Solar Cell Materials

Developing Technologies
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Solar Cell Materials
Developing Technologies

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This book is dedicated to our wives, Julie and Jenni, without whose support it would not have been possible.
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Series Preface

WILEY SERIES IN MATERIALS FOR ELECTRONIC AND OPTOELECTRONIC APPLICATIONS

This book series is devoted to the rapidly developing class of materials used for electronic and optoelectronic applications. It is designed to provide much-needed information on the fundamental scientific principles of these materials, together with how these are employed in technological applications. The books are aimed at (postgraduate) students, researchers and technologists, engaged in research, development and the study of materials in electronics and photonics, and industrial scientists developing new materials, devices and circuits for the electronic, optoelectronic and communications industries.

The development of new electronic and optoelectronic materials depends not only on materials engineering at a practical level, but also on a clear understanding of the properties of materials, and the fundamental science behind these properties. It is the properties of a material that eventually determine its usefulness in an application. The series therefore also includes such titles as electrical conduction in solids, optical properties, thermal properties, and so on, all with applications and examples of materials in electronics and optoelectronics. The characterization of materials is also covered within the series in as much as it is impossible to develop new materials without the proper characterization of their structure and properties. Structure-property relationships have always been fundamentally and intrinsically important to materials science and engineering.

Materials science is well known for being one of the most interdisciplinary sciences. It is the interdisciplinary aspect of materials science that has led to many exciting discoveries, new materials and new applications. It is not unusual to find scientists with a chemical engineering background working on materials projects with applications in electronics. In selecting titles for the series, we have tried to maintain the interdisciplinary aspect of the field, and hence its excitement to researchers in this field.

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1 Introduction

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1.1 INTRODUCTION

The environmental challenges to the world are now well known and publicised, and all but a small minority of scientists accept that a reduction on dependence on fossil fuels is essential for addressing the problems of the greenhouse effect and global warming. Everyone is aware of the limited nature of fossil-fuel resources, and the increasing cost and difficulty, as well as the environmental damage, of extracting the last remnants of oil, gas and other carbonaceous products from the earth’s crust.

Photovoltaics, the conversion of sunlight into useful electrical energy, is accepted as an important part of any strategy to reduce this dependence on fossil fuels. All of us are now familiar with the appearance of solar cell modules on the roofs of houses, on public buildings, and more extensive solar generators. Recently, the world’s PV capacity passed 100 GW, according to new market figures from the European Photovoltaic Industry Association (14 February 2013), which makes a substantial contribution to reducing the world’s carbon emissions.

It is the aim of this book to discuss the latest developments in photovoltaic materials which are driving this technology forward, to extract the maximum amount of electrical power from the sun, at minimal cost both financially and environmentally.

1.2 THE SUN

The starting point of all this discussion is the sun itself. In his book ‘Solar Electricity’ (Wiley 1994), Tomas Markvart shows the various energy losses to the solar radiation that occur when it passes through the earth’s atmosphere (Figure 1.1).

The atmosphere also affects the solar spectrum, as shown in Figure 1.2.

A concept that characterises the effect of a clear atmosphere on sunlight, is the ‘air mass’, equal to the relative length of the direct beam path through the atmosphere. The extraterrestrial spectrum, denoted by AM0 (air mass 0) is important for satellite applications of solar cells. At its zenith, the radiation from the sun corresponds to AM1, while AM1.5 is a typical solar spectrum on the earth’s surface on a clear day that, with total irradiance of 1 kW/m\textsuperscript{2}, is used for the calibration of solar cells and modules. Also shown in Figure 1.2 are the principal absorption bands of the molecules in the air. AM1.5 is referred to frequently in a number of the chapters in this book, and readers should be aware of its meaning.
Figure 1.1  Solar radiation in the atmosphere. (Reproduced with permission from Markvart, 2000. Copyright © 2000, John Wiley & Sons, Ltd.)

Figure 1.2  The solar spectrum. (Reproduced with permission from Markvart, 2000. Copyright © 2000, John Wiley & Sons, Ltd.)
1.3 BOOK OUTLINE

The book starts with a clear exposition of the fundamental physical limits to photovoltaic conversion, by Jean-Francois Guillemoles. This covers the thermodynamic limits, the limitations of classical devices, and develops this theme for more advanced devices. The identification of device parameters used in other chapters can also be found in this chapter.

