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Towards Sustainable Photovoltaics: the Search for New Materials

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Summary

The opportunities for photovoltaic solar energy conversion are reviewed in the context of projected world energy demands for the 21st century. Conventional single crystal silicon solar cells are facing increasingly strong competition from thin film solar cells based primarily on polycrystalline absorber materials such as cadmium telluride (CdTe) and copper indium gallium diselenide (CIGS). However, if PV is to make a significant contribution to satisfying global energy requirements, issues of sustainability and cost will need to be addressed with increased urgency. There is a clear need to expand the range of materials and processes that are available for thin film solar cell manufacture, placing particular emphasis on low energy processing and sustainable non-toxic raw materials. The potential of new materials is exemplified by copper zinc tin sulfide (CZTS), which is emerging as a viable alternative to the more toxic CdTe and the more expensive CIGS absorber materials.

Key index words

electrodeposition, photovoltaics, solar cells, sustainability, thin film

Photovoltaics in Perspective

According to BP's 2009 Statistical Review of World Energy (1), the annual primary energy consumption in 2008, was equivalent to around 11 gigatonnes of oil, an increase of around 30% compared with a decade earlier. In terms of primary (thermal) power rather than energy, the corresponding 2008 figure is 13.2 TW, of which less than 0.8 TW was generated by non-nuclear renewable resources (primarily hydroelectric). Estimates of future requirements vary, but a relatively optimistic scenario considered by the European Union (2) considers that energy consumption will at least double by 2050. If CO₂ emissions are to be pegged at current levels, we need to find an additional 13-15 TW of power from renewable resources by 2050. This represents a formidable challenge roughly equivalent to increasing the number of nuclear power stations in the world from the current 61 to 1,200. The question we may now ask is – can solar energy conversion make a substantial contribution towards filling the widening energy gap? The total power of the sun's radiation that is incident on the earth can be calculated from the solar constant (1.366 kW m^{-2}) and the cross sectional area of the earth. The result is 1.4×10^{17} W, i.e. around 5000 times the estimated primary power requirement for 2050. If we assume that we could cover 1% of the earth's land surface with solar arrays operating at a power efficiency of 10%, a rough calculation based on the land area illuminated by the sun and losses due to weather and seasons indicates that photovoltaics could generate around 25 TW. The constraints imposed by mineral scarcity become apparent from a calculation that shows that the amount of cadmium that would be required to fabricate enough CdTe solar cells to generate this power exceeds identified world reserves (3) by more than a factor of a hundred. In other words, resource limitations appear to restrict

the possible contribution of CdTe solar cells to less than 1% of the total additional power required by 2050. Clearly, planning for terawatt deployment of photovoltaics requires careful consideration of sustainability issues including materials scarcity and cost.

The availability and price of a range of elements used in photovoltaic cells are contrasted in Figure 1.

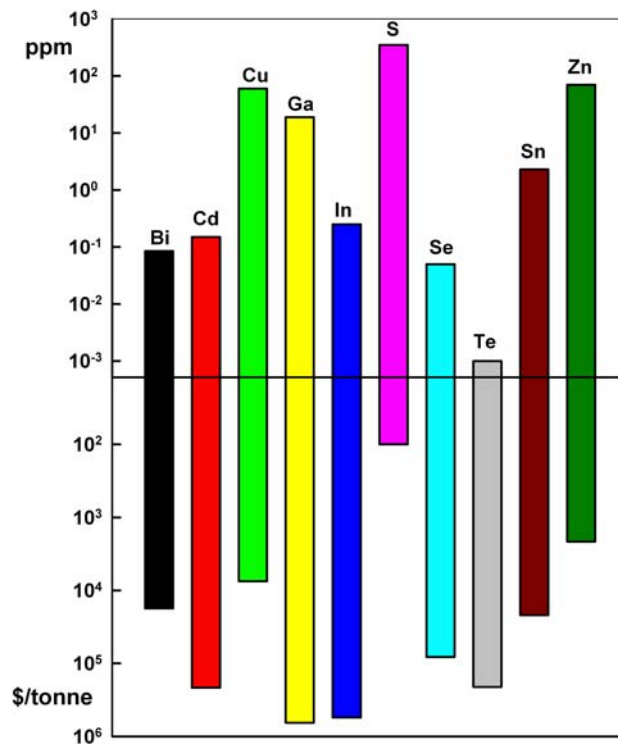


Figure 1. Occurrence in the earth’s crust and current costs of some of the elements relevant to thin film photovoltaics. Note that logarithmic scales have been used for both y axes. Current technologies include CIGS – copper indium gallium diselenide - and cadmium telluride (CdTe). Promising alternatives include copper zinc tin sulfide (CZTS). (Online version in colour).

As the preceding discussion of CdTe makes clear, the materials requirements for large scale deployment of PV are demanding. Figure 2 compares current annual production of the same set of elements. The impact on production requirements of increasing production of thin film PV would clearly be largest for CIGS, since the annual production of indium and gallium is tiny compared with metals such as copper zinc and tin, which could be used in the alternative material, CZTS.

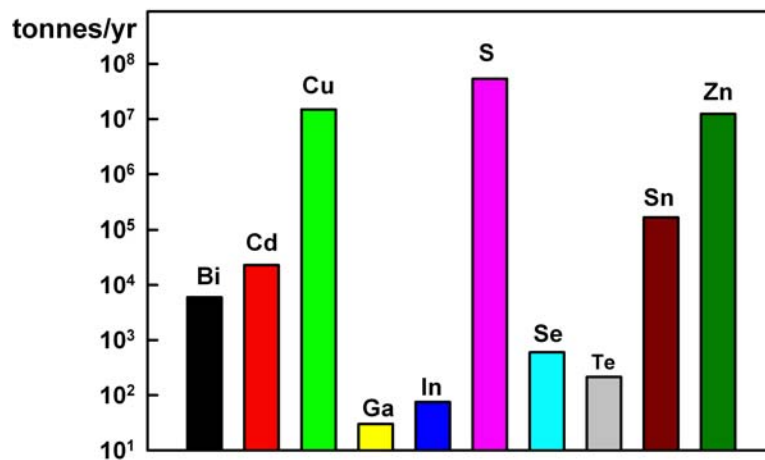


Figure 2. Annual production of some of the elements relevant for photovoltaics. Note the logarithmic y scale. (Online version in colour).

