CHAPTER 9

Photovoltaic Power Generation … the Impact of Nano-materials

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Abstract

Solar power is seen by many as a solution to the world’s energy problems. The earth receives $1.7 \times 10^{17}$ W from the sun compared to a total electricity generation capacity of $4.6 \times 10^{12}$ W (OECD prediction for 2010). However the average power density is low with a daytime average over the earth of 680 W/m$^2$. This makes centralised generation problematic but distributed photovoltaic generation by domestic and commercial users is a rapidly developing market. However typical commercially available modules have an energy conversion efficiency of less than 12%. Silicon cells with 24% efficiency have been produced in the lab while multi-junction tandem cells using different semiconductor materials (GaInAs, GaInP and Ge) to absorb different parts of the sun’s spectrum have reached 40%. This chapter describes some of the materials and device achievements so far and looks at possible ways in which higher efficiencies might be achieved with particular emphasis on nano-materials to use more of the solar spectrum efficiently. The possibility of using quantum slicing and multiple exciton generation to make more efficient use of high energy photons is considered and impurity band generation as a possible route to use low energy photons. One of the greatest challenges is to do this cheaply using semiconductors made from non-toxic abundant elements.

Keywords: solar, photovoltaic, silicon, nanomaterials, quantum dot CdSe, GaAs, GaInAs, GaInP, Ge

1. Solar Energy

The last ten years has seen a dramatic increase in research into renewable energy sources. The reasons are well publicised: increasing world energy demands particularly from countries with emerging economies, exhaustion of easily accessible oil resources and fears that global warming is a result of CO$_2$ emissions from fossil fuels. Solar power is the prime source of renewable energy and is very substantial. In one hour the sun delivers energy equivalent to an entire year of energy consumption by mankind. The problem is how to harness the sun’s massive energy output. One option is to produce electricity by photovoltaic cells.

The irradiance at the extremity of the earth’s atmosphere is $\sim 1360$ W m$^{-2}$ with a spectral distribution as shown in Figure 1 as (a). The spectrum is basically that of a 5762K black body radiator on which are superposed the fine detail of emission lines and Fraunhofer lines resulting from absorption in the peripheral solar gas. At the surface of the earth additional spectral detail is introduced by absorption in the earth’s atmosphere1 (line b) resulting primarily from water vapour, carbon dioxide and ozone. The available energy is also reduced by Rayleigh and Mie scattering processes with the result that the available power density at the earth’s surface after the light has passed through 1.5 atmospheres (typical of latitudes $\sim 50^\circ$) is around 900 W m$^{-2}$ at midday. These data have been published as ASTM standards from which Figure 1 is derived 2. However local variations occur due to climatic conditions in addition to the systematic variation with latitude, season and of course time of day. For Europe these values have been compiled under the PVGIS project3 and are available as interactive...
maps. As an example of the total of the solar energy available in an average year on an optimally inclined surface the value in Berlin is 1142 kWh/m².

Many approaches to using this energy have been proposed. In this chapter we focus on photovoltaics but this need to be considered in the context of other approaches. These have been reviewed with an emphasis on the materials requirements in a 2008 issue of the MRS Bulletin devoted solely to energy provision.

## 2. Photovoltaic Power Generation

### 2.1 Basic Concepts

Converting the power in sunlight to electricity efficiently is not simple. It can be seen in Figure 1 that there is quite a broad spectral distribution of the available energy. If the light is used to generate electrons in a semiconductor, photons with an energy greater than the bandgap will be absorbed and have a probability of producing a carrier which can be supplied to an external circuit. In conventional solar cells, often referred to as first generation cells, photons with an energy less than the bandgap will not be absorbed by the semiconductor and their energy will be lost. This also applies to second generation cells which are usually thin films of semiconductor deposited on low cost substrates. In a conventional p-n junction solar cell the output voltage is dependent on the bandgap of the absorbing semiconductor so the greater the bandgap the greater the voltage. However photons with an energy greater than the bandgap will only produce one carrier pair so energetic photons will not be used effectively in a simple p-n junction system.

These concepts are illustrated in Figure 2 which also shows some other energy loss mechanisms. Recombination at defects and impurities is normally small in high quality wafers of single crystal silicon grown by the Czochralski or float zone methods but is very significant in block cast polycrystalline material. Surface and interface recombination depends largely on cell design and fabrication technologies but is increasingly important in conventional second generation thin film cells. However the dominant loss mechanisms are the fundamental problem of not using below bandgap photons at all and not using photons with energies significantly above band gap effectively.

A consequence of the above issues is that there is an optimum bandgap for simple solar cells (ie first and second generation). A maximum possible efficiency for conversion of the solar spectrum can be calculated allowing for the lost photons of long wavelength and the partial energy conversion of the short wavelength radiation. This calculation was first published by Loferski in 1956 and subsequently refined by Shockley and Queisser. They assumed the sun was a black body radiator at 6000K and the solar cell temperature 300K. They derived a detailed balance limit of the
conversion efficiency for a semiconductor of gap 1.1eV of 30% assuming a perfectly matched load, 100% absorption of photons with energy greater than the band gap and no non-radiative recombination losses. Numerous variants on this calculation have been published and an “optimum” bandgap calculated at around 1.35eV determined but the general conclusion is that there is a fundamental limit to the achievable efficiency of a simple p-n junction solar cell of between 30 and 35%, the exact value in various publications being dependant on the assumptions made.