Material parameters, of course, also require a thorough understanding of characterisation tools, and the second chapter, by Daniel Bellet and Edith Bellet-Amalric, outlines the main material characterisation techniques of special interest in solar cell science. X-ray analysis, electron microscopy, ion-beam techniques and spectroscopy characterisation methods are discussed, including Raman, X-ray photoelectron and UV/Visible spectroscopy, which are rarely detailed in such a materials book.

The next chapter, by Martin A Green, concentrates on developments in crystalline silicon solar cells. Despite the fact that silicon is an indirect-bandgap semiconductor, and therefore is a much less efficient absorber of above-bandgap light than direct-gap semiconductors (such as GaAs), silicon is still the overwhelming choice for solar cell manufacture. As the second most abundant element in the earth’s crust, with a well-established technology, the chapter explores recent developments that have produced low-cost devices with efficiencies approaching the maximum physically possible.

Amorphous and microcrystalline silicon solar cells, are next reviewed by Ruud E I Schropp. These thin-film technologies are finding many exploitable applications with their lower usage of absorber materials and use of foreign substrates.

Turning next to direct-bandgap semiconductors, Nicholas J Ekins-Daukes outlines recent developments in III-V solar cells. III-Vs give the highest efficiencies of any solar cell materials. But despite their large absorption coefficients for above-bandgap light, the materials are relatively expensive, and often difficult and rare to extract from the earth’s crust. Their place in the technology is assessed, together with recent advances.

Chalcogenide thin-film solar cells are next reviewed by Miriam Paire, Sebastian Delbois, Julien Vidal, Nagar Naghavi and Jean-Francois Guillemoles. Cu(In Ga)Se₂ or CIGS cells have made impressive progress in recent years with the highest efficiencies for thin-film cells, while Cu₂ZnSn (S,Se)₄ or CZTS or kesterite uses less-rare elements than CIGS, and so has significant potential for large-scale production.

The field of organic photovoltaics (OPV) has become of great interest since the efficiency achieved rapidly increased from around 1% in 1999, to more than 10% in 2012 (Green 2013). The chapter by Claudia Hoth, Andrea Seemann, Roland Steim, Tayebeh Amin, Hamed Azimi and Christoph Brabec reviews this novel technology, concentrating on the state-of-the-art in realising a photovoltaic product.

Lastly, one of us (Gavin Conibeer) looks to the future, by outlining third-generation strategies that aim to provide high conversion efficiency of photon energy at low manufacturing cost. Approaches covered include multiple energy level cells (such as tandem cells and multiple exciton generation), modification of the solar spectrum (such as by down- and upconversion), and thermal approaches (such as thermophotovoltaics and hot-carrier cells). The emphasis in all these approaches is on efficiency, spectral robustness, and low-cost processes using abundant nontoxic materials. The book ends with some concluding remarks by the editors, looking to the future in this rapidly developing field.

Finally, no book in this very extensive field can claim to be complete. To explore the field further, readers are recommended to consult ‘Thin Film Solar Cells’ by Jef Poortmans.
and Vladimir Arkipov (Wiley 2006), a companion volume in this Wiley Series on Materials for Electronic and Optoelectronic Applications, which includes such areas as dye-sensitised solar cells (DSSCs), in the chapter by Michael Gratzel. We hope that this book, with its emphasis on technological materials, will be of use to all who are interested in this field.

REFERENCES

2 Fundamental Physical Limits to Photovoltaic Conversion

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2.1 INTRODUCTION

Where to stop the quest for better devices? What does better mean? The conversion efficiency arises prominently in this respect.

More efficient devices, everything kept equal, would first translate into cheaper solar electricity. Are there limits to reducing the cost of PV electricity? In 2012, modules were sold 0.5–0.7 €/W and the cost of solar electricity is around 20 cts/kWh. In the longer term, development of photovoltaics (PV) has to be based on a major technological breakthrough regarding the use of processes and materials at very low cost, or/and on the engineering of devices offering far higher performance, harvesting most of the available solar energy. Two approaches are targeted at this issue today: the first aims at low-cost materials and low-cost processes to reduce the surface cost of PV devices, possibly sacrificing some of the device efficiency, and the second, aiming at the maximal possible efficiency, at the same cost as today’s modules (see Figure 2.1). There is a major difference between these two approaches: the conversion concepts, the materials and the processes.