Solar cells need sun. The amount of solar radiation available for photovoltaic energy conversion varies considerably. In Europe, Spain and Italy have particularly high levels of sunshine that are not too different from those in North Africa. In the UK, irradiation levels are more modest but still usable. Figure 3 is the European Commission's map of annual irradiation levels for Europe (4), which shows that the South of the UK receives more than 50% of the annual amount arriving in North Africa. It is worth noting that the role played by PV in national energy strategies is not related simply to the local levels of

solar radiation. Germany - which receives a level of irradiation similar to that of the UK - had achieved an installed PV capacity of 9.8 GWp¹ by 2009, whereas the UK was far down the European list with only around 33 MWp installed.(5)

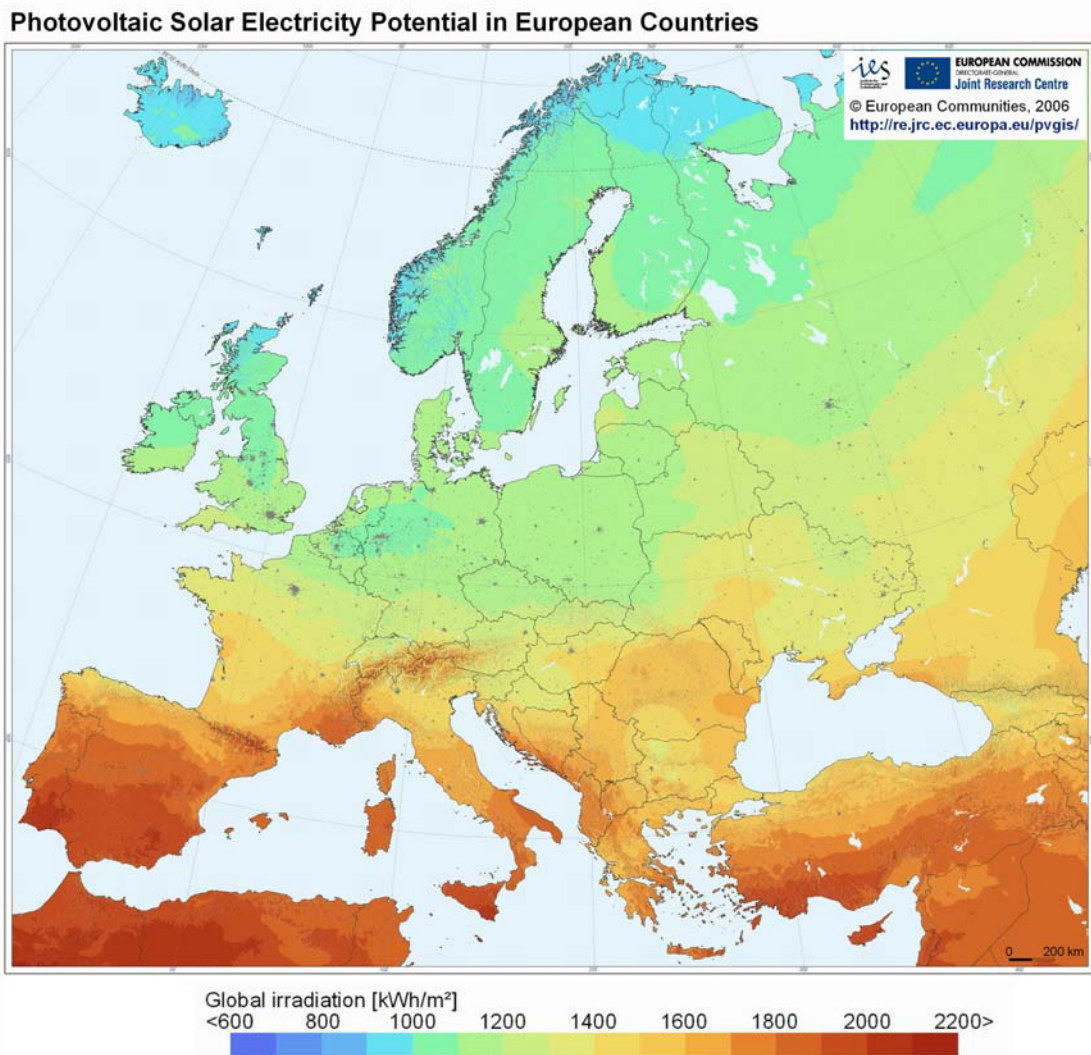


Figure 3. Yearly sum of global irradiation in Europe (adapted from reference (4) – see also <http://re.jrc.ec.europa.eu/pvgis/>). (Online version in colour)

¹ Wp (watts peak) refers to the nominal power output of a solar panel when illuminated with AM (air mass) 1.5 radiation at a power density of 1 kW m⁻².

The current contribution of PV to the total world energy requirement is still very small, with total worldwide installed capacity just over 20 GWp (6). However, as Figure 4 illustrates, the total installed PV capacity is rising steeply, and it is clear that consideration of the sustainability implications of further rapid expansion should already be influencing research directions. The search for new materials forms an important part of this emerging scenario.