In practice silicon with its bandgap of 1.12eV has received most technological attention and efficiencies over 24% have been achieved for small area optimised structures. Figure 3 illustrates a high efficiency silicon cell showing some of the measures necessary to reduce surface recombination, optimise absorption and reduce reflection. These issues are discussed in detail elsewhere. The silicon used to achieve these efficiencies was single crystal magnetically-confined Czochralski or float zone. These materials have a long minority carrier lifetime and so largely fulfil one of the Shockley-Queisser conditions of no non-radiative recombination. This is not the case for the low cost block cast polycrystalline silicon used for mass produced cells where typical efficiencies are 10%. In this material and in very lower cost metallurgical silicon purified by low energy methods the challenge is to reduce the non-radiative paths usually attributed, at least in part, to metallic contamination. This issue has received much attention and a substantial volume of literature exists quantifying the problem and proposing possible solutions.

In conventional silicon cells a long minority carrier lifetime is an essential prerequisite for high efficiency primarily because it provides the long diffusion length for minority carriers and hence enables effective collection of the carriers generated by absorption of photons. The fundamental requirements are to eliminate (or at least minimise) recombination in the bulk, at the surface and at interfaces.

Cells based on wafers of single crystal silicon are considerably more efficient than cells made from polycrystalline material or thin films deposited on glass or metal substrates. However the material cost is higher. In May 2008 SunPower announced that they had produced a production prototype large area cell (5inch) based on monocrystalline wafered silicon with an efficiency of 23.4% beating the previous year’s pre-production best from Sanyo by a small margin. This is probably very close to the achievable limit for commercial device designs.

It is well known that photovoltaic cells degrade under normal operating conditions. In the case of satellite cells the dominant mechanism is radiation damage which limits the useful life of the cell. In terrestrial cells there are a number of known mechanisms. A particular problem is the degradation of the efficiency of boron doped silicon cells containing oxygen which occurs during the first few days of operation. This is most significant in high efficiency cells made from Czochralski material but also occurs in multi-crystalline cast material.

Typical degradation is 10% relative so the efficiency of a 20% cell reduces to 18% after two or three days’ operation. Although this effect has been known for some time it is only recently that the mechanism has been explained as being due to the formation of a metastable boron-oxygen complex. The effect can be reversed by thermal treatments and avoided by doping with gallium instead of boron or reducing...
the oxygen content of the silicon. Unfortunately these alternatives have economic or practical difficulties and so this rapid initial degradation is of considerable practical importance.

2.2 Economic and Ecological Considerations

The economics of the generation of electricity from solar power are skewed by governments providing a “feed in tariff” This essentially guarantees domestic users and small enterprises a market for their solar electricity fed into the distribution grid at a price well above the 2008 cost of generation from fossil fuels. Some countries (for example Germany) guarantee the tariff for a fixed period making the purchase of solar panels a safe investment. In general the cost of this subsidy is met by increased tariffs to the electricity consumers. Estimates of the actual ratio of production costs vary but in the USA a figure which is often quoted is that electricity generated by a small photovoltaic installation (~ 2kW peak) if it were to be fed into the grid would cost five times as much as electricity generated from a coal station at the point of production. This assumes the photovoltaic system has a working life of 25 years. The calculation is only relevant for grid connected installations because it does not take into account the need for energy storage necessary for stand alone systems during the hours of darkness. This is more than the cost of the solar cells.

Feed in tariffs are a justifiable short term policy for the situation where photovoltaic generation is a small proportion of the total generation capacity. Such distributed power generation, usually at a domestic level, is based on the solar panel as a consumer good. A century of experience tells us that such markets have a high elasticity of demand. Mass production drives down the price which further stimulates demand. The norm early market situation is a 10% decrease in production cost for each doubling of market size.

At the present time system costs far outweigh material costs but in the future this will not be the case. Infrastructure costs also favour high efficiency devices because, although cheap lesser efficiency systems seem equivalent, the reality is that for urban applications the area available for solar cells is strictly limited and a larger area means larger land and installation costs. Inevitably the driving force is towards cost effective high efficiency systems.

A useful concept in assessing the ecological and economic value of solar cells is “payback time”. This can either mean the time to recover the financial investment in terms of the cost of energy produced or simply the time taken to recover the energy expended in producing the solar cell or more realistically the solar cell system including the voltage conversion and management circuits and devices. If we ignore the feed in tariff the reality of the situation in 2007 was that commercially available systems will take more than 20 years to pay back economically. Although some manufacturers claim a 30 year life expectation for their modules it is quite evident that both cost and efficiency improvements are essential. Much needs to be done in terms of materials research to achieve this.

Energy payback time has been studied recently for the case of silicon polycrystalline panels by Stoppato15. She analysed the production process in detail and identified the
most energy hungry steps. Assuming a commercial poly-silicon 100cm² panel manufactured by existing methods, installed on grid (all output used) in various locations, she calculated an energy payback time typically between 4 and 6 years.