If we think in terms of the manufacturing costs of PV modules, the target aimed at requires that the system needs to produce 1 MWh (comprising about 0.2 m² of high-end c-Si modules lasting 25 yr) cost less than €30 for parity with the base load or €120 for grid parity. For a very low-cost device, for instance based on polymers or organic–inorganic hybrids, with an expectation for conversion efficiencies on a par with those achieved by the amorphous Si line (on the grounds of similar structural disorder and a low carrier mobility) and shorter life durations, the budget is €7.5/m² (5-year life duration with 5% efficiency, including power electronics and installation), closer to the cost of structural materials than of functional electronic materials. Finally, for profitable electricity production, we need to pay attention to the system costs. Thus, one sees that it might be extremely difficult to attempt to reduce production costs far beyond what is currently being obtained with inorganic thin-film systems.

This chapter will deal with the scientific issues behind the photovoltaic conversion process, keeping in mind what would make a difference to having this technology more widely used.

The first of these questions is of course the efficiency of the processes. Since the appearance of the first PV devices, the question of the conversion efficiency limits arose, and for a good reason: not only does it have high scientific and technological visibility, it is also
one of the major factors in lowering the cost of generating solar electricity. Interestingly, this question of efficiency limit took quite a bit of time before being settled [Landsberg and Badescu, 1998].

The paper of Schockley and Queisser, devising an approach based on a detailed balance approach of photovoltaic conversion is still one of the most quoted papers on PV, yielding the limit of single-junction, standard PV devices. This question has also been approached on a more general basis, using thermodynamics (Landsberg and Tonge, 1980, Parrott 1992, De Vos 1992) to give device-independent or even process-independent limits (Section 2.1). These limits are essentially related to the source (the sun) characteristics and to the conditions of use (e.g. ambient temperature). Perhaps more useful, and practical, limits have been proposed for defined processes.

In very general terms, photovoltaic conversion in its simpler form supposes several steps:

1. solar photon transferred to the active part of the system;
2. absorption of the photons and energy transfer to the electronic system;
3. selective extraction of electrons to contacts (2 at least);
4. channelling of e-free energy to useful load whose impedance is adjusted.

These steps are illustrated in Figure 2.2 and describe PV process as it is working in all working devices, with nonessential modifications for organic PV (in which electron and holes are coupled as excitons) and multijunction cells (where the incident spectrum on a cell is a part of the total solar spectrum).
Figure 2.2 Photovoltaic action proceeds in 3 steps. (a) photons have to be collected and coupled to the converting system; (b) the converting systems contains occupied (VB) and empty states (CB) separated by a gap between which light induces transitions are allowed; (c) upon photon absorption, two populations of charge carriers are created; (d).

In this process, the work per absorbed photon is equal to the electromotive force between the electrodes (i.e. the voltage) times the elementary charge, that is the difference in the quasi-Fermi levels in the two contacts. In the absence of current extraction and when the mobility is high enough this quasi Fermi level (QFL) separation is that of electrons and holes in the absorber (see Section 2.4 for a more complete discussion).

Because the QFL is generated by the incoming flux, it increases with the light flux. This can also be understood as a larger generation rate per unit volume will create a larger density of electron–holes pairs, and therefore a higher conduction-band electron QFL and a lower valence-band electron QFL (that is a larger chemical potential of holes in the VB). This large QFL separation can be obtained in different ways, everything else being equal:

- by decreasing the recombination pathways for photogenerated carriers, for instance increasing the carrier lifetime;
- by increasing the generation of electron–hole pairs, for instance by concentration of the incident solar influx;
- by decreasing the generation volume, for instance by thinning down the cells, which requires light trapping to keep the total generation constant.

A large chemical potential can be seen as a large partial pressure: this helps the extraction of generated carriers and therefore a larger free energy per carrier can be collected, whereas, whatever the concentration of electron–hole pairs, their potential energy is always the same, near $E_g$. The collection of carriers depends on the chemical potential of the carriers in the contacts, that is, in fine, of the external conditions, and for instance the load into which the solar cell will deliver power.