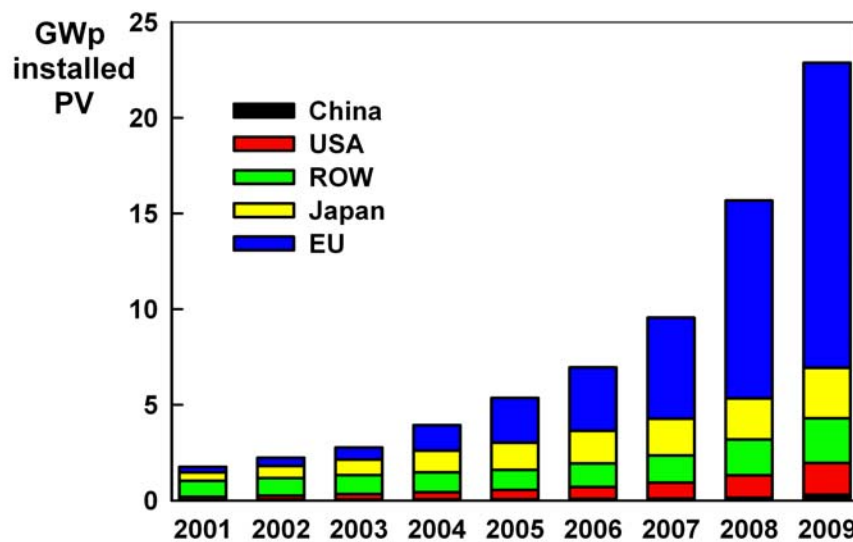


Figure 4. Total installed world PV capacity. (ROW – rest of the world). (6). (Online version in colour)

2. PV Basics

The PV market is still dominated by silicon solar cells, which come in several different forms: monocrystalline, multi-crystalline and amorphous. The market share for crystalline and multi-crystalline silicon solar panels in 2009 was just over 80%, with the other 20% made up from different types of thin film solar cells including CdTe, CIGS and a-Si. The market share gained by CdTe solar panels is increasing rapidly, doubling

from 6.3% in 2008 to 12.3% in 2009 (7), with First Solar currently the largest solar panel producer in the world. (8)

The basic principles of solar cells, which have been dealt with in detail in a number of books (9, 10), will not be reviewed here. The current commercial status of thin film technologies and materials has recently been surveyed by Schmidtke (11), and the interested reader is referred to the more comprehensive discussion of cells designs in this paper. Here we concentrate attention on thin film solar cells utilizing compound semiconductors rather than silicon since these are assuming increasing importance. One of the key advantages of these materials over silicon is that they absorb light more strongly because the optical transition is direct rather than requiring simultaneous absorption or emission of phonons (indirect transition). As a consequence thin layers of the order of a few microns suffice to harvest all of the incident photons at photon energies exceeding the bandgap of the materials.

Considerations based on detailed thermodynamic balance indicate that the optimum band gap for terrestrial solar cells is around 1.2 eV, which corresponds to an absorption onset in the near infrared at around $1 \mu\text{m}$ (1000 nm). The thermodynamic efficiency limit for photovoltaic solar energy conversion is known as the Shockley Queisser limit after its originators (12) who calculated it as a function of the bandgap of the semiconductor used in the solar cell. Under standard AM 1.5 conditions, the maximum efficiency is around 30% for single solar cells² with bandgaps in the range 1.2-1.4 eV. Suitable absorber materials that have bandgaps in this range include CdTe (1.44 eV), whereas the bandgap

² Multiple stacked cells with different bandgaps have a higher efficiency limit.

of CIS (CuInSe_2) is too low (1.02 eV) so that gallium is added to create a solid solution $\text{Cu}(\text{In,Ga})\text{Se}_2$ (CIGS) with higher bandgap close to the optimum value as shown in Figure 5. Monocrystalline silicon solar cells have already achieved efficiencies close to the Shockley Queisser limit, whereas thin film solar cells still have room for improvement.

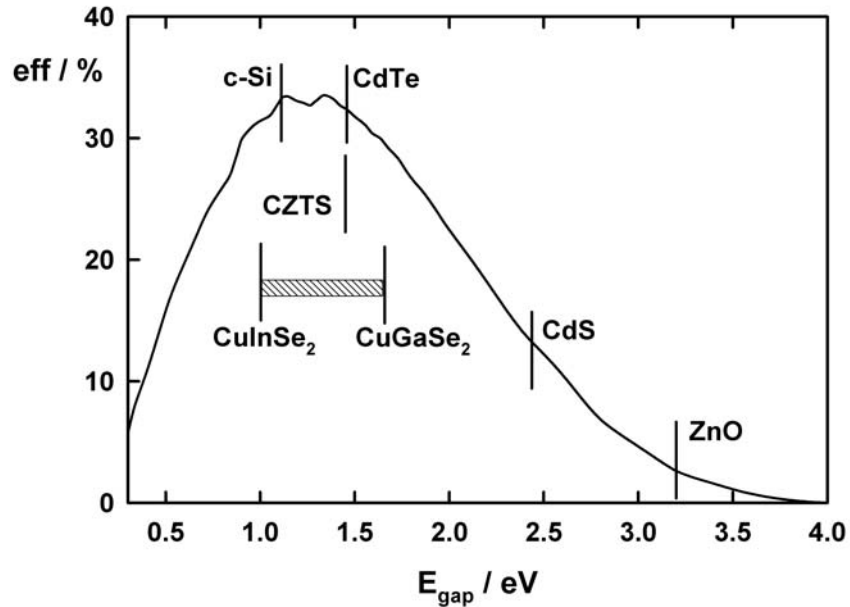


Figure 5. Maximum theoretical efficiency (Shockley Queisser limit) for solar cells under AM1.5 illumination without concentration. The bandgaps of absorber materials (c-Si, CdTe, CIGS, CZTS) and window materials (CdS, ZnO) are shown for comparison. Note that the bandgap of the CIGS system can be tuned by controlling the In/Ga ratio.

The range of solar cells continues to expand, with two relatively new entries – dye-sensitized solar cells (DSCs) and organic photovoltaic cells (OPV) making rapid progress in laboratory efficiencies. The remarkable progress in efficiencies over the last 35 years for a range of different types of solar cells is illustrated by the plot prepared (and

periodically updated) by Lawrence Kazmerski (NREL). The latest version is shown in Figure 6.

