The number of nodes increases with the increase in the energy level. Energy levels associated with a horseshoe shaped QD compared with that of a 6nm diameter spherical QD (left). The two morphologies give energies which are most similar for their ground states, with the horseshoe shape giving significantly lower energies than spherical for higher confined levels. The degeneracy in energy levels is lost in the horseshoe shaped dot.

**FIGURE 4.5.7**
4.5.2.2.3 3D EF-TEM tomography on Si QDs embedded in oxide matrix formed as multilayers (Collaboration with Cornell University)

Researchers:
Xiaojing Hao, Shujuan Huang, Lena Fitting, Kourkoutis (Cornell University), Ivan Perez-Wurfl, Tom Puzzer

A significant challenge to the design of nano-scale materials and devices arises from the difficulty of characterising complex three-dimensional structures on small length scales, which is nonetheless critical in understanding the material performance. Whilst a number of techniques, such as conventional transmission electron microscopy, provide sufficient two-dimensional (2-D) resolution, they have insufficient depth sensitivity to obtain internal three-dimensional (3-D) structure. Electron tomography can be applied to obtain such information by using high-angle dark-field scanning transmission electron microscopic (STEM) tomography and energy filtered transmission electron microscopy (EFTEM) tomography. We have applied this EFTEM tomography to investigate Si QDs embedded in an oxide matrix formed as multilayers, in order to better understand the dot size, shape and distribution for further optimization of Si QD device performance. Fig. 4.5.8 illustrates the ability of electron tomography to reconstruct the morphology and internal structure of a Si QD nanostructure. Fig. 4.5.8 (left) shows the aligned “on-axis” reconstructed EFTEM tomography, and Fig. 4.5.8 (right) shows a top-view of the Si QD size and shape distribution in one Si QD layer. With such information, we can confirm that inside the Si QD layer, most of the Si QDs are reasonably spherical and well separated from each other. This indicates that individual QDs have not merged to form larger particles under these conditions. This is important in designing the optimum concentrations to give minimum QD spacing whilst maintaining individual QDs.

4.5.2.3. 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. This approach has been carried out for both Si QDs in SiNx and in SiC. It is also possible to have asymmetric superstructures in which quantum confinement and hence enhanced band gap is maintained in the plane, but in which tunnelling probability is maximised in the direction normal to the plane such that transport of carriers to contacts is maximised. Interlayers use for such asymmetric structures can also act as diffusion barriers enhancing size uniformity of QDs.

Alternative group IV materials such as Ge offer the possibility of lower temperature precipitation of nanostructures 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 both QDs and QWs of Ge in either SiO2 or SiNx matrices.
4.5.2.3.1 Silicon QDs embedded in silicon nitride matrix

Researchers:
Yong-Heng So, Shujuan Huang

(i) Size-dependent optical properties of Si QDs in Si-rich nitride/Si$_3$N$_4$ superlattice

An approach similar to spectroscopic ellipsometry analysis has been proposed to determine the size dependent optical properties of silicon quantum dots (Si QDs) in Si-rich nitride/silicon nitride superlattice structure (SRN/Si$_3$N$_4$-SL) [4.5.26]. The optical properties of Si QDs are modelled using the Tauc-Lorentz (TL) model and Bruggeman effective medium approximation that can yield the energy bandgap of the Si QDs based on spectral fitting of the reflection ($R$) and transmission ($T$) of characterized samples, as shown in Fig. 4.5.9. A four-phase optical model as shown in the inset of Fig. 4.5.9 was employed for the spectral fitting.

Figure 4.5.10 shows that the dielectric functions of Si QDs are strongly size dependent. Sample S3, S4 and S5 correspond to SRN/Si$_3$N$_4$ thicknesses of 3/3 nm, 4/3 nm and 5/3 nm, respectively. The suppressed imaginary dielectric function of Si QDs exhibit a broad peak centred between transition energies $E_1$ and $E_2$ of bulk crystalline Si and which blue shift towards $E_2$ as the QD size reduces.

Figure 4.5.11(b) shows that the band gap expansion indicated by the TL model when the size of Si QD reduces is in good agreement with PL measurements (Fig. 4.5.11(a)). The bandgap expansion with the reduction of Si QD size is well supported by the ab-initio calculations of confined energy levels from [4.5.25].

(ii) n-type conductivity of nanostructured thin film composed of antimony-doped Si nanocrystals in silicon nitride matrix

Highly conductive thin films composed of antimony (Sb)-doped Si nanocrystals (Si-NCs) embedded in Si$_3$N$_4$ matrix were prepared by a co-sputtering technique. Results from structural characterizations suggest that doping with Sb concentration of 0.54 at. % has negligible affect on the crystallization properties of Si-rich nitride (SRN) films. The X-ray Photoelectron (XPS) data of Fig. 4.5.12(a) and (b) show the Si 2p and Sb 3d$_{5/2}$ spectra of the undoped and 0.54 at.% Sb-doped Si-NC. (c) Fitting of Sb 3d$_{5/2}$ spectrum by two peaks separated by ~0.8 eV in energy ($\delta_1$ and $\delta_2$).

Thus, the appearance of $\delta_2$ suggests the presence of Sb-Si bonds which implies that Sb atoms were either incorporated within the Si-NCs or located at the interface between the NCs and Si$_3$N$_4$ matrix.
The temperature dependent conductivity data of Fig. 4.5.13(a) indicate that the conductivity of 0.54 at.% Sb-doped SRN film (~2.8 × 10^-2 S/cm) is six orders of magnitude higher than that for undoped material (~7.3 × 10^-8 S/cm), which could be attributed to an increase in carrier concentration. Furthermore, n-type electrical behaviour with carrier concentration of 2.4 × 10^16 cm^-3 and mobility of 2.94 cm^2/V s in the doped films as observed from Hall measurements was attributed to free carrier generation due to the effective Sb doping.

The temperature-dependent conductivities of both undoped and Sb-doped samples are shown in Fig. 4.5.13(b). As can be seen, doping of the Si-NCs strongly influences the electronic transport properties of the films. Arrhenius-like temperature dependence is observed in the T range between 220 and 320 K, attributable to thermally activated conduction. From the slope of the Arrhenius plot, we found that the activation energy $E_A$ decreases to 0.182 eV for the Sb-doped Si-NCs film, suggesting effective n-type doping of the Si-NCs. Nevertheless, the extracted $E_A$ is much larger than that of bulk Si with the same dopant. One possible explanation for the large $E_A$ observed would be the deeper donor level expected in Si-NCs. Also, it is possible that the number of free carriers available for conduction may be limited due to a trap density distributed within the bandgap that is comparable to the doping density.

Interestingly, the conductivity for the Sb-doped sample at T < 220 K deviates from Arrhenius behavior and is best described by the expression $\sigma = \sigma_0 \exp \left(-\frac{T}{T_0}\right)^{1/2}$ as illustrated in Fig. 4.5.13(c). The charge transport mechanism can be explained well by a percolation-hopping model.

4.5.2.3.2 Si QDs in SiO$_2$/Si$_3$N$_4$ hybrid matrix

Researchers: Dawei Di, Ivan Perez-Wurfl, Gavin Conibeer

To improve the current transport properties in the vertical direction and to obtain better size control of Si quantum dots, we proposed a new design based on Si QDs embedded in a SiO$_2$/Si$_3$N$_4$ hybrid matrix [4.5.27, 4.5.28]. By replacing the SiO$_2$ tunnel barriers with the Si$_3$N$_4$ layers, the new material manages to constrain the growth of doped Si quantum dots effectively and enhances the apparent band gap. Also electrical characterisation on Si QD/c-Si hetero-interface test structures indicates the new material possesses improved vertical carrier transport properties.

Doped and undoped samples with different barrier dielectrics (SiO$_2$ and Si$_3$N$_4$) are compared. Samples were fabricated using the co-sputtering multilayer technique with layers containing excess Si consisting of SRO for both materials, with an SRO thickness of 4 nm. Samples were either undoped or co-sputtered with either P$_2$O$_5$ or B for n- and p-type doping respectively. After annealing at 1100°C the crystalline properties were characterised by X-ray diffraction (XRD), as shown in Fig. 4.5.14. For samples with Si$_3$N$_4$ barriers, the measured Si NC sizes are 4.3 nm when undoped, 3.5 nm when B doped and 5.0 nm when P$_2$O$_5$ doped. For samples with SiO$_2$ barriers, grain sizes are 7.7 nm when undoped, 7.2 nm when B doped, and 15 nm when P$_2$O$_5$ doped. The Si NC sizes vary significantly although all samples have the same silicon-to-oxygen ratio in the SRO layers and the same as-deposited layer thickness.

It can be observed from the experiment that samples with Si$_3$N$_4$ barriers contain generally smaller Si QDs than samples with SiO$_2$ barriers. This is because Si$_3$N$_4$ acts as a better diffusion barrier than SiO$_2$ [4.5.27]. It could also be thermodynamically related to the interface free energy between
the Si NC and the matrix dielectrics during the growth of the Si NCs. As a result, Si$_3$N$_4$ is able to constrain the growth of Si NCs very effectively, within ±1 nm of the intended diameter (i.e. 4 nm, the deposition thickness of SRO). In contrast, Si NCs with SiO$_2$ barriers are significantly larger than the as-deposited thickness of SRO - over 180% larger for undoped and B doped and 375% for P$_2$O$_5$ doped. Hence, it can be noted that samples with phosphorus (P$_2$O$_5$) dopants tend to form larger sized Si NCs than undoped samples, while introduction of boron doping tends to suppress this size increase and slightly reduces NC size. This phenomenon is more pronounced for samples with SiO$_2$ barriers (Fig. 4.5.14 (a)) than those with Si$_3$N$_4$ barriers (Fig. 4.5.14 (b)).

Si$_3$N$_4$ barriers have lower band gaps (~5.3 eV) than SiO$_2$ (~9 eV) therefore they should be more transparent to charge carrier transport because of the larger tunnelling probability for electrons and holes. To verify this hypothesis in practice, we compared the current transport of SiO$_2$ barrier structures with Si$_3$N$_4$ barrier structures via the measurement of vertical currents under a bias voltage.

The current-voltage characteristics of these test structures are shown in Fig. 4.5.15. It should be noted that these samples are not PV devices. Therefore, the dark currents measured are primarily affected by the materials' conductivities and are not related to carrier recombination. It can be clearly seen from the measurement that for B doped materials, Si$_3$N$_4$ barriers result in a current enhancement of approximately an order of magnitude over those with SiO$_2$ barriers (Fig. 4.5.15 (a)). This can be qualitatively explained by (4.5.19):

$$T_e = 16 \exp \left(- \frac{8m^*}{\hbar^2} \Delta E \right)$$

(4.5.1)

where $T_e$ is the tunnelling probability between quantum dots, $d$ is the barrier thickness or the separation between dots, $m^*$ is the effective mass of electron, $\hbar$ is the reduced Plank constant, $\Delta E$ is the energy difference between the conduction band edge of the barrier material and the conduction band edge of the confined QDs.

Although the difference in Si NC sizes would play an important role in the tunnelling event, the variation of $\Delta E$ is still the dominant factor for B doping. On the other hand, for the P$_2$O$_5$ doping, samples with Si$_3$N$_4$ and SiO$_2$ barriers have similar currents (Fig. 4.5.15 (b)). These apparently contradictory results can be explained by referring back to the XRD results. The P$_2$O$_5$ doped sample with SiO$_2$ barriers contains Si NCs with an average size of 15 nm, this suggests that a single Si NC is physically penetrating three thin layers on average (inset of Fig. 4.5.15 (b)).
This greatly reduces the number of barrier layers that the carriers need to tunnel through. This size effect becomes so significant that it effectively competes with and largely cancels the increased conductivity due to lower $\Delta E$ for the Si$_3$N$_4$ barrier material.