3. Beating the Shockley-Queisser Limit

Achieving truly high efficiencies (well above the Shockley-Queisser limit) at low cost is an essential pre-requisite to the widespread adoption of photo-voltaics for energy production. Many publications propose approaches to this problem. The most common short term solution is to split the spectrum into component parts and extract energy from the spectral segment with an appropriate band gap semiconductor. This can be done with dichroic mirrors feeding light to two separate independent cells or by using a number of solar cells stacked with the widest bandgap on top. Such a structure could consist of separate cells or a monolithic structure composed of semiconductors with multiple gaps again with the widest gap on top.

The design of such stacked multiple junction cells is very complicated. As the junctions are connected in series the same current flows though the entire structure. In consequence the band gaps need to be chosen so that each material system contributes the same current utilising the appropriate spectral region. This is compromised in the monolithic structures by practical considerations of available materials with either lattice matching or controlled strain … issues which will be considered later.

These structures are inevitably more expensive than a simple one bandgap cell so, although they are widely used as power supplies in communication satellites, for terrestrial applications they are looked at primarily for applications where the sunlight is concentrated via a lens or reflector system. However a key problem with concentrators is that in a focused system the optics must track the sun to retain the optimum advantage of concentration. This is typically done with mechanical systems although clever optics can eliminate moving parts at a cost of lower efficiency when the sun deviates by more than about 20º from the cell axis.

Cells operating under concentrated light are in general more efficient. This is partially because of the reduced significance of non-radiative processes but after such processes have saturated, the gain in efficiency with increased intensity is due to increased cell voltage. The photovoltaic current increases approximately linearly with solar intensity and because the current appears across a p-n junction the voltage increases logarithmically with voltage. Hence an increase in efficiency is observed until the increase in Ohmic voltage drop (which rise linearly with current and is due to series resistance effects) exceeds the increase from the diode I-V dependence.

The temperature rise of the cell has also to be considered because of its effect on the leakage current and the shift of band gap. The latter is a surprisingly large effect. At 20ºC the optimum gaps16 for a two band gap cell are 0.96 and 1.54eV while at 150ºC the gaps (measured at 20ºC) need to be 1.2 and 1.8eV respectively17. Because of these factors concentrator cells usually operate at or less than two hundred times the intensity of normal sunlight, referred to as 200 suns.
Henry\textsuperscript{18} has calculated the limiting efficiency of multiple energy gap solar cells using a very similar approach to Shockley and Queisser but using the true air mass 1.5 spectrum for a somewhat unrealistically high level of concentrated light of 1000 suns. Henry’s calculation for a single material cell with the optimum gap of 1.35eV under one sun is 31\% (very close to the Shockley and Queisser calculation) and under 1000 suns 37\% assuming a cell temperature of 300K. For multiple junction devices with optimum bandgap materials the maximum efficiency of a two junction cell was calculated to be 50\%, three junctions 56\% and 72\% for 36 energy gaps. Henry makes an important point that this efficiency although high is well below the thermodynamic limit for converting the energy of 1000 sun radiation into work (93\%). This is because energy is lost and entropy increases when light is emitted from the forward biased p-n junctions.

4. Multiple Cell Systems

4.1 Physically Separate Cells

Conceptually dual cell systems are the simplest way to utilise more of the solar spectrum effectively. Early proposals consisted of two separate cells of different materials In Figure 4a this is effected by a dichroic mirror. Using AlGaAs and Si as the materials an efficiency of 28.5\% was achieved as early as 1978\textsuperscript{19}. The wavelength separator system has also been proposed for use in conjunction with a thermoelectric generator\textsuperscript{20}. The more difficult to utilise long wavelength region could be concentrated on the thermopile while the shorter wavelength component would be directed onto a photovoltaic element. Current thermoelectric materials provide efficiencies around 8\% so much work must be done before such systems contribute much to the total system performance.

An approach which combines the concepts illustrated in Figures 4a and 4b is being followed in a current research programme using two tandem cells one of which filters the radiation with the remaining flux being incident on a silicon cell\textsuperscript{21}. By using a static concentrator and a dichroic prism designed to have an optical efficiency of 93\% in combination with GaInP/GaAs + Si and GaInAsP/GaInAs diodes the sum of the outputs from the cells (not connected in series and optimised independently) amounted to 42.9\%.

The structure shown in Figure 4b utilises the top cell to absorb the high energy photons which are filtered out leaving the remaining radiation to be used by the lower cell. This is the basis of the most widely used strategy for beating the Shockley-Queisser limit namely the monolithic tandem cell.

4.2 Monolithic Multiple Cell Structures
Monolithic tandem cells are based on well established technologies and have been used extensively in commercial space applications since the mid 1990s. These structures are typically made from InGaP/GaAs/Ge with bandgaps of 1.85/1.4/0.66eV. In 1997 such devices used in terrestrial applications achieved 30% efficiency at air mass 1.5 under 1 sun intensity\textsuperscript{22}. For concentrator applications under AM 1.5 and 200 suns such a cell has been demonstrated to give 39.2%\textsuperscript{23}.

The development of such devices presents immense challenges in terms of materials and design trade-offs. The concept is simple and expounded above. The two materials have to filter out a segment of the spectrum so that the combination of bandgap, thickness and efficiency produces equal current in each region which is also equal to the current generated in the germanium substrate. Direct gap materials are desirable for the upper layers because the absorption edge is abrupt resulting in the requisite absorption being produced by thinner (and hence in principle less expensive) layers. In addition thinner layers give good performance with shorter diffusion lengths. However in thin layers the surface and interface become more significant so that surface recombination needs to be actively suppressed.