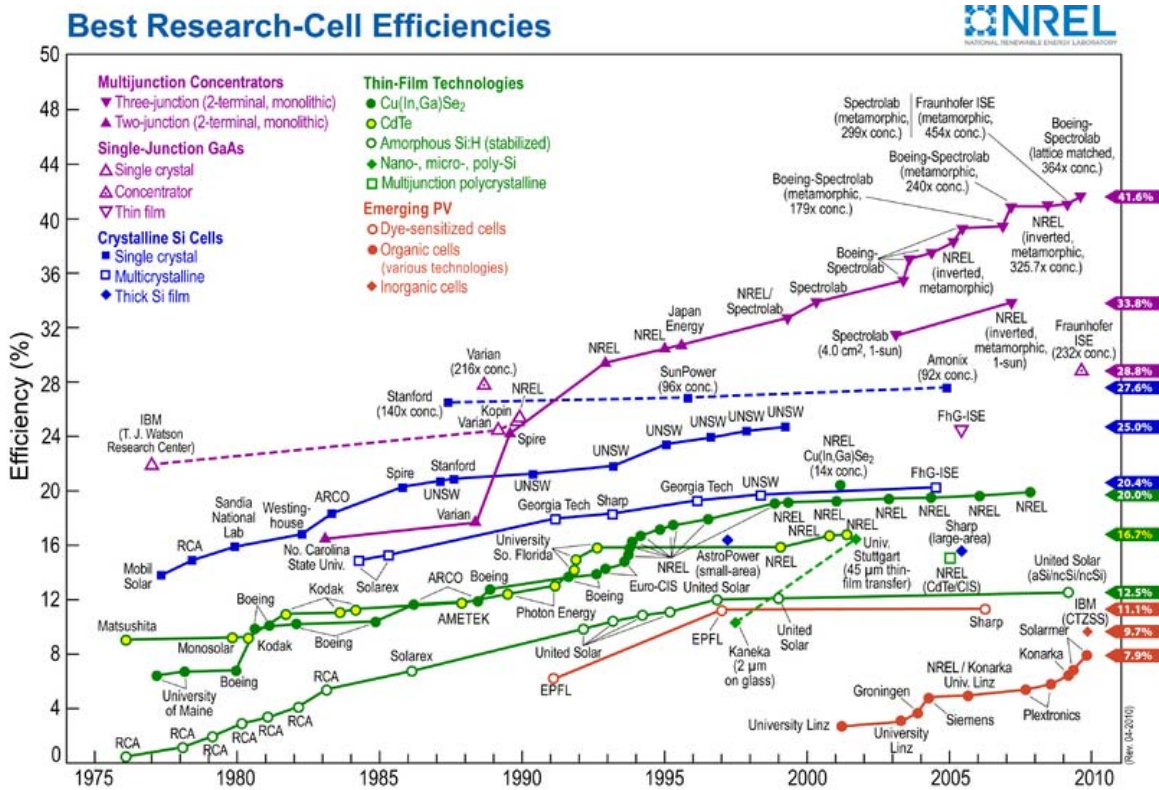


Figure 6. Best research solar cell efficiencies: compiled by Lawrence L. Kazmerski, National Renewable Energy Laboratory (NREL), Golden, Colorado. (Online version in colour).

It can be seen that the thin film technologies (CdTe and CIGS) are achieving efficiencies that are around 2/3 of the Shockley Queisser limit. Dye-sensitized and organic solar cells are late starters, but both of these low cost technologies have reached efficiencies that make them commercially interesting if scale up and acceptable lifetimes can be demonstrated.

3. An Overview of Non-Silicon Thin film PV Technologies

CdTe thin film solar cells

Cadmium telluride-based solar panels are currently the most rapidly expanding thin film PV technology, with module sales from First Solar reportedly passing the 1 GWp mark in 2009. The technology is particularly interesting since according to First Solar it currently offers the lowest production cost of any form of PV: \$0.76/Wp.(13) The cell design is based on the so-called substrate configuration, in which the active materials are deposited on a substrate that also acts as the transparent window to allow solar radiation to reach the device junction. The substrate is a glass sheet that is coated with thin film of a transparent conducting oxide, usually fluorine-doped tin oxide (FTO). Cell fabrication consists of sequential deposition of layers of CdS and CdTe followed by a conducting back contact. Possible deposition processes include closed space sublimation (CSS) as well as chemical and electrochemical methods. The BP Apollo cell (14), for example, was fabricated by depositing a thin CdS layer (around 100 nm) on FTO using a chemical bath method followed by electrodeposition of a thicker layer (around 2 microns) of CdTe from a solution containing Cd^{2+} and TeO_2 . BP discontinued development of CdTe solar cells after a high profile opening by Al Gore of a fabrication facility in Fairfield California in 1998. Current CdTe technologies do not use the BP process and are mostly based on CSS. The CdS|CdTe cell structure is illustrated schematically in Figure 7.

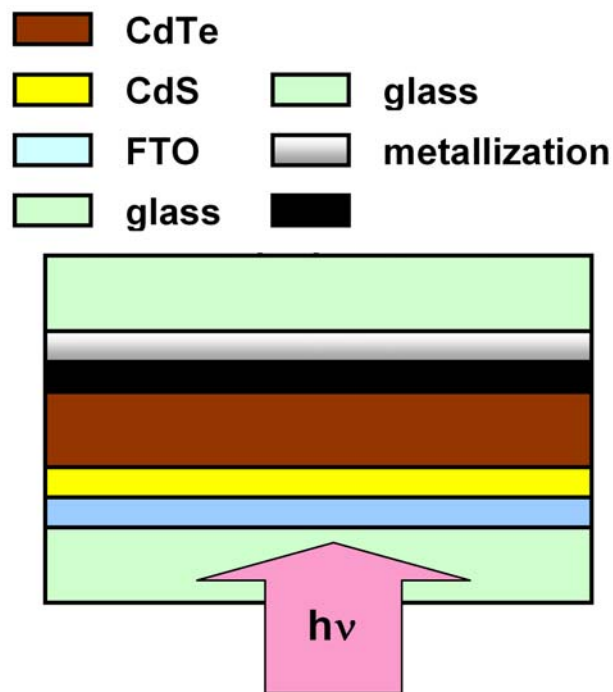


Figure 7. Cross-sectional diagram of the structure of a typical CdS|CdTe solar cell. Light enters the cell through the conducting glass substrate. (Online version in colour).