This result is very promising for both QD size control and increased vertical current transport in these nitride barrier interlayer Si QD materials.

### 4.5.2.3.3 Silicon QD nanocrystals embedded in silicon carbide matrix

Researchers:
Zhenyu Wan, Shujuan Huang, Gavin Conibeer

Silicon carbide (SiC) has a lower barrier height than either Si$_3$N$_4$ or SiO$_2$. Therefore it seems likely that it should offer a higher tunnelling probability between QDs and hence a higher conductivity matrix than either. In previous work, we have demonstrated that both Si and SiC have been crystallised by high temperature annealing of a single thick Si-rich SiC (SRC) layer or of a Si$_{1-x}$C$_x$/SiC multilayer structure [4.5.28, 4.5.29]. We believe that the formation of $\beta$-SiC nanocrystals may hinder the formation of Si QDs. Also they may cause current leakage via the SiC grain boundary traps to increase the shunt current in the solar cell. Therefore, the work in 2009 focused on studying the mechanism of the crystallisation of SiC and optimising the materials by comparing the annealing methods of rapid thermal annealing (RTA) and conventional furnace annealing. We found that RTA annealed samples revealed a better degree of crystallisation of Si nanocrystals with a smaller residue of amorphous Si [4.5.30]. The work in 2010 has been to further improve the structure by reducing the stress caused by RTA and by replacing SiC barrier layers with thin silicon nitride layers in order to suppress the growth of SiC crystals.

#### (i) Study of RTA induced stress

Two different annealing processes have been applied on all SRC amorphous samples: furnace annealing at 1100°C/1hr and RTA at 1100°C/30 sec. After annealing, Si and SiC nano-crystals were clearly observed in TEM and XRD. The peak positions of Raman spectra are down-shifted to lower wavenumbers for RTA samples ($\Delta = 5.4$ cm$^{-1}$ from bulk Si) as compared to furnace annealed samples ($\Delta = 2$ cm$^{-1}$ from bulk Si), indicating greater tensile stress in the Si nano-crystals, as shown in Fig. 4.5.16 (a). This is because of a different thermal expansion coefficient for Si and SiC crystals and the fast temperature ramping rate in RTA. In order to release the stress in RTA samples an additional annealing process was carried out. Raman analysis indicates that after an additional furnace anneal at 1100°C for 30 min, all samples with different Si concentrations could release most of their residual stress, as shown in Fig. 4.5.16 (b). However, an additional RTA could not release residual stress in low Si concentration samples due to insufficient duration [4.5.31].

#### (ii) Si QDs embedded in SiC matrix with Si$_3$N$_4$ barrier layers

Si$_3$N$_4$ is also considered preferable to SiO$_2$ in term of carrier transport. It has been proven as a good diffusion barrier to suppress inter-diffusion between silicon rich layers in multilayer structures during annealing [4.5.27]. In 2010, we have successfully introduced ultra-thin Si$_3$N$_4$ (UT-SiN) barriers (0.2nm-2.0nm) into a Si-NC in SiC matrix structure using sputtering followed by RTA. Crystallisation of the SiC matrix has been greatly suppressed and a clear layered superlattice structure can be observed as shown in the TEM of Fig. 4.5.17. The nanocrystal size of all samples was calculated using XRD peak analysis to quantitatively investigate the optimum thickness of the Si$_3$N$_4$ barrier layer required to produce confined crystalline Si-QDs, as shown in Fig. 4.5.18. It is seen that as the Si$_3$N$_4$ barrier layer thickness increases, the $\beta$-SiC peaks decrease, such that $\beta$-SiC-NCs almost disappear when the Si$_3$N$_4$ barrier thickness is over 0.8nm.
Optical characterization has been performed to investigate quantum confinement effects for different nanocrystal sizes. Optical analysis reveals a blue shift in the strong absorption edge, consistent with quantum confinement effects in small Si NCs matching qualitatively calculated results using effective mass theory from other groups, as shown in Fig. 4.5.19.

Temperature dependent I-V measurements were carried out to investigate the carrier transport mechanism. The conductivity is best described by the expression, $\sigma = \sigma_0 \exp\left(-\frac{T_0}{T}\right)^{1/2}$ when the Si$_3$N$_4$ barrier thickness is greater than 0.5 nm, as illustrated in Fig. 4.5.20. The charge transport mechanism can be explained well by the percolation-hopping model, similar to the result found in Section 4.5.2.3.1 for Sb doped SiQDs in Si$_3$N$_4$. Finally, we conclude that in future, a 0.5-0.8 nm thick layer of Si$_3$N$_4$ barrier layer would be optimum to achieve both good Si-NC confinement and minimal film resistivity for a candidate material for photovoltaic applications.

### 4.5.2.3.4 Germanium Nanostructures

Although the main focus has been on Si nanocrystals during the last decade, other group 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. This is indeed a significant advantage both for processing compatibility and for processing costs, although set against this are the greater cost and lower abundance of Ge as compared to Si.

### (i) Fabrication of Germanium quantum dots

The current work builds on earlier work on Ge nanocrystals carried out in our group [4.5.32]. The new work uses a different approach to annealing of the samples which gives a wider range of control of Ge NC formation. Ge NC samples have been fabricated by RF magnetron sputtering using a combination of sputtering with just an Ar background, whereas sputtering of the oxide layers, GeO$_x$/SiO$_2$, is performed by reactive sputtering with O$_2$. These layers are alternately deposited to obtain the desired multilayered structure. A thick oxide capping layer is deposited to prevent oxidation of the GeRO layers during subsequent annealing. Post deposition annealing of the samples was performed under a low pressure (in-situ in the growth chamber) during which Ge NCs are formed. Results
from structural characterization using TEM, Raman, XRD and PL have been obtained.

Figure 4.5.21 shows a high resolution TEM image of a section of a typical sample containing GeRO layers between GeO₂/SiO₂. The sample was annealed at 650°C. Ge nanocrystals of about 5nm diameter are evident. Although there is a slight variation, the NCs appear to be spherical in shape. The clear lattice fringes observed in the TEM image give direct evidence of the formation of the Ge NCs. It should be noted that the distance between the lattice fringes is 3.3 Å, which is consistent with the lattice spacing of the (111) planes of the Ge diamond structure.

Fig. 4.5.22 (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. 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 [4.5.33]. 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 NCs.

Figure 4.5.22 (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 2θ = 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 to 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.

The crystallisation of Ge NCs with annealing duration has been investigated with Raman spectroscopy. Fig. 4.5.23 shows Raman spectra for identical multilayer samples with each GeRO and GeO₂/SiO₂ layer 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 NCs, suggests an early stage of the crystallization process at this annealing duration. As annealing duration increases, Raman peaks become sharper and narrower indicating an 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 SiO₂ matrix [4.5.7, 4.5.34]. In our superlattice structure, Ge NCs are confined within the GeRO layers between GeO₂/SiO₂ 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.

Figure 4.5.24 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 studied here, just as in the case of annealing durations. The results also illustrate the formation of Ge NCs in SiO2 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. 4.5.25 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 GeO2/SiO2 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 previous work [4.5.32]. We tentatively consider that this is due to the band gap increase induced by the quantum confinement effect in Ge NCs [4.5.35].

(ii) 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 cheaper substrates such as soda-lime glass. 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 [4.5.36].

Figure 4.5.26 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) [4.5.37]. For the sample grown at Tg = 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 occur 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 Tg = 350°C and becomes sharper with increase in the growth temperature. This range of temperature is very close to the onset temperature for Ge crystallisation reported in [4.5.38]. However, when the growth temperature Tg 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 crystallised 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 GeO2/SiO2 films is shown in Fig. 4.5.27. In this case the sample was grown at Tg = 380°C without further post-deposition thermal treatment. The TEM image shows close to spherical Ge NCs with fairly uniform size, separated...
(iii) Electrical properties of Ge-NC thin films

Ge-NC thin films about 250 nm ~ 300 nm were deposited. The coverage of Ge was ~ 20% of the area of the composite target. XPS has shown that this resulted in a Ge atomic concentration of ~ 35% in the films. Undoped, Ga-doped and Sb-doped Ge targets were used. During the sputtering process the substrates were intentionally heated up to ~ 380 °C for in-situ growth of Ge-NCs. Finally, RTA treatments at different temperatures, including 650°C, 700°C, 750°C, 800°C were carried out in nitrogen [4.5.39].

The current conduction characteristics of i:Ge-NC thin films were measured using HP4140B pA Meter/DC voltage source with tri-axial wires to eliminate noise. The relatively high conductivity and carrier concentration in the i:Ge-NC thin films is quite surprising, taking into consideration that they were not intentionally doped. Temperature dependent measurement revealed a $\ln \sigma \propto T^{-4}$ relationship, suggesting a thermally activated nearest hopping conduction mechanism in these films. The carrier transport was considered to occur at the surface state energy level and a theoretical calculation predicts that the density of surface states of Ge can provide sufficient free holes to explain the observed conductivity. RTA treatments further increase the film conductivity without changing much the structural properties of nanocrystals. This improvement was tentatively attributed to the modification of surface structure of NCs and reduction of oxygen-deficiency-related defects in the SiO$_2$ matrix. The effect of incorporating moderate amounts of Ga and Sb dopants was also investigated. The doped films exhibit similar conduction properties to the intrinsic films, which means the films were still dominated by surface state induced hole conduction and that the dopants were not effectively activated. This is not surprising if one realizes the screening of shallow dopants in NCs due to the increase of binding energy and ionization energy. This effect together with the inherent hole generation effect can make it very challenging to produce n-type Ge-NC thin films.

(iv) Ge-nc/c-Si Heterojunction Devices

Heterojunction (HJ) devices employing Ge-NC thin films on lightly doped n-type crystalline silicon substrates with impurity concentration of ~ 1 x $10^{15}$ cm$^{-3}$ (n:c-Si) were fabricated to evaluate the compatibility of the nanostructured thin film and investigate the design parameters required for its application in photovoltaic devices. The schematic diagram of the HJ device is illustrated in Fig. 4.5.28. The total area of the device is 1 cm$^2$. The thickness of the Ge-NC layer is about 250 nm. The Ge-NC thin films were post-annealed by RTA at 800°C in order to achieve lower film resistivity and higher carrier concentration. The Al front fingers and rear contact were deposited by thermal evaporation. No passivation or sintering process was performed on the devices.

Figure 4.5.29 shows the dark I-V curves and suns $V_{oc}$ of a typical i:Ge-NC/n:c-Si HJ device at room temperature. The device shows good current rectification of three orders of magnitude at ± 1.5 V. Since both front and rear electrodes were ohmic contacts, the rectification effect can be attributed to the junction. The apparent photovoltage was detected from the illuminated device and the 1-sun $V_{oc}$ was found to be ~ 314 mV. The best fitting to the experimental data using a two diode model predicts an effective ideality factor of ~1.01 throughout the entire injection range, which is indicative of a dominating bulk and surface recombination in the heterojunction device. Whilst this HJ device does not demonstrate photovoltaic behaviour of the Ge NC material it does show good rectification and is
encouraging as a starting point for using Ge-NC in true photovoltaic applications.

4.5.2.3.4.2 Germanium QW and QD nanostructures embedded in silicon nitride matrix

Researchers:
Sammy Lee, Jian Chen, Shujuan Huang, Martin Green

As discussed above in section 4.5.2.3.1, a silicon nitride matrix (Si$_3$N$_4$) should increase tunneling probability and hence increase conductivity of Ge nanostructure materials. In addition a nitride will strongly suppress the possibility of oxidation of Ge. Ge QDs and QWs were fabricated by co-sputtering followed by post-annealing and self-organisation by substrate heating.

