Towards sustainable photovoltaics: the search for new materials

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The opportunities for photovoltaic (PV) solar energy conversion are reviewed in the context of projected world energy demands for the twenty-first 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 PVs are to make a significant contribution to satisfy 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 is 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 sulphide, which is emerging as a viable alternative to the more toxic CdTe and the more expensive CIGS absorber materials.

Keywords: electrodeposition; photovoltaics; solar cells; sustainability; thin film

1. Photovoltaics in perspective

According to BP’s 2009 Statistical Review of World Energy [1], the annual primary energy consumption was equivalent to around 11 gigatonnes of oil in 2008, an increase of around 30 per cent 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 1200. 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

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calculated from the solar constant (1.366 kW m\(^{-2}\)) and the cross-sectional area of the Earth. The result is 1.4 \times 10^{17} \text{ W}, i.e. around 5000 times the estimated primary power requirement for 2050. If we assume that we could cover 1 per cent of the Earth’s land surface with solar arrays operating at a power efficiency of 10 per cent, a rough calculation based on the land area illuminated by the Sun and losses owing to weather and seasons indicates that photovoltaics (PVs) could generate around 25 TW. The constraints imposed by mineral scarcity become apparent from a calculation which shows that the amount of cadmium that would be required to fabricate enough CdTe solar cells to generate this power exceeds the identified world reserves [3] by more than a factor of 100. In other words, resource limitations appear to restrict the possible contribution of CdTe solar cells to less than 1 per cent of the total additional power required by 2050. Clearly, planning for terawatt deployment of PVs requires careful consideration of sustainability issues including material scarcity and cost.

The availability and price of a range of elements used in PV cells are contrasted in figure 1.
As the preceding discussion of CdTe makes clear, the material requirements for large-scale deployment of PVs 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 PVs would clearly be largest for CIGS, as the annual production of indium and gallium is tiny when compared with metals such as copper, zinc and tin, which could be used as the alternative material, CZTS.

Solar cells need sun. The amount of solar radiation available for PV energy conversion varies considerably. In Europe, Spain and Italy have particularly high levels of sunshine that is not too different from those in North Africa. In the UK, irradiation levels are more modest but still usable. Figure 3 shows the European Commission’s map of annual irradiation levels for Europe [4], which shows that the south of the UK receives more than 50 per cent of the annual amount arriving in North Africa. It is worth noting that the role played by PVs 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].

The current contribution of PVs 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.

1Wp (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\(^{-2}\).
photovoltaic solar electricity potential in European countries

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

2. Photovoltaic 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 per cent, with the other 20 per cent made up of 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 per cent in 2008 to 12.3 per cent in 2009 [7], with First Solar currently the largest solar panel producer in the world (http://www.firstsolar.com/).

The basic principles of solar cells that have been dealt with in detail in a number of books [8,9] will not be reviewed here. The current commercial status of thin-film technologies and materials has recently been surveyed by Schmidtke [10], and the interested reader is referred to the more comprehensive discussion of cell designs in this paper. Here, we focus on thin-film solar cells

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using compound semiconductors rather than silicon as these are gaining 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 bandgap for terrestrial solar cells is around 1.2 eV, which corresponds to an absorption onset in the near infrared at around 1 μm (1000 nm). The thermodynamic efficiency limit for PV solar energy conversion is known as the Shockley–Queisser limit after its originators [11], who calculated it as a function of the bandgap of the semiconductor used in the solar cell. Under standard AM1.5 conditions, the maximum efficiency is around 30 per cent for single solar cells with bandgaps in the range of 1.2–1.4 eV. Suitable absorber materials that have bandgaps in this range include CdTe (1.44 eV), whereas the bandgap of CIS (CuInSe₂) is too low (1.02 eV) so that gallium is added to create a solid solution Cu(In,Ga)Se₂ (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.

The range of solar cells continues to expand, with two relatively new entries—dye-sensitized solar cells (DSCs) and organic photovoltaic cells (OPVs)—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.

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

Figure 6. Best research solar cell efficiencies. Compiled by Lawrence L. Kazmerski, National Renewable Energy Laboratory (NREL), Golden, CO. (Online version in colour.)
It can be seen that the thin-film technologies (CdTe and CIGS) are achieving efficiencies that are around two-thirds of the Shockley–Queisser limit. DSCs 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

(a) Cadmium telluride thin-film solar cells

CdTe-based solar panels are currently the most rapidly expanding thin-film PV technology, with module sales from First Solar reportedly passing the 1GWp mark in 2009. The technology is particularly interesting since, according to First Solar, it currently offers the lowest production cost of any form of PVs: $0.76 Wp⁻¹ [12]. 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 a 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 [13], 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 μm) of CdTe from a solution containing Cd²⁺ and TeO₂. BP discontinued the development of CdTe solar cells after a high-profile opening by Al Gore of a fabrication facility in Fairfield, CA, 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.

(b) Copper indium gallium diselenide cells

The record laboratory efficiency of CIGS cells has recently broken through the 20 per cent 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 coevaporation or sputtering processes involving reaction in a selenium atmosphere. Module efficiencies are currently at around 10 per cent, close behind First Solar’s CdTe [10]. 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 [14] to fabricate 12 per cent 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 per cent on 1 m² modules [15]. An electrodeposition route to CIS cells is also being explored in France by Nexcис, a spin-off company resulting from research carried out by EDF with CNRS and ENSCP [16].
Most CIGS cells are fabricated in the superstrate configuration. This means that the light enters in the opposite direction compared with substrate cells such as 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 \textmu m) 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.