CIGS cells

The record laboratory efficiency of CIGS cells has recently broken through the 20% barrier, and although commercial production is some way behind CdTe, large investment by companies such as Q-cells, Nanosolar and Miasolé indicates that CIGS cells are poised to make a market breakthrough. At present, most CIGS cells are fabricated by co-evaporation or sputtering processes involving reaction in a selenium atmosphere. Module efficiencies are currently at around 10%, close behind First Solar's CdTe.(11) In order to be able to compete with the cheaper CdTe technology, low cost preparation methods such as the solution-based route developed by the research group at IBM (15) to fabricate 12% efficient CIGS cells will need to be optimized and scaled up. An alternative fabrication

technology based on electrodeposition is also promising, with work at NREL leading to efficiencies of over 10% on 1 m² modules.(16). An electrodeposition route to CIS cells is also being explored in France by NEXCIS, a spin off company resulting from research on carried out by EDF with CNRS and ENSCP (17).

Most CIGS cells are fabricated in the superstrate configuration. This means that the light enters in the opposite direction compared to substrate cells like CdTe. The substrate in this case normally consists of a layer of molybdenum (500 nm) sputtered onto a soda lime glass substrate. The CIGS absorber (1.5-2.0 microns) is then deposited onto the molybdenum layer, followed by a very thin CdS layer (50 nm). The cell is completed by adding thin transparent layers of zinc oxide. The top zinc oxide layer is doped with aluminium to make it highly conducting so that it can collect the current and transfer it to the metallic contact grid. The cell structure is illustrated in Figure 8.

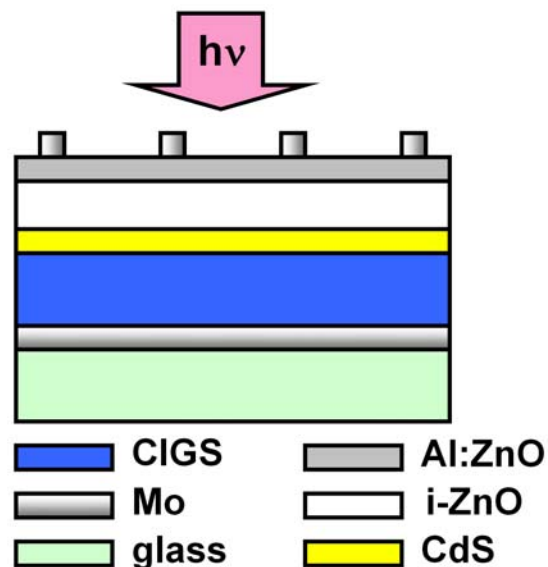


Figure 8. Cross-sectional diagram of the structure of a typical CIGS solar cell. Light enters the cell through the transparent ZnO top contact. (Online version in colour).

Dye-sensitized solar cells

Dye-sensitized solar cells (18) are often referred to as Grätzel cells after Michael Grätzel, who together with Brian O'Regan demonstrated that a low cost solar cell could be fabricated using the phenomenon of photosensitization of wide bandgap semiconductors.(19). These cells are a type of photoelectrochemical cell in which a semiconductor is in contact with a solution containing an ionic redox couple, in this case the I_3^-/I^- (iodide/tri-iodide) couple. Although photosensitization of monocrystalline semiconductors such as zinc oxide had been widely studied, the currents generated were limited very small because the monolayer of sensitizer dye adsorbs only a tiny fraction (0.1%) of the incident light (thicker dye layers are even less efficient due to internal

quenching mechanisms). The breakthrough to acceptable efficiencies was achieved by Grätzel's laboratory at EPFL by using a thin (ca. 10 μm) porous layer of mesoporous titania coated with a monolayer of a red ruthenium bipyridyl complex, which acts as a highly efficient light harvesting material (absorption approaching 100% in the green region of the spectrum). The porous oxide layer can be deposited on FTO glass from a colloidal paste of nanocrystalline TiO_2 by techniques such as screen printing, and the organic components of the paste are burnt off at 450-500 $^\circ\text{C}$, leaving a mesoporous titania film with a porosity of around 50%. Light absorption by the dye molecules adsorbed on the high internal surface area of the mesoporous titania film leads to rapid injection of electrons from the excited Ru(II) state of the dye into the conduction band of the TiO_2 (bandgap 3.2 eV), leaving the ruthenium complex in the Ru(III) state. Regeneration of the dye in its original Ru(II) state is effected by electron transfer from the iodide ions present in the electrolyte solution that permeates the mesoporous TiO_2 film. The tri-iodide formed in the regeneration process diffuses to a second platinized FTO electrode, where iodide ions are regenerated by electron transfer. The overall regenerative cycle is illustrated schematically in Figure 9. The separation between the titania coated anode and the platinized cathode is determined by the thickness of the polymer sealing gasket (typically 20-30 microns). This small gap ensures that the cell can deliver high currents under illumination without encountering problems due to diffusion of ions in the electrolyte. The liquid electrolyte can be replaced by a solid organic hole conducting material such as the bifluorene compound spiro-MeOTAD, although so far the efficiencies of these cells are lower than (around 6%) those of their liquid electrolyte counterparts, which have reached efficiencies of over 12%..