(i) Ge QDs embedded in silicon nitride matrix

Using a very similar approach to our previous work on Ge QDs in oxide and Sn QDs in nitride matrices, alternating layers of germanium-rich nitride (GRN) layers and Si$_3$N$_4$ layer were alternately co-sputtered on a heated substrate of either a silicon wafer or quartz slide. The Ge QDs crystallise due to minimisation of surface energy and the Si$_3$N$_4$ layer deposited on top of the GRN layer truncates crystal growth. The temperature of the substrate and the Ge content in GRN layers were the dominant factors in controlling the size of the NCs. The structure of the NCs was studied by GIXRD, Raman spectroscopy and TEM, and the optical properties were studied with transmittance and reflectance measurements analysed using a Tauc-plot.

Figure 4.5.30 shows the XRD spectra of samples of various Ge content in GRN. The Bragg peaks of (111), (220) and (311) planes sharpen with increasing Ge content, indicating the increase of the nanocrystal sizes. Using the Scherrer equation the size of the nanocrystals was estimated as shown in Table 1, with sizes in agreement with the NC size observed in TEM images.

<table>
<thead>
<tr>
<th>Ge vol%</th>
<th>$\Delta(2\Theta)$ of (111)</th>
<th>NC Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>5.62</td>
<td>NA</td>
</tr>
<tr>
<td>40</td>
<td>3.85</td>
<td>2.22</td>
</tr>
<tr>
<td>50</td>
<td>2.41</td>
<td>3.54</td>
</tr>
<tr>
<td>60</td>
<td>2.38</td>
<td>3.59</td>
</tr>
<tr>
<td>70</td>
<td>1.92</td>
<td>4.45</td>
</tr>
</tbody>
</table>

Figure 4.5.31 summarises the band gap engineering trend with the size of Ge QDs. The absorption edge shows a tendency to shift to high photon energy when Ge nanocrystal size decreases. The absorption coefficient was calculated by a simplified equation;

$$\alpha = \frac{1}{d} \ln \left( \frac{1 - R}{T} \right)$$

where $T$ and $R$ are the transmission and reflection and $d$ is the thickness of the film. With decrease in Ge content in the GRN layer, and hence in the diameter of the QDs, the absorption edge appears to increase by up to ~1.0 eV, as estimated with the Tauc-plot method. However, these data should be considered as indicative of the trend only as there is error in quantitative values for the shift in absorption edge due to uncertainty in extrapolating back to the energy axis.

(ii) Ge QWs with silicon nitride barriers

With a similar approach to the Ge QD fabrication, Ge QWs were fabricated by co-sputtering of alternating GRN and Si$_3$N$_4$ layers and followed by furnace annealing or RTA. The Ge content in GRN was higher in this case in order to give continuous layers. It was varied between 60vol% to 100vol% and the annealing temperature in N$_2$ was also varied from 600ºC to 900ºC for 1 hour. The structural and optical properties were studied by GIXRD, Raman spectroscopy, TEM and transmission and reflectance measurements.

Fig. 4.5.32 shows the continuous Ge layer with its QW-like-structure between amorphous Si$_3$N$_4$ barriers. Highly ordered lattice planes can clearly be seen in these Ge QW, indicating formation of large single crystal type structures. Based on Raman and XRD characterisation, the crystallisation temperature shows a significant dependence on the thickness of either Ge QW or Si$_3$N$_4$ barrier.
layers, varying from 700°C to 900°C. The absorption coefficient estimated from the transmittance and reflectance measurements also shows an apparent increase in band gap by up to 1.1eV when the thickness of the Ge QWs is 1.5nm.

Both Ge QDs and QWs nanostructures in Si₃N₄ show evidence of band gap enhancement. Further work will investigate electrical properties and the possibility of device fabrication.

### 4.5.2.4 Silicon nanocrystal devices on quartz substrates

**Researchers:**
Ivan Perez-Wurfl, Xiaojing Hao, Dawei Dai, Adrian Shi

As previously reported in the 2008 and 2009 annual reports devices have been fabricated using the SiQD in SiO₂ materials, with p-n junction formation using B or P of multilayers, respectively [4.5.9, 4.5.10, 4.5.40]. The fabricated p-n diodes consisted of sputtered alternating layers of SiO₂ 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. 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 0.12cm². The devices exhibit rectification and a photovoltaic response with VOC up to 493 mV, but with as yet very small currents and bad fill factors. These are partly due to the very high resistance of the material and in particular to the relatively long lateral paths to contacts at the back contact, necessitated by growth on an insulating quartz substrate. The device structure with appropriate contacting is shown schematically in Fig. 4.5.33. This also shows the current crowding effect which results from the high lateral resistance.

**4.5.2.4.1 Equivalent circuit model of nanocrystal devices on quartz substrates**

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 [4.5.41]. 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 [4.5.42], 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 [4.5.9]. It is further possible to linearise the expression around an average measuring temperature, $T_{avg}$, as follows:

$$
\frac{V_m}{Temp} = \sum_{i=1}^{N} \ln \left( \frac{I_{sat,i}}{I_{satAvg}} \right) + \frac{kT_{avg}}{q} \sum_{i=1}^{N} a_i
$$

(4.5.2)

where $k$ is Boltzmann's constant, $q$ is the electron charge, $T_{avg}$ is the temperature at which the saturation current, $I_{sat}$, is defined, $a_i$ is the diode ideality factor, and $N$ 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. 4.5.33, 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, $R_{sw}$, and a current dependent series resistance $R_{sc}$, arising from current crowding:

$$R_s(T, \phi) = R_{sw} + R_{sc}$$

(4.5.3)

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

$$\varphi(\tan \varphi - \frac{q}{8\pi kT} IR_{sw} \frac{W}{L}$$

(4.5.4)

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 have proposed 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. Figure 4.5.34 shows the circuit proposed.

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 ($V_1$ in Fig. 4.5.34) 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, $R_{sw}$, and inversely proportional to the area, $R_{sc}=R_{sw}/(1-\text{fraction})$, where the diffusion current occurs. The dark $I$-$V$ behaviour is modelled by the top branch of the circuit depicted in Fig. 4.5.34. $D_{QD1}$ and $D_{Sch}$ represent the series connection of diodes whose band gaps are extracted using Eq. (4.5.2). The series resistance, $R_2$, has the temperature and current dependence detailed in Eqs. (4.5.3) and (4.5.4).

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: $R_1=R_{sw}/\text{fraction}$. Since the photocurrent, $I_{ph}$, flows through $R_1$, 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 Fig. 4.5.35 show the reduction of $I_{ph}$ as the fraction, $f$, is varied from 99% to 1% of the total diode area.

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 circuited (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.

### 4.5.2.4.2 Demonstrator program for Si nanostructure devices

Using the approach described in Section 4.5.2.4.1, a device simulator has been developed in an MS Excel spreadsheet. The Demonstrator is a 2D simulator of the diodes fabricated from Si QD nanostructures. It is based on a simple diode model with a few fitting parameters and uses the method in section 0 and in [4.5.9].

There are three areas which the user can modify:

1. Measured parameters: these come from measured properties of the fabricated diodes. The base resistivity and its temperature dependence are measured. The device geometry is known. The default values are representative ones for the devices.
2. $J$, ideality factor, band gap and XTO can be varied to give flexibility in fitting to a specific diode properties.
3. The variation parameters are Current and Temperature.

The outputs are:

1. The $I$-$V$ curves for the range of temperatures chosen, in both log-lin and lin-lin output.
2. The variation of the ideality factor with current for various temperatures.
3. The series resistance with temperature.
4. The extracted band gap, using either a calculation incorporating a series resistance correction or with both a series resistance and a current modification term.

---

**FIGURE 4.5.34**

Equivalent Spice circuit representation of the fabricated devices.

**FIGURE 4.5.35**

Spice simulations of 1-sun $I$-$V$ characteristics based on the circuit depicted in Fig. 4.5.34. The fraction, $f$, represents the normalized area of the diode where the photocurrent is produced.
Some example outputs, using the default parameter settings, follow:

Figure 4.5.36 shows that a reasonable diode characteristic is shown, with good turn-on and rectification.

Figure 4.5.37 shows the increase in the ideality factor with current is as expected with a diode transiting from domination by radiative recombination ($n=1$) to being dominated by Shockley Read Hall recombination ($n=2$). But the large regime in which $n=3$ and then region where it goes to much higher values, are indicative of a non-physical aspect to the model. The most likely explanation is that rather than two diodes in series there are actually several, probably a variable number in different parts of the device, the combination of which lead to a composite ideality factor.

The demonstrator is useful as an iterative tool used to simulate the real measured data from a device. The parameters used for such a fit then define the values of the circuit elements in the EC model. Assignment of physical meaning to these elements will then require further development and interface with the EMA/quantum mechanical model.

### 4.5.2.5 Doping in Si QD nanostructures

Fabrication of a PV device from the Si QD materials requires a control of work function such as to allow separation of photogenerated electron-hole pairs. Methods by which this can be achieved include fabrication of a grown or diffused p–n junction or p–i–n junction with the Si QD multilayers as the i-region. These require careful control of the work functions of the p and n-regions. P–n junction devices have been fabricated and doping demonstrated. Progress on the theory explaining these doping effects using conventional dopants and the possibility of other modulation doping approaches has been made.

As discussed in Section 4.5.2.4, rectifying p–n and p–i–n structures can be fabricated with ‘conventional’ doping by incorporation of B and P during sputtering growth [4.5.9, 4.5.10]. Also, formation of p- and n-type materials is clearly demonstrated in the Si QD nanostructure materials with Si nitride interlayers doped with either P or B as discussed in Section 4.5.2.3.2; in the Sb doped n-type Si QDs in Si$_3$N$_4$, in Section 4.5.2.3.1; in the p-type Ge QD in SiO$_2$ material in section 4.5.2.3.4; and in MOS type devices doped with either P or B by a diffusion anneal discussed in [4.5.43].

However, the doping mechanisms taking place in these structures are not well understood. Theoretical work has shown that direct doping of the QDs is prevented by segregation of impurity atoms from the perfectly crystalline QDs [4.5.44, 4.5.23]. Experimentally this is supported by data on the free electron density in Si nanocrystals using Electron Paramagnetic Resonance (EPR), which show that 95% of P atoms are segregated to the surface of the nanocrystals and that their contribution to doping is at least an order of magnitude lower than the atomic concentration [4.5.45]. Further evidence that doping causes electronic changes comes from the quenching of luminescence on the incorporation of P (or Au) in Si nanostructures [4.5.46] and also from a small enhancement of luminescence observed at low P doping levels followed by quenching at higher levels [4.5.47]. This latter being explained by the passivation of QD surface states by low levels of P increasing luminescence and then the saturation of this mechanism by excess P. This also explains the non-monotonic behaviour of activation energy seen in P doped nanostructures [4.5.46] and also from a small enhancement of luminescence observed at low P doping levels followed by quenching at higher levels [4.5.47].

If direct doping of the QDs is not occurring, then another possibility is modulation doping of the matrix SiO$_2$, as is commonly used in III–V nanostructures; but this is ruled out because of the very high ionisation energies of about 5eV that would be required for the resultant deep defects in a dielectric matrix [4.5.48]. These clearly will not occur at room temperature, or even at higher temperatures.
4.5.2.5.1 Doping mechanisms in Si QD nanostructures

Researchers:
Dawei Di, Xiaoming Hao, Ivan Perez-Wurfl, Gavin Conibeer

As there is clear evidence for doping by P and B, a third possibility is that it is the sub-oxide QD/matrix interface region, with its shallower doping defect levels, that is doped by the P or B atoms, thus providing free carriers to be captured by the QDs [4.5.49]. As shown in Fig. 4.5.38, ab-initio calculation of the levels associated with B atoms associated directly with the interface region on the surface of a Si QD indicate that there are no shallow or deep levels introduced by the B within the effective band gap (HOMO-LUMO gap). The reason is that the strong affinity of B for O results in very strong B-O bonds, effectively splitting any available OMOs and UMOs a long way apart and well inside the already existing density of states.