To a large extent all these issues can be quantified and used in a design model. However what is much more difficult to predict is the effect of strain, relaxation and dislocations on the non-radiative recombination. An added complication is the interdiffusion between the layers which can occur during growth and subsequent processing. This can result in bandgap shifts or in unwanted donors and/or acceptors. The latter problem is relevant because the substrate is a group IV compound and the upper layers III-Vs.

A key issue in tandem cells is that it is necessary for current to flow through the entire structure. This necessitates passing current through a reversed biased junction without a significant barrier and minimal series resistance. The latter issue is particularly important for concentrator cells and is achieved by using a tunnelling junction relying on highly doped regions. This “contact” between cells must also be transparent.

### 4.3 GaInP/GaInAs/Ge Concentrator Cells

The material system GaInP/GaInAs/Ge has proved to be one of the most successful for concentrator cells produced at the time of writing. It has been used by several research groups and some designs are in an early production stage in concentrator systems. Figure 4 illustrates two very efficient monolithic tandem structures. One is a lattice matched cell and the other a metamorphic tandem cell. Both are designed by Spectrolab and have achieved over 40% conversion efficiencies\textsuperscript{24, 25}.

The metamorphic device was operated at 240 suns (24W cm\textsuperscript{-2}) at air mass 1.5. The device has an open circuit voltage of 2.9V and a short circuit current of 1A (current density 3.8A cm\textsuperscript{-2}) The cell consists of a Ga\textsubscript{0.44}In\textsubscript{0.56}P/Ga\textsubscript{0.92}In\textsubscript{0.08}As/Ge structure (1.8/1.3/0.66eV). Carrier confinement (to reduce surface and interface recombination) is effected in the top cell by the AlInP window and the AlGaInP back surface field (BSF) layer. At the time of writing the Spectrolab device holds the world record for efficiency of any solar cell. However other groups have achieved efficiencies close to
40%. The view has been expressed in both commercial and scientific literature that 50% is achievable using this technology. Metamorphic material systems offer greater design flexibility but are not as mature as lattice matched systems. Life tests on lattice matched systems designed for space use are remarkably stable under 1 sun under air mass 1.5. Certainly they do not suffer the 10% relative degradation in the first few days of operation seen in high efficiency boron doped Czochralski silicon cells. However detailed studies are required to discover the long term stability of high efficiency concentrator tandem cells.

There are however many doubts surrounding these well developed tandem cell materials. The high cost restricts their use to concentrator systems. To maintain a high system efficiency throughout all hours of daylight mechanical tracker systems have to be used. Although these are acceptable for central generator installations they are less attractive for domestic use because of maintenance and the impact on the appearance of homes. Passive concentrators compromise efficiency over a large part of the day and are only highly efficient for around two hours each side of noon. However a crucial point to bear in mind is that the ultimate or thermodynamic limit on efficiency is 68% at one sun but rises with concentrated sun light. As the subject progresses it seems inevitable that we will move towards the thermodynamic limit making concentrator cells a certainty for large scale commercial generation on fundamental as well as economic grounds.

If solar cells are to contribute a major part of our electricity requirement very large amounts of the solar cell material will be required and the question has been raised as to whether accessible resources of indium and germanium are adequate for such widespread application. The question is even more acute in non concentrator systems.

5. Thin Films and Hetero-junctions

Many other ways of making solar cells are being explored. The so called second generation solar cell projects are focussing on reducing costs by using thin films usually with a single p-n junction but sometimes with wider band gap confining layers. The technological target is to reduce material and manufacturing cost while attaining high efficiency in an evolutionary rather than revolutionary way. A very large number of systems and materials have been explored including amorphous Si, thin film Si, CuInxGa(1-x)Se2, CdTe, and a range of organic materials. The latter will be considered in detail in section 6.5.

These second generation cells are based on inexpensive supports, soda glass, metal or in some cases plastics and encapsulated with low cost materials. In some cases good efficiencies have been achieved in the lab. However wafer based crystalline silicon still remains the dominant material system commercially constituting more than 85% of sales. Among the thin film devices CdTe has achieved greatest market penetration (although others have considerable potential) because of reasonable efficiencies and the possibility of depositing thin films very cheaply and with little energy expenditure. However the long term future of CdTe as a major technology is
questionable. The primary reason for this is the toxicity of cadmium. CdTe cells contain more than 1% Cd and so are technically illegal in Europe. They can only be sold because of a special temporary dispensation. In addition Te has the problem referred to above of being a material with very limited abundance which could not sustain widespread use in non-concentrator applications. The market leader in the field, First Solar, has attempted to overcome these difficulties by providing recycling as part of their module supply contracts. An overview of the development of thin film technologies has been published by Green26 and a review of confirmed best efficiencies across all technologies compiled on a regular basis and published in Progress in Photovoltaics27.

An interesting variant on solar cell design is to use a pn hetero-junction. Here the different bandgaps of the two materials can absorb a wider spectral region than a single material and so can beat the Shockley-Queisser limit. However there is a fundamental difference when compared to the tandem cell. Carriers generated in both materials contribute to the current so that the current contributions from the two materials are in parallel. The output voltage is the voltage from the single junction. In the tandem cell the junctions are in series (hence the need to balance the currents) but the junction voltages are additive. This is conceptually important in relation to the next section in which nano-materials are discussed.