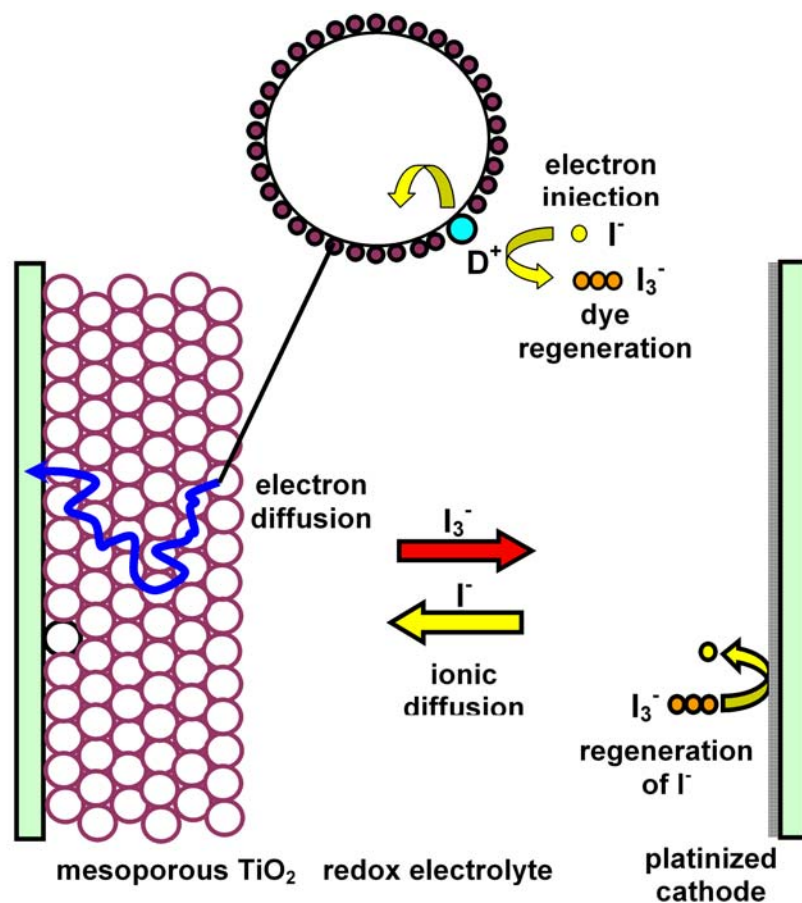


Figure 9. Schematic diagram to illustrate the electrochemical and electronic processes taking place in a dye-sensitized solar cell under operating conditions. Electrons injected into the titania film diffuse to the FTO contact, where they are transferred to the external circuit. Tri-iodide ions formed during regeneration of the sensitizer dye diffuse to the platinized cathode on the right, where they accept electrons to reform iodide ions, completing the regenerative cycle. (Online version in colour).

DSC modules with efficiencies of over 8% have been fabricated (20) using the same design as that used for laboratory cells, which employ the substrate configuration with light entering through the titania anode. A different approach has been taken by G24i Innovations, a company based in Cardiff. It has developed a reel to reel process for

fabrication of flexible DSC modules on titanium foil. In this case the light enters the DSC through the cathode, which consists of a transparent plastic sheet coated with TCO. The company shipped its first commercial consignment of DSC modules to Hong Kong in June 2006.(21). Also in Wales, Corus Colours and Dyesol are working on a project funded by the Welsh Assembly to develop building integrated photovoltaics systems based on dye-sensitized solar cells. (22)

Bulk Heterojunction Organic Cells

Progress on thin film organic photovoltaic devices (OPV) has been rapid in recent years. The cells are based on formation of a 'bulk heterojunction' between a fullerene derivative, which acts as an electron acceptor, and a conducting polymer such as P3HT (poly-3-hexyl thiophene), which acts as an electron donor. These two components are dissolved in a solvent such as chlorobenzene and spin-coated onto ITO (indium tin oxide) conducting glass. As the solvent evaporates, the two components appear to phase separate spontaneously into contiguous nano-domains forming the so-called bulk heterojunction (23). Illumination of the cell creates mobile molecular excited states (excitons) in the polymer. These excitons can diffuse a short distance (typically only 10 nm) before the excitation energy is lost and the molecule returns to the ground state. If an exciton manages to reach the interface with the fullerene, an electron is transferred to the fullerene phase, creating an electron-hole pair. Electrons are collected at the ITO anode by transport through the fullerene phase and the holes are collected at the aluminium cathode by transport through the polymer phase. The ITO electrode is coated with layer

of PEDOT:PSS (poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate)) to make it selective for the transfer of holes. Efficient electron hole pair formation requires the dimensions of the phase-separated nano-architecture of the system to be similar to the exciton diffusion length (the average distance that the exciton moves before losing its electronic excitation energy) (24). The polymeric materials used in OPV have very high absorption coefficients, so that ultra-thin films (a few hundred nm) suffice to harvest light efficiently. The main focus of present research is to develop new polymers to extend the response of the cells into the near infrared to correspond to the Shockley-Queisser optimum. The OPV cell structure is illustrated in Figure 10.

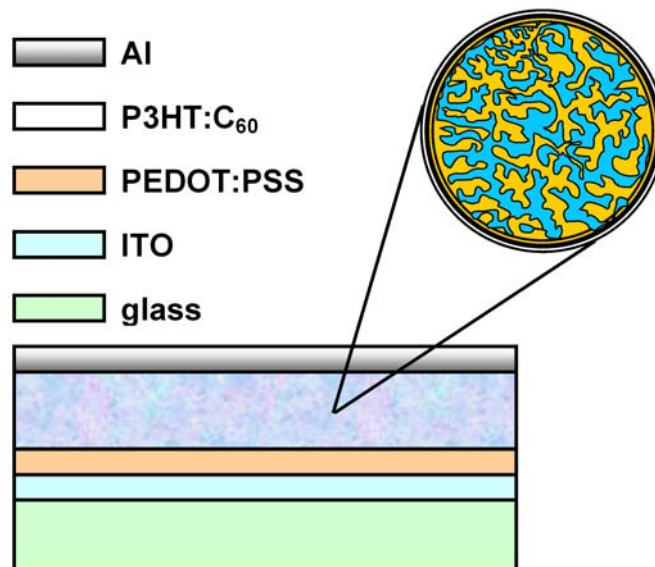


Figure 10. Structure of an organic bulk heterojunction solar cell. The magnified area shows the nanostructure of the contiguous P3HT and C₆₀ phases. Mobile excitons reaching the phase boundary generate electron hole pairs. (Online version in colour).