However, this approach considers the interface between Si QD and SiO₂ matrix to be very abrupt. In fact there is highly likely to be an extended transition region of a sub-oxide around the QD. If this region is a sufficiently extended silicon sub-oxide (Si₉ₓO₉₋ₓ) it could provide flat Bloch bands able to be doped in a pseudo bulk-like regime. In order that B and P doping levels are shallow enough to be ionised in such a region, x would need to be less than about 0.5. Such a region would be amorphous and hence not able to be modelled with ab-initio methods. But the presence of such regions can be determined from absorption measurements.

There is some support for this theory in the absorption data for Si QDs in SiO₂ [4.5.5] shown in Fig. 4.5.39. This shows a region of strong absorption with an absorption edge which blue shifts as the O to Si ratio increases, which translates to an increase in QD size. But there is also an additional weakly absorbing tail which extends well into the effective band gap region. This tail is likely to be due to an amorphous region around the Si QDs. An explanation for the band gap of this being larger than bulk Si is if this region consists of sub-oxide material. If this region were doped with B or P, it could provide free carriers to be captured by the QDs in a modulation doping mechanism, thus giving rise to the p- or n-type behaviour observed. (This is illustrated schematically in Fig. 4.5.40 (a).)

An alternative explanation for the rectifying character of the junctions obtained can be based on the modification to the Si QD crystallisation discussed in Section 4.5.2.3.2, for P and B doping of Si QDs in oxide with nitride interlayers [4.5.49]. The fact that P (B) doped material produces larger (smaller) QDs means that its confined energy levels and hence effective band gap will be smaller (larger) than undoped material under otherwise similar conditions. Thus a junction between a P and a B doped region will actually be a type-I heterojunction between small and large band gap materials, respectively, as illustrated in Fig. 4.5.40 (b).

It is also very likely that the mobility of electrons in these materials, whilst not big, will still be much greater than that of holes. Hence photogenerated electrons near the junction would experience a drift field sweeping them into the P doped material with its lower conduction band edge, whilst holes with their very limited mobility would be immobile. This would result in electrons accumulating in the P side of the junction and hence effective band gap will be smaller than bulk Si is if this region consists of sub-oxide material.
material and being collected in the external circuit as if from an n-type material, with electrons injected back into the device through the B doped material where they would recombine with the immobile holes, thus making the B material appear p-type. This qualitatively mirrors the behaviour observed, but will require corroboration. As it relies on the difference in electron and hole mobilities, it is essentially the same as the Dember effect, which is known to produce a photovoltaic effect through carrier separation, albeit not very efficiently.

It is also possible that both the sub-oxide doping effect and the mismatched QD size effects operate in the device. The fact that both mechanisms act in the same direction is fortuitous as both could therefore contribute to the observed rectifying photovoltaic behaviour. Differentiation between these or a determination of the relative strengths will require further study on the effects of doping, interlayers and band alignments. These will also further optimisation of the devices and lead to better photovoltaic performance from these Si QD nanostructure devices.

4.5.2.5.2 Ab-initio modelling of modulation doping possibilities in Si QDs nanostructures

As discussed in Section 4.5.2.5, direct doping of QDs by dopants is thermodynamically very unlikely. The alternative of modulation doping of the SiO₂ matrix is also not feasible due to the strong anionic nature of O leading to very deep ionisation energies [4.5.48]. We have concentrated recently on possible candidates for more efficient acceptor doping of Si QDs. Modulation acceptors must have an energetic position below the confined hole level, 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. The transition metal scandium (Sc) fulfils the last two requirements. It also has a very suitable valence state configuration which consists of a full (doubly occupied) 4s shell and one electron in the 3d¹ state located within the 4s shell. On the energy scale, the 4s electrons have a higher binding energy which is able to take up a much bigger proportion of an electron if the Si QD is slightly bigger (e.g. d_qd = 11 Å). The Sc-doped nanocrystals are shown with the iso-density plots of 1.35×10⁻³ e/Å³ for j-LUMO 1193 (lower left) and j-LUMO 1194 (lower right). The atoms of the Si₁₀ QD and the Sc atom are highlighted in cyan. Si atoms in SiO₂ are grey, O atoms are red, H-atoms terminating the outermost O-bonds are white. All DFT computations carried out with a Hartree-Fock 3-21G(d) optimisation and B3LYP/6-31G(d) electronic structure calculation [4.5.23].

![Figure 4.5.42](image)

**FIGURE 4.5.42**

**Researchers:**

Dirk König, James Rudd, Daniel Hiller (IMTEK, University of Freiburg, Germany)

Ab-initio Density Functional Theory calculations on a Si₁₀ QD in 2 mono layers (ML) of SiO₂ have been carried out, with a Si atom at the outermost position with full O termination replaced by a Sc atom. The Si₁₀ cluster is the smallest size which still behaves as a Si QD [4.5.23]. Such a nanoparticle allows us to directly observe the electronic structure of Sc as a modulation acceptor in SiO₂ in the proximity of a Si QD, see Fig. 4.5.41.

Figure 4.5.42 shows that 0.07 electrons stemming from the Si₁₀ QD (dₐ = 7.3 Å) are localized at the Sc atom over two 2 ML (6 Å) of perfect SiO₂. Technological relevant QD sizes start at dₐ = 20 Å, with a much lesser degree of quantum confinement as compared to a 7.3 Å QD. It is thus reasonable to assume that a Si QD with dₐ ≥ 20 Å will be positively ionized to a much greater extent, ensuring that holes are majority carriers in a Si QD super lattice (SL) embedded in SiO₂. Experimental verification of this doping mechanism is being carried out. The difference to conventional acceptor modulation doping as used in III-V electronic devices is the way the Si or Ge QDs are ionised by Sc in SiO₂. As Sc induces a deep acceptor level in SiO₂, it cannot be thermally ionized from the SiO₂ valence band. Instead, the Sc acceptor state takes up the electron directly from the initially occupied state at a lower binding energy presented by a nearby QD, see Fig. 4.5.43. This requires the Sc acceptor to be within 50 Å of the Si QD in order to exploit field emission.
Acceptor modulation doping:
Conventional example with GaS QD in AlAs matrix and electron thermally emitted into acceptor (Mg), such that holes are captured by the QD (left). In SiO₂, charge transfer occurs directly as the Sc state is too deep within the band gap to be thermally ionized. Instead, the acceptor state is ionised directly from the QD by field emission of an electron into the Sc acceptor state.

which is a consequence of the energy difference between the QD HOMO and the Sc acceptor state.

Acceptor modulation doping of SiO₂ can be accomplished by incorporation of a small amount of Sc, say one monolayer of Sc, into the SiO₂ barriers between the SRO QD array layers. During the segregation anneal, Sc is incorporated into the SiO₂ matrix and thereby activated as an acceptor. Ab-initio calculation indicates that Sc attached to the Si QD does not create any levels within the HOMO-LUMO gap of a Si₈₄(OH)₆₄ QD. We can therefore assume that a Sc atoms bonded onto a Si QD does not result in a detrimental change in its electronic structure. This concept is now being investigated experimentally.

4.5.3 Hot Carrier cells

Researchers:
Shujuan Huang, Santosh Shreshtha, Dirk König, Robert Patterson, Pasquale Aliberti, Binesh Puthen Veettil, Lara Treiber, Ivan Perez-Wurfl, Andy Hsieh, Yu Feng, James Rudd, Stephan Michard, Martin Green, Gavin Conibeer

Hot carrier solar cells offer the possibility of very high efficiencies (limiting efficiency above 65% for unconcentrated illumination) but with a structure that could be conceptually simple compared to other very high efficiency PV devices – such as multi-junction monolithic tandem cells. For this reason, the approach lends itself to ‘thin film’ deposition techniques, with their attendant low costs in materials and energy usage and facility to use abundant, non-toxic elements.

An ideal Hot Carrier cell would absorb a wide range of photon energies and extract a large fraction of the energy to give very high efficiencies by extracting ‘hot’ carriers before they thermalise to the band edges. Hence an important property of a hot carrier cell is to slow the rate of carrier cooling to allow hot carriers to be collected whilst they are still at elevated energies (“hot”), and thus allowing higher voltages to be achieved from the cell and hence higher efficiency. A Hot Carrier cell must also only allow extraction of carriers from the device through contacts which accept only a very narrow range of energies (energy selective contacts or
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 [4.5.50]. The limiting efficiency for the hot carrier cell is over 65% at 1 sun and 85% at maximum concentration – very close to the limits for an infinite number of energy levels [4.5.1, 4.5.51, 4.5.52]. Fig. 4.5.44 is a schematic band diagram of a Hot Carrier cell illustrating these two requirements.

**Figures**

4.5.45 (a) Schematic representation of energy and particle fluxes interactions used in the model (Particle fluxes - full line arrow, energy fluxes- dotted line arrow). (b) 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. \( J, F \) and \( E \) are current density and particle and energy fluxes as denoted by subscripts for \( A \) absorption, \( E \) emission and \( IA \) Auger processes.

4.5.46 Carriers transmission probability versus energy for (a) ideal ESC, (b) non-ideal ESC.

In 2010 modelling of Hot Carrier efficiencies has progressed with implementation of real material properties to give more realistic efficiencies for InN which include Auger processes and more realistic contact structures. Significant progress has been made on demonstrating resonance in double barrier selective energy structures. Further work on triple barrier double Si QW structures has been carried out for rectifying ESCs. This is complemented by improvements in 2/3D modelling of transport in these ESC structures. For absorbers, modelling of nanocrystals superlattice arrays has bee applied to real material systems. The growth of such systems in both III-V QD superlattices with collaborators and with colloidal Langmuir-Blodgett dispersion of Si nanocrystals has produced structures which are now being characterised for their modulation of phononic properties. Also measurement of carrier cooling rates has been extended to other large phononic gap bulk materials including InN, demonstrating the importance of material quality. Design of structures for hot carrier cells which should be practical and realisable has developed, with the device properties more carefully specified and plans for fabricating such structures in real devices.

**4.5.3.1 Modelling of Hot Carrier Solar Cell Efficiency**

Researchers:
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Collaboration with:
Yasuhiro Takeda (Toyota Central Research Laboratories, Nagoya)

Previous work was focused on developing a new model to calculate limiting efficiency of a real HCSC based on an Indium Nitride (InN) absorber layer. InN has been chosen as a potential material because of its narrow electronic band gap for absorption of a wide range of photon energies, whilst also having a wide phonon band gap. This is good for suppression of phonon decay, and hence for slowing carrier cooling [4.5.53, 4.5.54]. Calculation of limiting efficiency was performed taking into account real optical and electronic properties of InN, removing most of the ideality assumptions used in other models [4.5.51, 4.5.52, 4.5.55, 4.5.56]. The detailed band structure
of wurtzite bulk InN has been considered in performing computation of carrier densities, pseudo-Fermi potentials and II-AR time constants \((4.5.57)\). Results have been calculated considering ideal energy selective contacts for the HCSC, which means that contacts have a very high conductivity and a discrete energy transmission level.

Recently the limiting efficiency for the hot carrier InN solar cell has been calculated considering non-ideal ESCS. In this case the carriers are not extracted on a single energy level, but in a finite energy window. Calculations have been performed taking into account contact resistance and entropy generation effects.