6. Nano Materials to the Rescue?

The primary importance of nano-materials in opto-electronics is that the small dimensions confer quite different properties on the material. Such structures bridge the transition between bulk semiconductors and individual atoms. If the physical size of the semiconductor sample is reduced the interaction between the atoms differs from the bulk solid and the properties become very interesting from the point of view of electronic materials and novel applications particularly in the area of opto-electronics.

Such concepts are not at all new. The ideas expressed above have been known in terms of quantum wells for more than twenty years and are widely used today in semiconductor LASERs in consumer goods. Quantum wells are planes of semiconductor material usually within a wider band gap host. Carriers are confined to move in two (as distinct to three) dimensions. A structure which is of fundamental interest in relation to nanostructures is the quantum well solar cell. Mazzar28 describes a strain-balanced GaAsP/InGaAs multi-quantum well structure grown on GaAs with a AM 1.5 efficiency under 200 suns of 26%. The spectral response is extended considerably beyond that of GaAs. An important factor in these structures is the recombination in the quantum wells which is believed to be predominantly radiative resulting in photon recycling. However there are inevitably losses involved in such recycling and this may present an insuperable barrier to obtaining very high efficiencies in such cells.

Much more interesting are structures which confine carriers to motion in one or zero dimensions referred to historically as quantum wires (1D) or quantum dots (0D). For the purposes of this chapter these later structures are our nano-materials.
A key advantage in optoelectronics (and indeed in several other semiconductor device applications) is that the material properties can be adjusted or in some cases continuously tuned by simply changing the size of the structure. The most obvious property is the effective band gap which increases as the dimensions decrease. The use of such structures in solar cells have potential advantages over conventional materials in several important applications but represent immature explorations or in some cases little more than proposals. The primary hurdle to application is the fabrication of the nano-material with controlled structure. For example quantum dots can be fabricated by simple self organising techniques but the wide size distribution renders such materials difficult to use in applications where close control of specific properties is required.

The requirements for a successful nano-structured solar cell which will be widely adopted follow quite logically from the discussion in earlier sections. Essentially:

1) It should have high conversion efficiency. This necessitates using as much of the solar spectrum as effectively as possible and being able to extract the carriers with minimal losses from recombination, series resistance etc.
2) It must be inexpensive to manufacture using abundant non-toxic materials.
3) It must not degrade substantially during a working life of 20 to 30 years.

In the remainder of this chapter we will explore a range of approaches which either use nanostructures as the key enabling technology or material systems which might benefit from nanomaterials. This is a very fast moving area and many proposals regarding the potential of nanostructures for solar energy have been made. The review below covers some of the key approaches and gives a brief overview of each with selected state of the art examples. Where possible references are given to comprehensive reviews.

6.1 Tandem and Heterojunction Cells using Nanomaterials

Being able to tune the bang gap of a nano-structured material suggests a solution to matching the solar spectrum. Silicon nano-crystals smaller than 6nm exhibit quantum confinement. It is quite easy to grow such dots in a matrix of SiO₂. If they are sufficiently densely packed the overlap of the wavefunctions produces a miniband which results in a nano-structured material having an effective bandgap larger than that of silicon and in consequence could be used as the upper (short wavelength absorbing) layer in an “all silicon” tandem cell. One could envisage multiple layers with varying sizes of nano-particles resulting in a multiple tandem structure.

Silicon is an indirect bandgap semiconductor so needs phonon participation in the absorption process. This results in weaker absorption and a less steep dependence of absorption coefficient as a function of wavelength in bulk materials. In quantum dots the k-conservation requirement is relaxed and so the material behaves more like a direct gap material with, effectively, greater absorbance. However a major problem is the extraction of carriers and, as in the cases of the III-V tandem cells described earlier, the difficulty of matching currents in the series combination of layers.
A less demanding task would be to produce a hetero-structure cell as shown in Figure 6. Here the shorter wavelength light generates carriers in the wider bandgap nano-material while longer wavelength light is absorbed in the substrate. The carrier current in the two regions is additive while the open circuit voltage will depend on the bandgaps, their alignment and the location of the Fermi levels in the two materials. Such a cell need not necessarily have a uniform size distribution of quantum dots which is difficult to achieve if reliance is placed on random nucleation. However the layer must carry current and the carriers must be extracted from the dots. This has proved to be extremely difficult to achieve with any reasonable efficiency in practical systems.

The optimum bandgap for the top absorber in a silicon based two cell device at AM1.5 is 1.7eV. Photoluminescence studies indicate that 2nm quantum dots in an SiO₂ matrix would have an effective bandgap close to this. Cho et al have fabricated such a nano-material in silicon by producing by thermal treatment of a sputtered silicon rich SiOₓ layer between 2 and 5nm thick on an p-type silicon substrate. Phosphorous was co-sputtered in order to produce n-type conduction in the dot layer although the actual mechanism is unclear.