Commercial development of OPV is proceeding rapidly. In 2009, Konarka produced test cells with NREL-validated efficiency of 6.9% (25), and in 2010 Solarmer announced an

efficiency in excess of 8%. (26) Roll to roll plastic PV technology has the potential for low cost fabrication with costs below \$1/Wp. An important goal is to achieve long term stability. In the UK, Cambridge has just announced that the Carbon Trust PV Research Accelerator programme has resulted in formation of a new spin off company – Eight19 Ltd (named after the time taken for light to reach the earth from the sun) – that will commercialize OPV, building on the expertise at the Cavendish Laboratory.(27)

PV Myths and Facts

The discussion of photovoltaics is sometimes marred by careless statements that can distort the debate about renewable energy policy. For example, ‘solar cells never pay back the original investment, so they are a waste of time’ and ‘the advantage of PV is that it is CO₂ free’. This section briefly examines both of these generalizations.

The most important payback time for any photovoltaic system is the energy payback time (EPT). The fabrication, deployment and eventual recycling of a photovoltaic system all consume energy. The amount of energy consumed must be calculated for a complete life cycle of the type shown in Figure 11. The same life cycle is used to find the CO₂ emission rate.

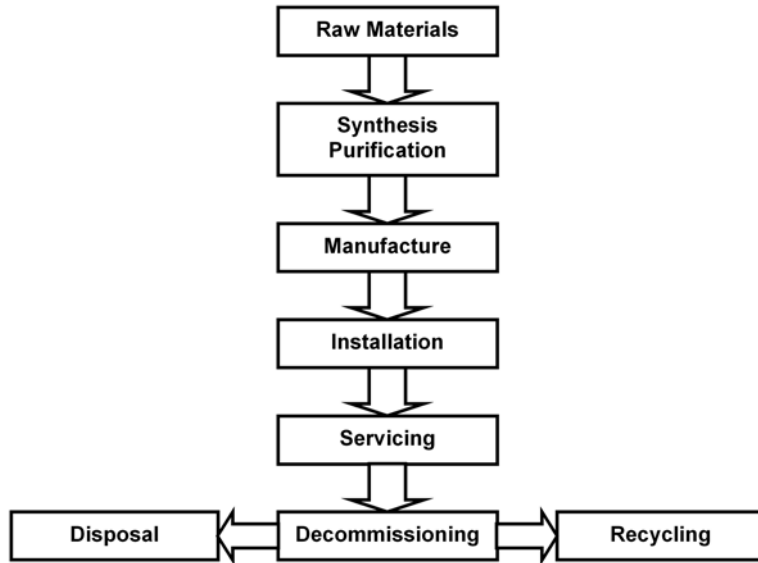


Figure 11. Life Cycle of PV array used to calculate the energy payback time (EPT, years) and CO₂ emission rate (g C per kWh).

The EPT is defined as

$$\text{EPT}(\text{years}) = \frac{\text{total primary energy requirement of PV system throughout lifecycle}}{\text{primary energy saving per year using PV system}}$$

and the CO₂ emission rate is defined as

$$\text{CO}_2 \text{ emission rate}(\text{g/kWh}) = \frac{\text{total CO}_2 \text{ emission during lifecycle}}{\text{annual power generation} \times \text{lifetime}}$$

A recent example of the calculation of the EPT for a CdTe solar module carried out by ECN is given by de Wild-Schoten (28). The primary energy input derived from the life cycle analysis is 12236 MJ/kWp. Based on irradiation levels for southern Europe, the

annual primary energy saving is 14535 MJ/kW. This means that the payback time is $12236/14535 = 0.84$ years. Based on the irradiation levels shown in Figure 3, the payback time in the UK would be about twice as long. The energy payback times calculated by de Wild-Schoten for CIGS modules is higher, at around 1.4 years, and Veltkamp and de Wild-Schoten (29) have calculated the EPT for dye-sensitized for glass-based solar modules as 0.8 years. Figure 12 - taken from the data given by Wild-Schoten (28) - illustrates the breakdown of the contributions to the EPT for crystalline silicon, CIGS and CdTe modules. A striking feature of this breakdown in the case of the CIGS and CdTe modules is the high energy cost of the glass/laminate encapsulation of the cells and modules which dominate the EPT. By contrast, the energy input need to produce silicon is the main reason for the higher energy payback for c-Si modules.

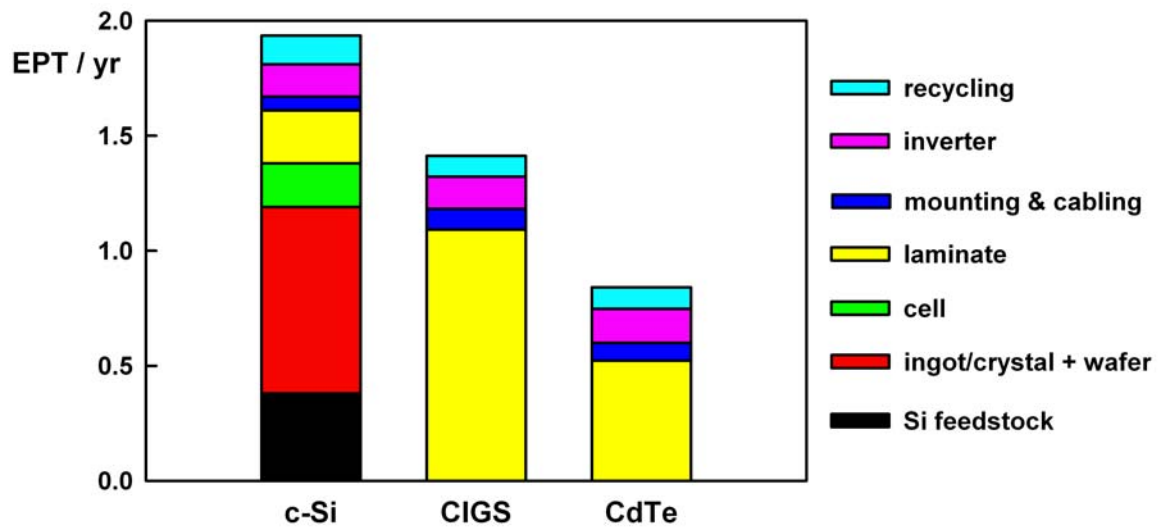


Figure 12. Breakdown of EPT for three PV technologies based on data given by Wild-Schoten (28). (Online version in colour).