The flux of current travelling through the ESCs towards the cold metal electrodes can be described using the following relation.

\[
J_{ch}(\epsilon) = T_{ch}(\epsilon) \left[ f_{\epsilon,\epsilon_{ch}}(\epsilon) - f_{\epsilon,\epsilon_{ch}}(\epsilon) \right] 
\]

\[
\left( 4.5.5 \right)
\]

The current density in this case is proportional to the occupation probability at the two sides of the ESC. Equation \((4.5.5)\) has been derived assuming no correlation of energy of electrons in three different directions as shown in \((4.5.6)\). This assumption is acceptable if there is a parabolic dispersion relation at minimum energy point along the three different directions.

\[
\tilde{E} = \epsilon_x \tilde{x} + \epsilon_y \tilde{y} + \epsilon_z \tilde{z}; \quad \tilde{k} = k_x \tilde{x} + k_y \tilde{y} + k_z \tilde{z} 
\]

\[
\left( 4.5.6 \right)
\]

Based on the energy and carrier conservation, \(\Delta \mu\) and TC at steady state are calculated.

\[
F_A - F_{\epsilon k} + F_{\epsilon k} - \frac{J}{e} = 0; \quad E_A - E_k - E_{\epsilon k} - \frac{E_{\epsilon k}}{e} = 0 
\]

\[
\left( 4.5.7 \right)
\]

[quantities as defined in Fig. 4.5.45 (a).]

The maximum efficiency has been found for a \(\Delta \epsilon\) between 1.15 eV and 1.2 eV with a transmission energy window \(\delta \epsilon\) of 0.02 eV. The value of limiting efficiency is 39.6% compared to 43.6% calculated in the previous section using ideal ESCS. The drop in efficiency is mostly due to the decrease of open circuit voltage related to the decreased extraction level, equation \((4.5.7)\). This is partially compensated by an increase in extracted current due to increased II rate.

Figure 4.5.47 (a) shows calculated efficiency as a function of for several values of extraction energy. In all the curves two different trends can be identified. If the value of \(\delta \epsilon\) is too close to zero, the efficiency is very low due to low carrier extraction, thus a very small value of short circuit current. The conductivity of the contact in this case is indefinitely large. Enlarging \(\delta \epsilon\), the number of carriers available for extraction increases, improving \(J_{sc}\), and so the maximum efficiency. In general the efficiency peak has been found for values of \(\delta \epsilon\) from 0.02 eV to 0.1 eV depending on the extraction energy \(\Delta \epsilon\). For the configurations which show higher efficiencies, \(\Delta \epsilon < 1.35\) eV, the optimum value of \(\delta \epsilon\) goes from 0.02 eV to 0.05 eV. This optimum value for \(\delta \epsilon\) of between is very close to \(kT_{\epsilon r}\). This represents the variation in energy in the contacts such that approximately the \(kT_{\epsilon r}\) will inevitably be lost anyway by carriers thermalising within the contacts. Thus it sets a lower limit on a reasonable \(\Delta \epsilon\). Therefore this result indicates that the transmission energy range has to be very small and confirms once again the high selectivity requirements of ESCS for HCSC \((4.5.58)\). In Fig. 4.5.47 (b) the value of maximum efficiency as a function of \(\Delta \epsilon\) is reported for different values of \(\delta \epsilon\). It can be observed that for small transmission energy window the extraction energy which allows maximum efficiency is lower compared to the one calculated using ideal ESCS. This effect is related to the higher occupancy at lower energies, which increases the value of \(J_{sc}\) for contacts with a small transmission window.
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

We developed a robust 2 dimensional model for describing the transport properties through quantum dot structures and have used this model to understand the filtering characteristics of Energy Selective Contacts (ESCs). In this way we are able to compute the effective filtering in 2 dimensions by running numerical simulations. The model is developed from a discretized Schrödinger equation by considering the sample volume as a collection of discrete points and using an effective mass approximation method over the entire volume.

During fabrication of the quantum dots in a dielectric matrix for selective energy contacts, different kinds of irregularities can be present in the structure, the major disorders being configurational (disorders in the position of the dots) and morphological (disorders in the size of the dots). The extent to which configurational and morphological disorders determine the electrical properties of the overall structure is investigated using simulation runs of the model. The disorders are assumed to follow a normal distribution from the mean position and size. The results show the outcome of an average of 1000 simulation runs with different standard deviation (σ) values.

Figure 4.5.48 shows the simulation results for resonance in 2.6nm Si dot in SiO₂ matrix under different orders of configurational disorders. As the disorders increases from σ =0 to σ =1 the conductance decreases by 53%, but the resonant energy remains the same at 1.205eV. This shows the confined energy in the QDs does not change as their size is fixed but the effective filtering reduces dramatically. Figure 4.5.49 shows the simulation results for a 2.2 nm Si dot in a SiO₂ matrix under different orders of morphological disorders. As the disorder increases from σ =0 to σ = 1, the conductance decreases by 60% and the resonant peak remains the same at 1.573eV. But the morphological disorders cause major impact compared to configurational disorders because of the widening of the energy selection window. This is due to the distribution in size of the QDs, since QDs with different sizes have different resonant energies which are slightly different from the mean resonant energy, the average of them all increase the spread of the resonant peak thus reducing the efficiency of the double barrier structure as energy selective contacts.
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 to give the same conductance as SiO$_2$, for which the very thin barriers are difficult to fabricate.

Figure 4.5.49 (right) shows the I-V characteristics for the double barrier QD structure with SiO$_2$ dielectric and SiC barriers at temperature 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 voltage in structures with SiC barrier than that in structures with SiO$_2$ barrier. This is due to the increased leakage and thus the lower confinement energy for the SiC.

### 4.5.3.2.2 Characterization of Energy Selective Contacts using ‘Optically assisted I-V’

#### Researchers:

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Collaboration with:

Daniel Hiller (IMTEK, University of Freiburg, Germany)

Optically assisted IV (oa-IV) is a new characterisation method which investigates an energy selective contact (ESC) fabricated on a Hot Carrier Absorber material with optical excitations in a pre-defined wavelength range. If a very large optical generation rate G$_{opt}$ exists adjacent to the ESC, it can probe this HC population immediately next to the contact. Alternatively, if the HC population within the absorber is known, the ESC can be tested for its energy selectivity. The basic principle is to provide free carriers with additional energy by optical means, see Fig. 4.5.50. The resonant level of the ESC can then be reached by carriers at a lower bias field, shifting the tunnelling resonance of the ESC – here a QD array – to lower bias voltages $V_{bias}$. Samples based on Si were provided by the University of Freiburg, see Fig. 4.5.51. Si is very far from being an ideal Hot Carrier Absorber due to the complete lack of a gap between optical and acoustic phonon modes and hence no propensity to slow carrier cooling. Furthermore, Si has an indirect band gap in the spectral range of optical excitation which renders the interpretation of measured data rather complex due to the absorption coefficient $\alpha_n$ changing over two orders of magnitude. However, for initial proof of concept it is adequate providing the excitation of hot electron-hole pairs in the material is sufficiently large and collection can be made from very close to the ESC.

A Xenon (Xe) arc lamp is a continuous light source with one of the most constant photon fluxes $\Phi_\nu$ in the spectral range 1000 to 500 nm. Nevertheless, there are significant deviations in particular in the long wavelength region (> 800 nm). We therefore compare oa-IV curves which have the same $V_{bias}$ for the current transition from forward to reverse direction, $V_{bias}^{-}$ ($V_{bias} < 0$), indicating a constant carrier product (constant quasi-Fermi level positions) at the ESC. Under these conditions, the current density as a function of quasi-Fermi level position can be assumed to be identical for these curves and this current density can be treated as a constant offset for each $V_{bias}$ value.

For liquid nitrogen (LN$_2$, T = 77 K) measurements, resonant tunnelling behaviour (negative differential resistance – NDR) was detected for all spectral ranges. With the method mentioned above, only the oa-IV curves from 800 – 750 nm and 650 –
600 nm with $\Phi_{\text{hv}} = 50$ Suns for each interval could be directly compared to each other. In addition, we evaluated the curves with optical excitations in the range of 1000 – 500 nm ($\Phi_{\text{hv}} = 600$ Suns) and 550 – 250 nm ($\Phi_{\text{hv}} = 140$ Suns). The former is near the practical high concentration limit for solar cells of 1000 Suns.

As shown in Fig. 4.5.52, for the curves in the 800 to 600 nm region at LN$_2$ temperature, the potential difference between $V_{\text{bias}}$($j \rightarrow 0$) and the average voltage of the resonance ($V_{\text{Res,avg}}$) shows a decrease of 48 mV with increasing photon energy (decreasing $\lambda$ range). As carrier densities (quasi-Fermi level positions) are identical for these curves, this potential drop corresponds to an increase in free hole energy of 48 meV. As this energy difference is equal to the effective $kT$, it can be interpreted as an increase in carrier temperature of $D_T = 560$ K when going from 800 – 750 nm (1.55 – 1.65 eV) to 650 – 600 nm (1.91 – 2.06 eV). Even at $F_{\text{hn}} ≈ 50$ Suns, this effect is small. This is due to Si being a very unsuitable absorber material, further corroborated by the ratio of peak to valley current densities (quality factor of NDR – QFNDR) dropping from 2.2 to 1.5. Si does not have a phononic band gap so that optical phonons undergo a rapid decay which tremendously accelerates carrier cooling.

For the 1000 – 500 nm and 550 – 250 nm ranges, the QFNDR increases significantly to 4.1 and 3.2, respectively. A quantitative comparison of both curves to each other or to the curves in the spectral range from 800 – 600 nm is thus not feasible. However, it shows that the energy selectivity may increase under high concentration $\Phi_{\text{hv}}$.

For all $\alpha$-$\psi$ curves, a tunnelling feature for electron extraction can be seen at 760 mV forward bias. However, the background current density is much higher than the tunnelling portion of the current density in this forward bias range, so no NDR can be seen.

At room temperature ($T = 300$ K), NDR was detected only for $\lambda$ ranges ≤ 600 nm, while the impact of resonant electron injection is still visible for curves in the 800 – 600 nm range. The background current density in the bias range around the tunnelling event increases by about an order of magnitude when going from LN$_2$ to room temperature. This is due to thermal activation of trap states and increased thermal scattering during carrier transport through the QD array. It has the same effect on NDR suppression as explained above for electron injection under forward bias.

The QD arrays were processed by segregation anneals, comprising some $10^{10}$ QDs as ESCs under the contact pad. It is very encouraging to see resonant tunnelling transport even at room temperature in a material system which was not grown epitaxially. At LN$_2$ temperature (77 K), an increase in carrier temperature of $D_T = 560$ K was detected when increasing the photon energy from $1.6 ± 0.05$ eV to $1.985 ± 0.075$ eV under a constant photon flux of $F_{\text{hn}} ≈ 50$ Suns. More suitable Hot Carrier Absorber materials will be investigated.

**4.5.3.3 Hot Carrier Absorbers: slowing of carrier cooling**

Researchers:
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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 [4.5.59].

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 [4.5.60]. 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 [4.5.61] using a simple 1D force constant model and complemented by high accuracy DFT computation [4.5.62] indicated that GaN, InN and InP all have large phononic band gaps, which are close to those found experimentally [4.5.63]. We are using time resolved photoluminescence (tr-PL) to investigate the carrier cooling rates in these materials.

4.5.3.3.2 Time resolved photoluminescence measurements of bulk phononic band gap materials

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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 Hot Carrier cells. The efficiency of an InN based hot carrier solar cell has been calculated using a complex theoretical model, see Section 4.5.3.1.1 was found that the limiting efficiency is strongly related to hot carriers relaxation velocity in the absorber [4.5.57].