(c) Dye-sensitized solar cells

DSCs [17] 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 [18]. 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 and 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 owing to internal quenching mechanisms). The breakthrough to acceptable efficiencies was achieved by Grätzel’s laboratory at EPFL by using a thin (ca 10 \textmu m) 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$_2$ using techniques such as screen printing, and the
organic components of the paste are burnt off at 450–500°C, leaving a mesoporous titania film with a porosity of around 50 per cent. 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\textsubscript{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 affected by electron transfer from the iodide ions present in the electrolyte solution that permeates the mesoporous TiO\textsubscript{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 \textmu m). This small gap ensures that the cell can deliver high currents under illumination without encountering problems owing 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 per cent.

DSC modules with efficiencies of over 8 per cent have been fabricated [19] 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, UK. It has developed a reel-to-reel process for the fabrication of flexible DSC modules on titanium foil. In this case, the light enters the DSC through the cathode, which
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.)

(d) Bulk heterojunction organic cells

Progress on thin-film OPV devices has been rapid in recent years. The cells are based on the 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 indium tin oxide (ITO)-conducting glass. As the solvent evaporates, the two components appear to phase-separate spontaneously into contiguous nanodomains forming the so-called bulk heterojunction [22]. 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
Figure 10. Structure of an organic bulk heterojunction solar cell. The magnified area shows the nanostructure of the contiguous P3HT and C_{60} phases. Mobile excitons reaching the phase boundary generate electron–hole pairs. From bottom to top: glass, ITO, PEDOT:PSS, P3HT:C_{60}, Al. (Online version in colour.)

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 a 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) [23]. The polymeric materials used in OPVs have very high absorption coefficients, so that ultra-thin films (a few hundred nanometres) 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.

Commercial development of OPVs is proceeding rapidly. In 2009, Konarka [24] produced test cells with NREL-validated efficiency of 6.9 per cent, and in 2010 Solarmer Energy [25] announced an efficiency in excess of 8 per cent. Roll-to-roll plastic PV technology has the potential for low-cost fabrication with costs below $1 W_p^{-1}. An important goal is to achieve long-term stability. In the UK, the University of Cambridge has just announced that the Carbon Trust PV Research Accelerator programme has resulted in the formation of a new spin-off company—Eight19 Ltd (named after the time taken for the light to reach the Earth from the Sun)—which will commercialize OPVs, building on the expertise at the Cavendish Laboratory [26].
4. Photovoltaic 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 PVs is that they are CO\textsubscript{2} free’. This section briefly examines both of these generalizations.

The most important payback time for any PV system is the energy payback time (EPT). The fabrication, deployment and eventual recycling of a PV 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 CO\textsubscript{2} emission rate.

The EPT is defined as:

\[
\text{EPT (years)} = \frac{\text{total primary energy requirement of PV system throughout life cycle}}{\text{primary energy saving per year using PV system}}
\]

and the CO\textsubscript{2} emission rate is defined as:

\[
\text{CO\textsubscript{2} emission rate (g kW\textsuperscript{-1} h\textsuperscript{-1})} = \frac{\text{total CO\textsubscript{2} emission during life cycle}}{\text{annual power generation \times lifetime}}.
\]

A recent example of the calculation of the EPT for a CdTe solar module carried out by ECN is given by de Wild-Schoten [27]. The primary energy input derived from the life cycle analysis is 12 236 MJ kW\textsuperscript{-1}. Based on irradiation levels for southern Europe, the annual primary energy saving is 14 535 MJ kW\textsuperscript{-1}. This means that the payback time is 12 236/14 535 = 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 EPTs calculated by de Wild-Schoten for CIGS modules is higher, at around 1.4 years, and Veltkamp & de Wild-Schoten [28] have calculated the EPT for dye-sensitized glass-based solar modules as 0.8 years. Figure 12—taken from the data given by Wild-Schoten [27]—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 dominates the EPT. In contrast, the energy input needed to produce silicon is the main reason for the higher energy payback for c-Si modules.

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 CO\textsubscript{2} emissions is also substantial. Even for a DSC with an efficiency of 8 per cent and lifetime of only 5 years, the life cycle analysis shows that the rate of CO\textsubscript{2} release is 100 g kW\textsuperscript{-1} h\textsuperscript{-1} [28]. 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 20 g kW\textsuperscript{-1} h\textsuperscript{-1} [29]. So, while PVs are certainly not CO\textsubscript{2}-free, its carbon footprint is so small, when compared with conventional power generation from fossil fuels, that large-scale deployment of PVs can make a substantial contribution to meeting the world energy needs while addressing the problems of climate change.
5. Photovoltaics in the context of sustainability: the search for new materials

The resource implications of large-scale terrestrial PVs 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 technologies promise to provide low-cost low-energy routes to solar energy conversion, innovation in inorganic thin-film PVs still has a role to play as 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, Cu$_2$ZnSnS$_4$ [30]. This material is quite closely related to CIGS, as shown in figure 13. 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 time, Se is replaced by abundant and cheap S because the bandgap of Cu$_2$ZnSnS$_4$ (1.45 eV) is closer to the optimum value than the corresponding selenide compound, which has a narrower bandgap.

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

Several routes to CZTS are being explored. In our laboratory, stacks of the three metal components have been prepared by electrodeposition.

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onto molybdenum-coated glass substrates. Subsequent annealing in a sulphur atmosphere produces the CZTS absorber film. The cells are then completed with the same layers as those used for CIGS cells (figure 8) [32–34]. 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. [35] in which the authors demonstrated that CZTS cells with efficiencies approaching 10 per cent 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 [36, 37].

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 [38]. It is clear that, as PV solar energy conversion begins to make a major contribution to renewable energy, material chemistry will play an important role in driving innovation in PVs.

6. Conclusions

This brief review has attempted to show that thin-film PVs are 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 of comprehensive cost–benefit analyses 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 PVs supply a substantial fraction of the planet’s energy needs.

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