The role of dopants in quantum dots is rather debatable but Cho does observe n-type conduction in the nano-layer provided the spacing of the dots is less than 2nm. The open-circuit voltage increased with reductions in QD size, which was attributed to bandgap widening effect in the Si QDs and an improved hetero-junction field allowing a greater split of the Fermi levels in the Si substrate. Photovoltaic conversion efficiencies of ~10% were observed but at this stage it is not possible to say if the nano-layer made any contribution to this.

A silicon substrate is not the ideal material for such a structure as, apart from cost, photons longer than the Si bandgap are lost in this type of cell. Some work has also been done on other materials but work is at a very early stage. However other very different approaches are being investigated to utilise the longer wavelength photons.

### 6.2 Intermediate Band Cells

All the cells we have considered so far use photons to effect excitation from the conduction to the valence bands. If we were to introduce an impurity band in the gap then carriers generated by longer wavelength photons could be used and the energy of two photons summed to produce carrier energies comparable with an excitation across the full band gap. This process was observed for discrete energy levels by Grimmeis and calculations undertaken in relation to its predicted application in solar cells by Wolfe. The concept is illustrated in Figure 7. Ideally the band should be offset so that effectively the material has three absorption edges. The position of the band should be chosen so that the carrier flux in process (b) matches the carrier flux in process (c) so maintaining sufficient occupancy of the intermediate level to maximise absorption. The combination of the processes a, a', b and c could cover the absorption range of a triple junction tandem cell although some of the energy involved in a' would be lost.
Detailed balance calculations for an idealised case have been undertaken by Luque and Marti\(^{33}\) who show that assuming the cell has perfect contacts and is thick enough to assure complete absorption of the photons with enough energy to induce the transitions in Figure 7 the cell will outperform a tandem cell. They also make the assumption that there is no non-radiative recombination. This is somewhat unrealistic because of recombination via the intermediate band similar to a Shockley Hall Read process.

Attempts to use impurities in silicon to produce the intermediate energy level in such solar cells have been notably unsuccessful. The negative effects of non-radiative recombination always outweigh the effects of increased absorption. This is largely predictable as such near mid gap impurity states tend to have low oscillator strength but are often powerful non radiative centres when present as point defects. Recently however two proposals have been put forward which may avoid this seemingly fundamental barrier and the most promising route ahead appears to be via nanomaterials.

Macdonald et al\(^{34}\) have proposed locating the impurity band in a region of the cell which has a larger band gap than the base cell material. The effect of this is that the carriers generated by interaction of the photons with the mid gap impurity band are swept away from the impurity doped region and hence are spatially remote from the potential recombination path. Initial trials used Si implantation damage in a-Si deposited on Si as the optically active region. A very marked increase in absorption of below bandgap light (1100 to 1600nm) was observed but no additional carriers were delivered to the crystalline silicon.

Luque et al\(^{35}\) have developed the model referred to above and applied it to an intermediate band prototype fabricated from InAs quantum dots in a GaAs matrix. The analysis shows evidence of splitting between the conduction and intermediate band quasi-Fermi levels, one of the basic hypotheses on which operation of such cells must depend. These ideas have been used by Wei and Forrest\(^{36}\) to consider Quantum dots embedded in an energy fence barrier to eliminate charge trapping and hence non-radiative recombination. A p⁺ i n⁺ cell with QDs buried in a high band gap barrier layer has been proposed and analyzed by them. The maximum solar power conversion efficiency under AM1.5 of a GaAs-based photovoltaic cell employing 10-20 layers of InAs QDs surrounded by a Al\(_x\)Ga\(_{1-x}\)As barriers in the depletion region is calculated to be as high as 45%. Higher efficiencies are anticipated for InP-based cells.

Kechiantz et al\(^{37}\) have considered similar issues using an intermediate band effected with type II quantum dots in the Si/SiGe system. A barrier layer promoting the separation of the quasi-Fermi levels is modelled around the QDs. Conditions for the separation of the quasi-Fermi levels and the activation of the two-photon generation of mobile carriers were found. Under these conditions the photocurrent and the conversion efficiency of the Ge QD buried Si solar cell exposed to concentrated sunlight was postulated to be 25% larger than that of conventional Si solar cells. However such devices have not been realised in practice.
6.3 Quantum Cutting

In cases where the photon energy exceeds the band gap the difference in energy is lost in a conventional photovoltaic cell. The tandem cell moves towards solving this problem by the series combination of different gaps and of course in the limit the loss could be eliminated completely by an infinite number of band gaps. Even with a nanostructure to produce tuneable gaps it seems unlikely that this could be done economically. Figure 2 summarises the problem … essentially how do we capture the energies shown as $\Delta E_e$ and $\Delta E_h$? Several proposals have been put forward. One of these is the process of quantum cutting. The term was introduced in relation to the luminescence of Eu$^{3+}$ doped LiGdF$_4$ where the excitation of Gd$^{3+}$ with a vacuum UV photon resulted in two visible photons being emitted by Eu$^{3+}$ through a two-step energy transfer from Gd$^{3+}$ to Eu$^{3+}$, with a quantum efficiency that approached 200 percent$^{38}$.

Early indications are that similar processes can occur in silicon nanocrystals at longer wavelengths. Timmerman et al$^{39}$ have undertaken proof of principle experiments which result in the spatial separation of the two lower energy excitonic states so eliminating the very rapid Auger recombination and carrier cooling effects that normally occur. If this can be translated into a practical device it provides a potentially very effective way of using higher energy photons.