A comparison of femtosecond time resolved photoluminescence (tr-PL) spectroscopy between InP and GaAs was reported in last year's annual report and is also now published [4.5.64]. This showed a distinctly longer carrier cooling time constant for the wide phononic gap InP as compared to almost zero phononic gap of GaAs. It also showed further evidence for excitation into higher side valleys for both GaAs and InP for appropriate excitation wavelengths. In 2010 the hot carrier cooling in InN has been investigated using tr-PL. The wide gap between optical and acoustic branches in the InN phononic dispersion relation (wider than that for InP) prevents the Klemens decay of optical phonon into acoustic phonons. This can lead to slower carrier cooling due to “Hot Phonon Effect” [4.5.65]. The decay of hot carriers for different excitation wavelengths InN has been investigated.

Tr-PL experiments have been performed on InN samples using the measurement configuration shown in Fig. 4.5.53. 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 collected from the sample, after a 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 is a three dimensional representation of PL as a function of time for all the probed wavelengths. It can be observed that the PL sharply rises when the carriers are photo-excited by the laser pulse. The fast decay of the PL shows the thermalisation of carriers towards respective band edges. The decay is faster for highly energetic carriers compared to carriers closer to the bandgap. Thus the carrier population quickly degenerates towards the band edges during the thermalisation process. In InN the thermalisation is most probably due to interaction of highly energetic electrons and holes with LO phonons [4.5.66].

To investigate the rate of the carrier cooling process, the effective temperature of the carrier population has been calculated fitting the high energy tail of the PL spectrum for every single time during the cooling transient. The PL has been fitted assuming that carriers form a Boltzmann-like distribution in a femtosecond time scale using the following equation.

\[ L(\varepsilon) \propto \alpha(\varepsilon) \varepsilon^2 \exp \left( \frac{E_G - \varepsilon}{k_B T_C} \right) \]

\[ L(\varepsilon) \] represents the measured PL intensity at energy \( \varepsilon \), \( \alpha(\varepsilon) \) is the measured sample absorption coefficient, \( E_G \) is the InN energy gap, 0.7 eV in this
case, and $k_B$ is the Boltzmann constant. $T_c$ is the fitted parameter and represents the hot carrier temperature. Figure 4.5.55 shows the carrier temperature transient, which seems to follow an exponential behaviour quite well (blue line – fit).

The fitting of the calculated temperature data has been performed using a single exponential.

$$T(t) = C \cdot \exp\left( -\frac{t}{\tau_{TH}} \right) + K$$

Here $\tau_{TH}$ represents the carriers thermalisation time constant, whereas $C$ and $K$ are two constant parameters. The fitted value for $\tau_{TH}$ is 7 ps. This long cooling constant can be attributed to the hot phonon effect due to the long lifetime of the A1(LO) phonon [4.5.64, 4.5.66]. This hot carrier relaxation velocity is still too high to achieve a considerable efficiency gain in an InN hot carrier solar cell. However, it has been demonstrated that, for InN, the carrier cooling velocity is strictly related to the quality of the material and slower carrier cooling constants compared to the ones calculated in this chapter have been reported in the literature [4.5.67].

4.5.3.3.3 Nanostructures for absorbers

Nanostructures offer the possibility of modification of the phonon dispersion of a composite material. III-V compounds or indeed most of the cubic and hexagonal compounds can be considered as very fine nanostructures consisting of 'quantum dots' of only one atom (say In) in a matrix (say N) with only one atom separating each 'QD' and arranged in two interpenetrating fcc lattices. Modelling of the 1D phonon dispersion in this way gives a close agreement with the phonon dispersion for zinc-blende InN extracted from real measured data for wurtzite material.

Similar 'phonon band gaps' should appear in good quality nanostructure superlattices, through coherent Bragg reflection of modes such that gaps in the superlattice dispersion open up [4.5.61]. There is a close analogy with photonic structures in which modulation of the refractive index in a periodic system opens up gaps of disallowed photon energies. Here modulation of the ease with which phonons are transmitted (the acoustic impedance) opens up gaps of disallowed phonon energies.

4.5.3.3.3.1 Force constant modelling of III-V QD materials by SK growth

Researchers: R. Patterson, Y. Kamikawa, G. Conibeer

Collaboration with: Yoshitaka Okada – University of Tokyo

3D force constant modelling, using the reasonable assumption of simple harmonic motion of atoms in a matrix around their rest or lowest energy position, reveals such phononic gaps [4.5.68]. The model calculates longitudinal and transverse modes and can be used to calculate dispersions in a variety of symmetry directions and for different combinations of QD sub-lattice structure and super-lattice structure.

III-V Stranski-Krastinov grown QD arrays of InAs in InGaAs and InGaAlAs matrices are fabricated at the University of Tokyo using MBE. We are investigating these for evidence of phonon dispersion modulation and potential slowed carrier cooling. In order to understand the expected phonon dispersions these are being modelled using the 3D force constant technique.

Lattice matched and strain compensated material pairs that may produce large phonon bandgaps are of interest. Previous iterations in the design of these structures indicated the importance of separating "light" and "heavy" atoms to different parts of the nanostructure. Initially, the lightest atom in the system, As, was present in both the QD and the matrix. This meant that the reduced mass of both regions (proportional to the sum of the inverses
of each atomic mass) was very similar as the light element dominates in this case.

On this iteration structures with an \( \text{In}_{0.5}\text{Ga}_{0.5-x}\text{Al}_x\text{As} \) matrix (with \( x=0.4 \)) and InAs QDs were grown. Significant Al content was introduced into these structures with the expectation that this light element, segregated to the matrix material, might produce appreciable phonon bandgaps. A schematic of the structure is shown in Fig. 4.5.56. Some images derived from characterisation of the structure are presented in Fig. 4.5.57. The superlattice of QDs has a simple hexagonal structure. Extraordinary periodic out-of-plane stacking is achievable and largely defect free structures can be grown on the order of microns.

Force constant modelling of this structure predicts an appreciable phonon bandgap, as shown in Fig. 4.5.58 and Fig. 4.5.59. This bandgap is due almost entirely to the presence of the Al in the system. A small bandgap is present due to the mass difference between In, Ga and As, but it is less than a quarter of the size shown in Fig. 4.5.58 and Fig. 4.5.59. Due to computational constraints the size of the QDs is quite small, only about a nanometre in diameter. While actual sizes for these structures are too computationally intensive to model without extreme effort, recent modelling with gradually increasing size suggests that the dispersion relations scale linearly with size. That is, once the discrete distances (bond lengths) are small relative to the superlattice unit cell dimension, the dispersion should look exactly the same when scaled such that the relative dimensions are preserved. This will be investigated in greater detail in further work.

4.5.3.3.2 Fabrication and characterisation of highly ordered nanoparticle arrays for Hot Carrier absorber

Researchers:
Lara Treiber, Shujuan Huang, Gavin Conibeer

As demonstrated by the work on modelling phonon modulation, periodic core-shell QD arrays 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. Deposition methods are being investigated to fabricate such highly ordered QD arrays.

The Langmuir-Blodgett (LB) technique fabricates thin films from colloidal dispersions of quantum dots (QDs). The LB technique allows for controllable, uniform film formation and subsequent transfer onto a solid substrate, such as quartz [4.5.69]. Through surface passivation of the QDs, interparticle spacing can also be controlled. Figure 4.5.60 illustrates the set-up of the LB apparatus and the functionalized QDs.

In 2010 work has focused on fabrication of periodic thin films of Si nanoparticles (NPs) provided by the University of Minnesota. The Si NPs under investigation are surface passivated with dodecane (\( \text{C}_{12}\text{H}_{26} \)), a long chain hydrocarbon rendering the surface hydrophobic. The particles were dispersed in chloroform and investigated using TEM, UV-vis spectroscopy and photoluminescence (PL). Using TEM imaging the average diameter was found to be 3.0 ±0.5 nm. Fig. 4.5.61 shows a droplet of solution (dispersed in chloroform) and the inset highlights the lattice fringes confirming the presence of silicon - a 3.14 Å lattice spacing corresponding to the (111) planes.

Densities of states (DOS) for the dispersion curve immediately to the left. Note small changes in the DOS could be due to pseudo-random locations of the Ga and Al particles or to differences in crystalline direction. (Far left): <100>, (Centre): <110>, (Left): <111> directions respectively.

FIGURE 4.5.58

FIGURE 4.5.59

Luburn-Blodgett set-up for film fabrication with surface functionalized Si NPs.

FIGURE 4.5.60

(Upper) TEM images of Si NPs dried on a grid. (Lower) TEM image of Si NP monolayer deposited at 50 mN/m of SP.

FIGURE 4.5.61
Selective energy contact: double (or triple) barrier QD resonant tunnelling

Slowed carrier cooling absorber layer:
- Periodic QD array tuned to block optical phonon decay by Klemens mechanism;
- Core shell QD for ease of tuning;
- Must also allow renormalization of carrier energy by e-e & h-h scattering.

Proof of concept with MOVPE/MBE III-V QD array.
Transfer to thin film or self-assembled QD array.

External contact

Selective energy contact: double (or triple) barrier QD resonant tunnelling
Slowed carrier cooling absorber layer:

- Periodic QD array tuned to block optical phonon decay by Klemens mechanism;
- Core shell QD for ease of tuning;
- Must also allow renormalization of carrier energy by e-e & h-h scattering.

Proof of concept with MOVPE/MBE III-V QD array.
Transfer to thin film or self-assembled QD array.

Selective energy contact: selecting opposite carrier type

External contact

Monolayer structures of Si NPs have been successfully deposited using the LB method and characterisation has been on-going using TEM, UV-vis, PL and Raman spectroscopy. Figure 4.5.61 (right) illustrates TEM image of the Si films fabricated at 50 mN/m surface pressures (SP) of the water trough. As noted, high contrast is difficult to achieve due to the small density difference of Si and the carbon-passivating chain. As a result, to further quantify the coverage and regularity, computer recognition software is required; on which work is on-going. It is difficult to see for this reason, but Fig. 4.5.61 (right) appears to show a dense packing of Si NPs.

UV-Vis spectroscopy was used to study the optical absorption of the films. As illustrated in Fig. 4.5.62 (left) for single layers of Si NPs at varying compression surface pressures (SP), the absorption clearly increases when SP increases, corresponding to higher packing densities of Si NPs. The PL spectra of the above films show narrow and symmetric peaks at 1.6 ~1.7 eV, as shown in Fig. 4.5.62 (right), which are in good agreement with the estimated bandgap using the 'effective mass approximation'.

The red shift in emission energy from Si NP films as compared to the solution corresponds to the electronic energy transfer from small particles to larger ones when they are closely packed (4.5.70).

Investigation of the electronic and phononic properties of the monolayer and multilayer structures are on-going using low-wavenumber Raman and time resolve PL spectroscopy.

4.5.3.3.3 Implementation of nanostructures for Hot Carrier cells

In order to use a nanoparticle array as a Hot Carrier absorber, and hence utilise slowed carrier cooling due to modified phonon dispersion, then a way to fabricate a complete structure with ESCs must be established. A structure in which nanoparticles are arranged in a uniform 3D array should give the required phononic band gap. The degree to which this needs to be ordered is still under investigation. Certainly a large difference between masses is beneficial between the nanoparticles and the matrix and this can be best achieved in an array of ‘core shell QDs’ in which the core and shell have very different acoustic impedance in order to promote coherent reflection and hence confinement of phonons [4.5.61]. The matrix in which such an array is embedded needs to allow transport of carriers to contacts and also electron-electron and preferably hole-hole scattering to renormalise carrier energies. Such a structure should also have a narrow electronic band gap so as to absorb a wide range of photon energies. This combination of properties is challenging but not mutually exclusive because phononic properties are largely independent of electronic properties. Energy selective contacts are also required for such a structure. These would most likely be arranged at the top and bottom of the absorber. (A hole contact might not need to be selective because the hole population only contains a small fraction of the hot carrier energy and hence thermalisation of holes is less important.) These ESCs would be QD or QW double barrier structures. (Addition of an extra layer to give double QD/QW triple barrier structures should also give rectification at the contact.) Such a QD array / double barrier QD ESC structure is shown schematically in Fig. 4.5.63.
Physical picture of the ND HC Solar Cell (upper) with a carrier diffusion field (core/shell thickness ratio not to scale), embedded into a wide band gap solar cell [4.5.71]. Iso-valent impurities provide an energy selective level for electrons. Band diagram of the ND HC Solar Cell matched to the physical structure (lower). Direct generation of hot exciton (1), energy selective extraction of hot electron from Hot Carrier absorber (2), thermionic emission/diffusion of holes over the barrier (3), electron-electron-scattering with renormalization of carrier energies and possible energy loss by phonon emission (4), free carrier re-absorption (5), impact ionization (6) and carrier generation in the wide band gap matrix (7).