It is clear from these calculations that thin film PV installations begin to make a positive impact on the primary energy requirement from fossil fuels in a short time. The corresponding amelioration of CO₂ emissions is also substantial. Even for a DSC with an efficiency of 8% and lifetime of only 5 years, the life cycle analysis shows that the rate of CO₂ release is 100g/kWh.(29). This is only a fifth of the average emission rate for electricity generated from conventional fossil fuels. Similar calculations for CdTe modules give values of 20g/kWh (30). So while PV is certainly not CO₂ free, its carbon footprint is so small compared with conventional power generation from fossil fuels, that large scale deployment of PV can make a substantial contribution to meeting the world energy needs while addressing the problems of climate change.

PV in the Context of Sustainability: the Search for New Materials

The resource implications of large scale terrestrial PV have already been mentioned. There is a need to expand the range of materials that can be incorporated into low cost thin film solar cells. While DSC and OPV technology promise to provide low cost low energy routes to solar energy conversion, innovation in inorganic thin film PV still has a role to play since inorganic materials are generally more stable than organic compounds. In this context, our laboratory has been looking at new absorber materials as sustainable alternatives to CdTe and CIGS. The main focus has been on CZTS, Cu₂ZnSnS₄.(31) This material is quite closely related to CIGS, as Figure 13 shows. In essence, the expensive and scarce elements indium and gallium are replaced by a 50:50 combination of much cheaper Zn and Sn. At the same, Se is replaced by abundant and cheap S because the

bandgap of $\text{Cu}_{22}\text{ZnSnS}_4$ (1.45 eV) is closer to the optimum value than the corresponding selenide compound, which has a narrower bandgap.

		13	14	15	16
		5 B	6 C	7 N	8 O
		13 Al	14 Si	15 P	16 S
11	12	31 Ga	32 Ge	33 As	34 Se
29 Cu	30 Zn	49 In	50 Sn	51 Sb	52 Te
47 Ag	48 Cd				

Figure 13. Section of the Periodic Table showing the logic of changing from $\text{CuIn}(\text{Ga})\text{Se}_2$ to $\text{Cu}_2\text{ZnScS}_4$ by moving from Group 13 to Groups 12 and 14. (Online version in colour).

The most stable crystal form of CZTS is the kesterite structure shown in Figure 14.

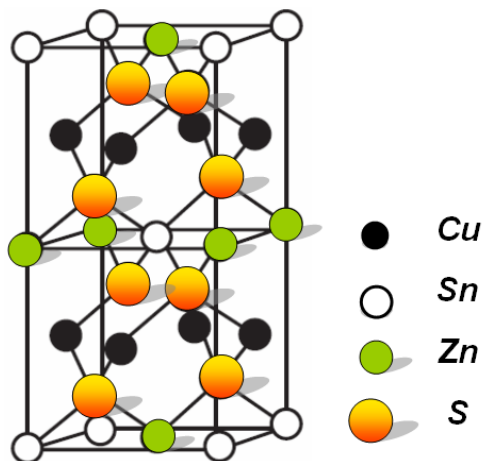


Figure 13. Crystal structure of copper zinc tin sulfide (CZTS) which is a promising sustainable alternative to CIGS. (32) (Online version in colour).

Several routes to CZTS are being explored. In our laboratory, stacks of the three metal components have been prepared by electrodeposition onto molybdenum coated glass substrates. Subsequent annealing in a sulfur atmosphere produces the CZTS absorber film. The cells are then completed with the same layers as those used for CIGS cells (see Figure 8).(33-35) Alternative routes include sputtering and wet chemical processes. CZTS has recently become the focus of intense interest following publication of a paper by Todorov et al. (36) in which the authors demonstrated that CZTS cells with efficiencies approaching 10% can be made by a wet chemical processing method followed by annealing. The fundamental properties of CZTS remain largely unexplored, and for this reason much of our current research effort is focused on growing well-defined single crystal samples for structural and optoelectronic characterization. CZTS has also attracted the attention of computational chemists, and several recent papers have

presented the results of calculations of the structural, electronic and defect properties of the material. (37, 38)

CZTS is only one example of alternative PV and sustainable materials, and several other potential candidates are currently being investigated in our laboratory. The rapidity with which CZTS has been developed in the last few years demonstrates the potential for new materials to make an impact on PV technology by exploiting the extensive database of knowledge on analogue materials that are already well established. At the same time, modern computational methods will allow rapid screening of candidate materials for appropriate electronic properties in order to narrow the search. (39) It is clear that as photovoltaic solar energy conversion begins to make a major contribution to renewable energy, materials chemistry will play an important role in driving innovation in PV .

Conclusions

This brief review has attempted to show that thin film PV is having an increasing impact on renewable energy strategies. Existing technologies based on well known semiconducting materials are driving down cost and carbon footprint, and novel technologies are moving towards the market. As the different technologies jostle for market share, the examples given here highlight the importance of basing comparisons on comprehensive cost benefit analyses based on full life cycle analysis of PV systems. As far as the research chemist is concerned, the imperatives imposed by sustainability provide the rationale for work in an area in which innovation holds the key to new

technologies that can underpin a sustainable future in which PV supplies a substantial fraction of the planet's energy needs.

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