6.4 Hot Electrons, Multiple Exciton Generation and Carrier Multiplication

A process with a similar end result to the above but which is conceptually quite different is to utilize the hot carriers produced by absorption of above band gap photons directly. There are several possible ways to do this. If the higher energy electrons can be extracted an enhanced photo-voltage will be produced. This process necessitates the fabrication of selective energy contacts from which the higher voltage can be obtained. This might be accomplished using resonant tunnelling and although such schemes have been proposed and proof of concept of selective energy contacts has been demonstrated for double barrier resonant structures using Si quantum dots$^{40}$ the problems of efficient extraction and electrical linkage to energy generated by the equilibrium carrier population have not been resolved.

If the photon energy is sufficient a second electron–hole might be produced and if the bandgap energy is small enough then it is possible that many electron hole pairs could be generated. This approach was considered in silicon by Kolodinski et al$^{41}$. They presented experimental evidence that the excess photon energy shown in Figure 2 can be utilized for the generation of a second electron/hole pair. The hot carriers of the primary electron/hole pair generate secondary pairs and so can result in a quantum efficiency exceeding unity. In their case they observed a quantum efficiency of 1.3 and propose a band structure which would optimise the effect.

This process has attracted much interest recently and there is now overwhelming evidence that multiple electron hole pairs are produced in many materials and that the process is very effective in quantum dots$^{42}$. What has emerged in recent publications
is that the process can be very highly efficient even at low excitation densities and is extremely fast. This is very important if it is to compete effectively with other processes which might result in energy loss. Much work has focussed on PbS, PbTe and PbSe nanocrystals which have sufficiently low band gap for the effect to be of practical value in relation to the solar spectrum. The generation of eight excitons from a single photon has been observed and the threshold energy of the photon to produce two excitons need only be twice the band gap energy. The process seems to be remarkably efficient in many nano materials including silicon.

It is evident that such processes have great potential and estimates of ultimate efficiencies have been suggested in the scientific press of such third generation cells achieving efficiencies of 80%. However the problem of extracting the carriers from the quantum dots and using them efficiently remains unsolved and presents considerable fundamental difficulties.

### 6.5 Organic Composites

Very remarkable success has been achieved in recent years in the development of organic light emitting diodes. This is a major factor in stimulating investment in small molecule organics and polymers for solar cells. The big attraction of these materials is that some of them can be made and deposited very cheaply, often from solution on flexible substrates and with a very low expenditure of energy. This is a major area of research and has been the subject of several comprehensive reviews and of journal special issues in recent years.

It is possible to produce organic and polymeric materials with appropriate band gaps for use as solar cell materials. These are often referred to as low band gap organics (sometimes called small molecule materials in this context) or polymers. The band gap in these materials is considered to be the difference between the highest occupied molecular orbital and the lowest unoccupied molecular orbital energy levels. The absorption spectra are distinctly different to conventional inorganic semiconductors and are typified by broad peaks rather than an abrupt absorption edge. As a result the utilisation of the solar spectrum is not as effective as inorganics of appropriate band gap. The absorbancy of the solar spectrum in organics is typically rather low and so thick layers are required to achieve appropriate absorption. This is a major problem as the low carrier mobility of organic materials results in unacceptable series resistance in thick layers.

Early attempts at using organic materials were typified by very low efficiencies and rapid degradation. The present position is that reasonable efficiencies have been demonstrated (~5%) and lifetimes of tens of thousands of hours although it seems that often the most efficient materials degrade quite rapidly and so it is not usual to obtain both long life and high efficiency in the same material at the present time. The degradation process has been the subject of a recent comprehensive review.

A promising approach which may go some way to resolving the conductivity and absorption problem is to combine nano particles with organic materials. Various material systems have been explored by several research groups. A very early report of reversible photoinduced electron transfer from poly[2-methoxy,5-(2'-ethyl-}
hexyloxy)-p-phenylene vinylene] (MEH-PPV) onto C$_{60}$ was published by Sariciftci$^{53}$ and has stimulated many investigations of C$_{60}$, which can act as an acceptor of up to six electrons, in polymers and small molecule organics. This system has been reviewed by Davenas et al$^{54}$ who has compared it with TiO$_2$ nanoparticles in poly[vinylcarbazole] (PVK) and silver particles in MEH-PPV to provide enhanced charge separation by plasmon resonance at the metal/polymer interface.

Alternative approaches include C$_{60}$ with zinc-phthalocyanine$^{55}$, polymers using graphene as the acceptor$^{56}$ and poly phenyl azo methane thiophene (PPAT) using ZnO nano-particles$^{57}$. These and related systems offer considerable promise but as yet have not shown the expected increase in efficiency over the engineered polymer devices referred to previously.

### 6.6 Dye Sensitisation

The term sensitisation is used to convey the idea of separating the absorption process from the carrier transport process so that appropriate materials can be selected separately for the two functions. The approach has similarities to film based photography where the spectral response of silver halides is modified by the co-location of dyes which have absorption spectra in the visible part of the spectrum. Solar cells base on dye sensitisation have been pioneered by O’Regan and Grätzel$^{58}$ but conceptually the subject is a very broad. It includes two disparate aspects: the general area of sensitisation, which can be achieved by organic dyes or by quantum dots, and the topic of photochemical cells$^{59}$ which also embraces the idea of direct photo-generation of hydrogen.