FIGURE 4.5.64

Nanoparticle cell design incorporating ESCs and absorber

Researcher:
Dirk König

A full Hot Carrier cell requires control of optical, electronic and phononic properties in the same structure. One possible approach is the ‘nano-dot (ND) Hot Carrier cell’ embedded into the i-region of a wide band gap solar cell as shown in Fig. 4.5.64.

Hot Carrier solar cells must have a continuous electronic density of states (DOS) to maximise maximum photon absorption and elastic electron-electron scattering. The latter refills the depleted electronic energy levels from which electrons are extracted through the ESC. On the other hand, if they do not have a phononic band gap themselves the NDs must not be much bigger than the ballistic mean free path in order to prevent inelastic scattering by which carriers cool down rapidly. However, optical phonons can be confined in the nanocrystals as mentioned in Section 4.5.3.3 by arranging for a mismatch between optical phonon energies in the two materials. Core shell nanocrystals can be used to realise this [4.5.61, 4.5.62]. In addition the shell can be doped with iso-valent impurities which form split-off subbands within the electronic band gap of the material, such as boron replacing gallium in gallium nitride (GaN) [4.5.71]. Such an ESC would only work for one carrier type as co-doping of a thin nano-shell appears not to be technologically feasible. For some III-V compounds with a very high effective mass ratio between holes and electrons such that most of the excess energy during optical generation is taken up by the electron, thermalisation of holes does not represent a large loss in energy. Hence thermionic emission of holes over a low barrier can be used to transport holes into the bulk of the device to be collected by the junction with little loss in efficiency.

4.5.3.3.4 Hot Carrier Absorber: Choice of Materials

Researchers:
G. Conibeer, R. Patterson, P. Aliberti, S. Huang, Y. Kamikawa, D. König, Binesh Puthen-Veettil, S. Shrestha, M.A. Green

The properties required for a good hot carrier absorber material are listed below in order of priority.

1. Large phononic band gap \( (E_{\text{max}} - E_{\text{OA}}) \) - in order to suppress Klemens decay of optical phonons this must be at least as large as the maximum acoustic phonon energy. Hence a large mass difference (or large force constant difference) between constituent elements is required [4.5.61].

2. Narrow optical phonon energy dispersion \( (E_{\text{LO}} - E_{\text{OA}}) \) – in order to minimise the loss of energy to TO phonons by Ridley decay. This requires a high symmetry atomic or nano-structure, preferably cubic with degenerate optical phonon energies at zone centre.

3. Small electronic band gap – to allow a wide range of photon absorption. This should be less than 1eV. For 1 sun concentration the optimum is 0.7eV - as a band gap below this energy gives no advantage in the balance between absorption and emission. As the concentration ratio increases this optimum band gap decreases to zero at maximum concentration [4.5.1].

4. A small \( E_{\text{LO}} \) optical phonon energy (\( E_{\text{LO}} \)). This reduces the amount of energy lost per LO phonon emission, requiring a greater number to be emitted for a given energy loss [4.5.62]. However, it is difficult to have both a small \( E_{\text{LO}} \) and the large phononic gap required in 1. This condition requires further investigation, but does still argue for a small \( E_{\text{LO}} \).

5. An absolute small maximum acoustic phonon energy \( (E_{\text{OA}}) \). This maximises the phononic gap if \( E_{\text{OA}} \) is also small. A small \( E_{\text{OA}} \) requires a large mass for the heavy atom and/or small force constant for its bonds.

6. Good renormalisation rates in the material, i.e. good e-e and h-h scattering (\( e=\text{electron,} \).
This requires a reasonable DOS at all energies above $E_g$, or at least only very narrow gaps between energy levels, $s \Delta E$. This in turn requires a good overlap of wavefunction for carriers through the material, i.e. poor electronic confinement or a reasonable conductor. This condition is met in all inorganic semiconductors quite easily, with $e-e$ scattering rates of less than $100fs$ for reasonable carrier concentrations. It may not be met in organic semiconductors or in nanostructures with large barrier heights.

7. Good carrier transport in order to allow transportation of hot carriers to the contacts. This is similar to 6, except that it only needs to be in direction of the contacts, probably the z growth direction. A reasonably low resistance is probably good.

8. It should be possible to make good quality, highly ordered, low defect material. Preferably it should be easy and cheap to do this.

9. Earth abundant and readily available and processable constituent elements and processes.

10. No or low toxicity of elements, compounds and processes.

[IE$_{opt}$, $E_{min}$, $E_{max}$ are the maximum optical, minimum optical and maximum acoustic phonon energies respectively.]

InN has most of these properties, except 4, 8 & 9, and is therefore a good model material for a hot carrier cell absorber.

**Analogue of InN**

As InN is a model material, but has the problems of abundance and bad material quality, another approach is to use analogues of InN to attempt to emulate its near ideal properties. These analogues can be II-IV-nitride compounds, large mass anion III-Vs, group IV compounds/alloys or nanostructures.

**II-IV-Vs: ZnSnN, ZnPbN, HgSnN, HgPbN**

With reference to Fig 4.5.65, it can be seen that replacement of In on the III sub-lattice with II-IV compounds is analogous and is now quite widely being investigated in the Cu$_2$ZnSnS$_4$ analogue to CuInSe$_2$ [4.5.72].

ZnGeN can be fabricated [4.5.73] and is most directly analogous with Si and GaAs. However, its band gap is large at 1.9eV. It also has a small calculated phononic band gap [4.5.74]. ZnSnN has a smaller electronic gap (1 eV) and larger calculated phononic gap [4.5.74]. It is however difficult to fabricate, and also its phononic gap is not as large as the acoustic phonon energy making it difficult to block Klemens decay completely. HgSnN or HgPbN should both have smaller $E_g$ and larger phononic gaps. These materials have not yet been fabricated [4.5.75].

**Large mass cation:**

The Bi and Sb compounds have large predicted phononic gaps and Bi is a relatively abundant material, with only low toxicity [4.5.75]. BiB has the largest phononic gap but AlBi, Bi$_2$S$_3$, Bi$_2$O$_3$ (bismuthine) are also attractive. Similarly SbS has a large predicted phononic gap. That for AlSb is the same size as the acoustic phonon energy and its band gap is 1.5eV, making it marginal as an absorber material and similar to InP.

**Group IIIA III-Vs**

LaN and YN both have large phononic gaps whilst that for ScN is too small.

The Lanthanides can also form III-Vs. ErN and other RE nitrides can be grown by MBE. The phononic band gaps of the Er compounds are predicted to be large, because of the heavy Er cation, but its discrete energy levels make it not useful as an absorber, although the combination of properties in a nanostructure could be advantageous.

**Group IV alloy/compounds:**

All of the combinations Si/Sn, Ge/C or Sn/C look attractive with large gaps predicted in 1D models. However being all group IVs they only form weak compounds. Unfortunately SiC, whether 3C, 4H or 6H, has too narrow a phononic gap. Nonetheless GeC does form a compound and is of significant interest [4.5.76].

There are also several other inherent advantages of group IV compounds/alloys all of which are associated with the four valence electrons of the group IVs which result in predominantly covalent bonding:

a) The elements form completely covalently bonded crystals primarily in a diamond structure (tetragonal is also possible in $\beta$Sn). However for group IV compounds the decreasing electronegativity down the group results in partially ionic bonding. This is not strong in SiC and whilst it tends to give co-ordination numbers of 4, can nonetheless result in several allotropes of decreasing symmetry: 4c, 4h, 6h. However, as the difference in period increases for the as yet theoretical group IV compounds, so too does the difference in electronegativity and hence also the bond ionicity and the degree of order. For a hot carrier absorber this is ideal because it is just such a large difference in the period which is needed to give the large mass difference and hence large phononic gaps. All of GeC, SnSi, SnC (and the Pb compounds) have computed phononic gaps large enough to block Klemens decay, and should also tend to form ordered diamond structure compounds.

b) Because of their covalent bonding, the group IV elements have relatively small electronic band gaps as compared to their more ionic III-V and much more ionic II-VI analogues in the same period: e.g. Sn 0.15eV, InSb 0.4eV, CdTe 1.5eV. In fact to achieve approximately the same electronic band gap one must go down one period from group IV to III-V and down another period from III-V to II-IV e.g. Si 1.1eV, GaAs 1.45eV, CdTe 1.5eV. This means that for group IV compounds there is greater scope for large mass difference compounds.
whilst still maintaining small electronic band gaps. A small band gap of course being important for broadband absorption in an absorber - property 3 in the desirable properties for hot carrier absorbers listed above.

c) The smaller $E_g$ would tend to be for the larger mass compounds of Pb or Sn. Which, to give large mass difference, would be compounded with Si or Ge. This trend towards the lower periods of group IV also means that the maximum optical phonon and maximum acoustic phonon energies will be smaller for a given mass ratio - the desirable properties 4 and 5.

d) Furthermore, unlike most groups, the group IV elements remain abundant for the higher mass number elements – desirable property 9. Property 10 is also satisfied because the group IVs have low toxicity.

**Nanostructures:**
As discussed in section 4.5.3.3.3 QD nanostructures can be viewed in the same way as compounds. Their phononic properties can be estimated from consideration of their combination force constants. Hence it is possible to engineer phononic properties in a wider range of nanostructure combinations.

Of the materials discussed above the Group IVs lend themselves most readily to formation of nanostructures instead of compounds due to their predominantly covalent bonding, which allows variation in the coordination number. Therefore the nanostructure approaches of section 4.5.3.3.3 are consistent with a similar description as analogues of InN, whether it be III-V QDs, colloidally dispersed QDs or for core shell QDs.

**4.5.3.3.5 Summary of Hot Carrier solar cell research**
2010 has seen significant development in most areas of Hot Carrier solar cell work. The modelling of efficiencies not only now includes real material parameters for highly promising absorber materials such as InN, but also is now extended to Energy Selective contacts of finite width. The transport across such contacts has now been modelled for a range of QD matrix combinations. Work on ESCs has seen further more detailed demonstration of the necessary resonance in double barrier resonant tunnelling structures, with additional evidence for hot carrier populations, albeit very small, from illuminated I-V measurements with the optically assisted I-V technique. Measurement of InN with time-resolved PL has indicated some evidence for slowed carrier cooling, further corroborating the importance of a large phonon band gap to block optical phonon decay, but also highlights the importance of material quality. Modelling of nanostructures for absorber materials has focussed on real III-V QD structures, showing phonon bandgaps which will soon be measured in phonon dispersion measurements. Progress on the Langmuir-Blodgett approach to ordered nanoparticle arrays has seen development of ordered single layer arrays of Si nanoparticles. The potential application of nanostructures to fully integrated devices has started to be investigated conceptually, with various designs considered. Similarly the possibility of absorber materials which are analogous to InN is also being investigated. These many aspects of Hot Carrier cells will see further development and consolidation in 2011 with recent success in significant additional funding.

**4.5.4 Up-conversion**

**Researchers:**
Craig Johnson, Gavin Conibeer

**Collaboration with:**
Peter Reece (Physics, UNSW)

**Up-conversion in novel silicon-based materials**
Up-conversion (UC) in erbium-doped phosphor compounds (particularly NaYF$_4$:Er) has been shown to be a promising means of enhancing the sub-band-gap spectral response of conventional Si solar cells without modification of the electrical properties of the cell (4.5.77). In this scheme, a layer containing the phosphor is applied to the rear of a high-efficiency bifacial cell. After absorbing two long-wavelength (~1500nm) photons - which are transmitted by the cell - the excited Er ions can relax by emitting a photon with an energy greater than the Si band gap, thereby increasing the current that can be extracted from the cell.

While phosphors have demonstrated high-efficiency UC behaviour, their use presents particular challenges with regard to fabrication and cost. Our work in the last year has focused on the development of Er-doped porous Si (PSi:Er) as an alternative UC material. PSi is unique in that its porosity - and hence the material refractive index - can be varied as a function of depth, allowing for the elaboration of high-quality monolithic Si optical structures such as distributed Bragg reflectors (DBRs). A cross-sectional electron micrograph of such a structure is shown in Fig. 4.5.66. Its porous substructure also allows for deep infusion of dopant atoms via techniques such as electroplating.
We have previously reported room-temperature UC luminescence from Er-doped nanoporous Si when excited at very high power densities with a 1550nm laser. In the past year we have focused on increasing the efficiency of this UC luminescence by modifying the PSi structure as described above.

The dependence of the efficiency of the UC process on irradiance is non-linear in the range of "sun-like" incident power. That is, the concentration of the incident radiation into a small Er-doped region results in greater efficiency than for non-concentrated radiation over a proportionally large-area device. Typically, concentration is achieved using lenses or non-imaging optics, but we have examined an analogous electromagnetic field enhancement in the vicinity of optically-active Er ions by the excitation of slow-light modes in these PSi:Er DBRs.

Field enhancement in 1D PSI:Er photonic crystals

Though their use preceded the advent of the photonic crystal concept, DBRs can be described as one-dimensional photonic crystals. The regular variation of the optical thickness of multiple alternating layers results in wavelength-dependent interference behaviour manifesting as discrete bands of allowed and disallowed electromagnetic modes, as shown in the left panel of Fig. 4.5.67. The "edge" of a photonic band is a spectral region in which the effect of coherent scattering processes changes abruptly between transmission and reflection of incident photons as determined by the superposition of Bloch waves. Insofar as the group velocity $v_g$ of an incident wave can be said to transition between "positive" and "negative" values - implying energy propagation into and out of the structure, respectively, in bands of strong transmission and strong reflection - there exists an inversion point at which $v_g$ is zero, corresponding to a standing wave established by the superposition of scattered Bloch components. As can be seen in the right panel of Fig. 4.5.67, group velocity is drastically suppressed across a broad region near the zero-point. For steady-state equilibrium conditions, this slowing of energy propagation requires a proportional increase in energy density, that is, an enhancement of the electromagnetic field strength within the structure. It can be shown that the efficiency increase for a two-step UC process is proportional to $(c/nv_g - 1)I_0$, where $c$ is the speed of light in vacuum, $n$ is the average refractive index of the multilayer material, and $I_0$ is the incident field intensity [4.5.78]. In this way the slow-light mode acts to augment the interaction that converts energy from the field into atomic potential energy, resulting in a boost in the efficiency of the process until saturation is reached.

Simulation of field enhancement in 1D PC structures

Using a 1D transfer matrix calculation, we simulated the reflectivity characteristics of a series of PSi DBRs with 10, 20, 30 and 40 high-/low-porosity bilayers. As shown in Fig. 4.5.68, the reflectivity characteristic of a DBR contains a wide photonic stop-band. The structural parameters were tuned slightly in each case as the number of bilayers increased to produce a short-wavelength band edge minimum at 1550nm, the excitation wavelength of interest (marked with a dashed red line).

Maximum transmission of ~1550nm light into the structure is clearly required for efficient coupling into the Er ions. From Fig. 4.5.68 it is evident that an increased number of layers "compresses" the reflectivity characteristic, resulting in a steeper
Intensity-valued mode profile in DBRs with varying numbers of high/low-porosity bilayers for a leading band edge fixed at ~1550nm. All intensities are normalized to the incident field intensity and each plot is independently color-scaled to show maximum detail. The air and substrate interfaces with the DBR are indicated by the dashed black (upper) and red (lower) lines, respectively.

**FIGURE 4.5.69**

4.5.5 Plasmonics for 3rd Generation structures

Researcher:
Supriya Pillai

Plasmonics is the study of the interaction of light on a thin metal dielectric interface resulting in the collective oscillation of the free electrons in the metal. This gives rise to exciting properties that are very different from the bulk metal. It is an emerging area of technology for photovoltaic applications with potential for light management at the nanoscale. Ever since our proof-of-concept results were published in 2007 [4.5.79], there has been a huge increase in interest in incorporating nanoparticles on solar cells due to their demonstrated light trapping properties. The large optical polarisation associated with the nanoparticles results in a strong enhancement of the electric field around the vicinity of the particles along with strong scattering. This optical property is being utilised for improving light trapping in thin-film solar cells.

The scattering or near field enhancement is strongest at the surface plasmon resonance (SPR) frequency and this can be tuned by changing the size, shape, dielectric medium around the particles. SPR tunability offers control in manipulating light in the regime where the absorption of the solar cells are weak. Our recent work (see section 4.4 Thin Film) has shown the benefits of having the particles on the rear as opposed to previous work with front located particles [4.5.80]. By having the particles on the back of the cell any potential loss due to absorption in the metal or losses due to sub-resonance photocurrent suppression resulting from destructive interference of the scattered and transmitted light into the semiconductor layer can be avoided [4.5.81]. An additional advantage is that because the scattering plasmonics layer is electrically decoupled from the cell, the antireflection layer on the front and the plasmons...
can be optimised independently of each other. Our recent work has also made use of an additional reflecting layer (paint) along with the nanoparticle layer on the rear side of the cell to maximise the randomisation of light and to ensure no light is lost [4.5.80].

In this study we focus our interest on the use of plasmonics for low-dimensional structures like quantum dot structures for possible applications in tandem solar cells. PL measurements were used to characterise the samples. The analysis is based on the reciprocity of light that a good absorber can be a good emitter and the proof-of concept established with EL measurements in an earlier study [4.5.82]. Hence the PL enhancement would be synonymous to an increase in photocurrent for an optimised QD cell.

The tunability of plasmon resonance allows the possibility of increasing the photocurrent of each cell in a tandem cell configuration. Optimising the nanoparticle parameters can help achieve wavelength dependent light trapping which will be an encouraging step towards increasing the performance of a tandem solar cell. Figure 4.5.70 shows one way of achieving the SPR tunability by varying the size of the nanoparticles in a tandem cell configuration.

The sample under study is a 4nm single layer silicon QD structure in an oxide matrix with a 6nm capping oxide layer with an emission wavelength of 930nm (~1.3eV). Mass thicknesses of 10, 14, 18 and 22 nm silver were deposited and the particles annealed at 200°C in nitrogen for an hour. A 532nm, 10mW Nd:YAG laser was used to illuminate the samples for both the front (incident on QD layer) and rear side (incident on the quartz slide) locations of the silver nanoparticles and the PL plots studied. PL measurements were carried out on these samples and the effect of different size particles were investigated both before and after the deposition of the nanoparticles.

The self assembly techniques of nanoparticle fabrication give a varied size and shape distribution suitable for a broadband response. This is particularly noted for particles corresponding to thicker Ag layers as can be seen from the PL plots in Fig. 4.5.71. The red-shift of the enhancement peaks with larger particles are also clearly evident. More details of this work has been reported in [4.5.83].

Rear located nanoparticles perform better than front located nanoparticles, consistent with the results from thin-film cells. We believe this is because of the change in scattering cross-section of the nanoparticles due to the changes in the driving field and also due to the change in the mode of excitation (from air for front located nanoparticles and from Si for rear located nanoparticles) for the two different locations on the samples. More work need to be done to better understand the mechanism. Further work will also concentrate on using alternate approaches for tuning the resonance position close to the band-edge (emission wavelength for PL) to increase the scattering properties and hence absorption in the weakly absorbing range.

4.5.6 Concluding remarks for the Third Generation section

In 2010 work has proceeded significantly in all the areas of Third Generation research, with improved fabrication and characterisation of materials and complexity of modelling which together give an overall better understanding and optimisation of devices.

Group IV based nanostructure materials have seen significant improvement in device design. With interlayers, in both SiN$_x$ and SiC matrices, used to effectively control both the uniformity of size of Si QDs and carrier transport in the growth direction. Modelling now allows the confined energy levels of complex QD shapes to be calculated and their overlap to form mini-bands estimated in more detail. At the same time improved characterisation is giving a much clearer idea on the shape and distributions of Si QDs and is now allowing choice of growth parameters to give uniform size spherical QDs to be grown. Ge nanostructure materials have seen improved control of p-type conductivity in...
Ge QDs and very highly crystalline growth of Ge QWs. Homojunction Si nanostructure devices have demonstrated improved conduction, there has been continued demonstration of rectifying properties for heterojunctions with c-Si and heterojunctions between two nanostructured materials are now starting to exploit the advantages of both. Hot carrier cells have seen further development of efficiency modelling which now not only includes material parameters such as Auger coefficients for real promising absorber materials such as InN, but also includes the effects of real non-ideal energy selective contacts. There has been significant improvement in measurement of negative differential resistance in Si QD based energy selective contacts is now allowing and this overlaps well with continuing improvement in modelling the transport through such structures in various matrices. Carrier cooling measurements on the candidate absorber material InN have shown evidence for phonon bandgaps building on the slowed carrier cooling seen in InP previously. Modelling of analogues of these materials in nanostructures now predicts the phonon properties of real III-V QD arrays grown by collaborators. In addition colloidal nanoparticles have now been fabricated as coherent single layer nanoparticle arrays and are progressing towards multi-layer structures. Theoretical work on the potential for absorption with controlled phon dispersion and hence slowed carrier cooling has progressed on approacatable analogues for InN and devices involving various nanostructure configurations are being analysed conceptually.

Up-conversion has seen a further significant development of the use of porous-Si as a host for Er up-converting species. The porosity of porous-Si can be controlled to give layers of alternating refractive index which can be used as distributed Bragg reflectors to modify the photonic density of states such that there is strong enhancement of photonic modes at the critical Er absorption at 1500nm. This has been demonstrated and can lead directly to large increase in the up-conversion efficiency, thus tackling one of the key problems of rare earth up-conversion that it is inherently non-linear and dependent on concentration.

Plasmonics, which has previously been shown to enhance emission and absorption from both 1st and 2nd generation cells, has now been applied to the Si nanostrung layers of 3rd generation materials. This has shown significant enhancement in luminescence demonstrating the strong potential to achieve local concentration with a global 1 sun illumination. This is particularly useful for several of the non-linear 3rd generation approaches.

The development of all the 3rd generation projects in 2010 now allows much greater understanding of the materials and devices. Work in 2011 will see consolidation of this into improved devices. Several new areas of funding will contribute to this and also allow development of new project areas.

References:
4.5.8 X.J. Hao, I. Perez-Wurfl, G. Conibeer, M.A. Green, 19th PVSEC, Korea, Nov 2009.
S. Huang, MA. Green, "Evolution of Si (and SiC) quantum dots in Si-rich nitride/Si3N4 superlattice Gentle, "Size dependent optical properties of Si quantum dots" , Physical Review B, 2008. 4.5.35