A sensitised cell uses a material to effect the absorption of a photon to form an exciton, a mechanism to separate the hole and electron constituting the exciton, and material(s) to transport the holes and electrons to contacts to the external circuit. There is in this system an important fundamental difference from the conventional photovoltaic cell in that not only can the materials be optimised for their specific function but if total separation of the hole and electron can be achieved at the absorber/conductor interface recombination can be eliminated and so the only competing process is the recombination of the exciton inside the absorber. If the extraction rate is very fast compared to this (and evidence in quantum dots and dye molecules suggests that this can be the case) then in principle the efficiency is only limited by the spectral absorbance.

Grätzel’s early cells$^{58}$ were based on a thin (~10μm) film of TiO$_2$ particles (~15nm in size) coated with a monolayer of a trimeric ruthenium dye complex. TiO$_2$ has a band gap of 3.2eV but the cell absorption onset was at 750nm (due to the dye) and wavelengths shorter than 550nm were almost completely absorbed resulting in 46% of the incident solar energy being used. The carrier transport mechanism was a result of an electron being transferred from the dye to the n-type TiO$_2$ and the electron being replaced in the dye by an iodide/tri-iodide redox electrolyte. The cell voltage is the difference between the quasi-Fermi level in the TiO$_2$ under illumination and the...
electrochemical potential of the electrolyte. For the cell described this is ~0.65V and an overall efficiency at AM1.5 at slightly less than one sun was ~7%.

Numerous variants on dye sensitised cells exist and efficiencies greater than 10% have been achieved\textsuperscript{60}. TiO\textsubscript{2} appears to work well because of its large surface area for holding the dye however the close packed structure does not conduct well so this has led some groups to consider quantum wires. Law et al used a dense array of close packed ZnO nanowires which provides better conductivity but the overall efficiency reported\textsuperscript{61} was less (1.5%) than the TiO\textsubscript{2} nano particle structure due to reduced absorbancy as a direct result of the involvement of less dye.

Dye cells suffer from various degradation processes but probably the most vulnerable aspect is the electrolyte. Attempts are in progress to replace the liquid with a solid or stable gel. In general this reduces the rate that carriers can be replenished in the dye reducing the efficiency at higher intensities. However Wang et al\textsuperscript{62} have obtained efficiencies of ~7% with a “quasi-solid-state” electrolyte and it seems that further progress is likely. Dye sensitised cells are a very attractive system both from a commercial and scientific viewpoint and considerable investment is now being committed to this approach.

7. Conclusions

It is evident that there is considerable political and commercial pressure to develop effective sources of solar energy. Photovoltaics have many advantages over other approaches and seem to have the potential to achieve high efficiencies for both distributed and central electricity generation.

At the present time the market is dominated by wafer based silicon technologies but second generation cells using thin films at lower cost per watt are likely to take a significant market share as demand increases. Longer term, high efficiency cells must inevitably replace these first and second generation systems. Already concentrator cells with efficiencies > 40% have been fabricated and higher efficiencies seem possible although at the present time these use very expensive technologies. It is evident that the community is now searching for revolutionary approaches as the evolutionary approach can already be seen to yield diminishing returns in terms of performance and ultimately in cost per delivered kWh. Many new ideas have flooded the literature in the last few years most revolving around nanostructures and it would seem that some of these have the potential to provide very high efficiencies at low cost ... an essential prerequisite to large scale adoption of photovoltaic energy generation.

Should this happen it is then inevitable that a massive market for solar cells will develop with conservative estimates of the value of the solar materials market exceeding the present day requirements of the semiconductor industry by more than a factor of ten.
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Figure Captions

Figure 1 Spectral distribution of the sun’s irradiance on earth at a) air mass 0 (top curve) and b) air mass 1.5. For a simple pn junction silicon solar cell only photons with an energy greater than 1.12eV are absorbed.

Figure 2 Representation of some important energy loss mechanisms in first and second generation pn junction solar cells.

Figure 3 PERL (passivated emitter, rear locally-diffused) solar cell structure (reproduced with permission from Zhao et al7).

Figure 4 Two approaches to spectrum splitting a) dichroic mirror with two cells b) cascaded cells using a wide gap cell on top with a transparent rear connection allowing longer wavelength light to be transmitted.

Figure 5 40% efficient InGaP/GaAs tandem cells with InGaP tunnel junctions and an AlInP barrier layer acting as a window layer (reproduced with permission from King et al25).

Figure 6 Conceptual representation of a silicon quantum dot heterostructure solar cell. The silicon quantum dots absorb shorter wavelengths to create carriers while the crystalline silicon substrate acts as a conventional photovoltaic material in the heterostructure.

Figure 7 Intermediate band cell showing absorption processes which might be engineered to provide effective absorption of photons and carrier generation over a very wide range of energies.
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Figure 2 Representation of some important energy loss mechanisms in first and second generation pn junction solar cells

- Energy lost due to relaxation and carrier cooling
- Energy lost due to recombination at defects, surface and interfaces
- Open circuit photovoltage
- Energy loss due to series resistance and load matching

Photon with energy greater than bandgap creates hot carriers $E_{hot} - E_g$ is lost

Energy of below bandgap photons lost
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