The maximum power is delivered when the load impedance matches the differential impedance of the generator (as is true by the way for any generator).

Indeed, if the device has a current–voltage characteristic $I(V)$, the power $P = I \cdot V$ is maximum for

$$\frac{dP}{dV} = 0 \text{ and, as } \frac{dP}{dV} = I + \frac{dI}{dV} \cdot V$$ (2.1)
this yields:

\[ R_{\text{Load}} = \frac{I}{V} = -\frac{dI}{dV} \]  

(2.2)

which is the relation announced.

The current at \( V = 0 \) (short-circuit) is noted \( I_{\text{sc}} \), while the voltage at \( I = 0 \) (open circuit) is noted \( V_{\text{oc}} \).

One can write a relation such that:

\[ \eta = \frac{I_{\text{sc}} \cdot V_{\text{oc}} \cdot \text{FF}}{P_{\text{inc}}} \]  

(2.3)

where \( \eta \) is the efficiency, \( P_{\text{inc}} \), the solar incident power and FF, the fill factor, is a number close to 0.85 and slowly dependent on the working point for an ideal cell.

Importantly, each carrier has to be collected at a specific contact, that is, ideally, the contact should be selective for one of the carriers, and prevent collection from the other. Selective contacts usually take the form of barriers for one of the contacts, as for instance in a p/n junction.

There are general relationships based on thermodynamics that fundamentally limit the efficiency of conversion of light into work. They have been discussed extensively in the literature and are presented in Section 2.2.

Photovoltaic conversion, as sketched in Figure 2.2, starts with a good coupling between the conversion device and the sun. We therefore start to explore limits to photon management. This limit is essentially given by the 2nd thermodynamic principle: a PV device does not become hotter than the sun (Section 2.2). It is then important to know how good the absorption of the material can be as this determines the dimensions and geometry of the device as its thickness has to be the best compromise between being

- large enough so that light is efficiently absorbed;
- small enough so that excited carriers are transported to the contacts before recombination.

Progress in material science has been extremely fast in the past decades, and that knowledge may help us to get closer to the above limits. So, it becomes more important to understand precisely what these are. We therefore look in more detail at the working of a standard (even if somewhat idealised) PV device (Section 2.3).

The next question is then: can we come up with practical approaches to get closer to the thermodynamic limits? A variety of such approaches have been proposed, although they sometimes come at the expense of increased device complexity. They fall into several categories that will be described below (Section 2.4).

### 2.2 THERMODYNAMIC LIMITS

Thermodynamics sets the most fundamental limits to any energy-conversion process via its two fundamental laws: energy conservation and maximum entropy for closed systems.

The thermodynamic framework captures perfectly the fact that the useable energy (called work, \( W \)) that can be extracted from a body is only a fraction of its total internal energy (\( E \)).
2.2.1 The Sun is the Limit

Common sense tells us that the energy source is certainly essential in delving into the limits of the extractible power, but thermodynamics teaches us that since we deal not with energy creation but energy conversion, we have to look at both the source and the sink. Our sink is the earth, whose ambient temperature is around 300 K, which we will take as the sink temperature.

How should we characterise the source? The sun emits a considerable power as electromagnetic radiation \(4 \times 10^{23} \text{ kW}\) into space burning some \(10^{15} \text{ g/s}\) of hydrogen in nuclear reactions and converting some 5000 t/s of matter into pure energy. This radiation is, to a good approximation, thermal and described as blackbody radiation of a temperature of 5800 K (often approximated as 6000 K in the literature). The resulting solar spectrum (Figure 2.3) is rather broad, with most energy being radiated in the near-infrared and in the visible ranges.

As was discussed in Section 2.1, the conversion efficiency of a solar cell depends on the incoming flux: more flux (of the same spectral density) means more power out. In principle, light from the sun can be concentrated using, for instance, lenses and mirrors. By such systems, the solid angle under which the cell sees the sun changes increases by the concentration factor, due to the conservation of étendue.

The maximum concentration of solar flux is limited to a factor of \(C_m = 42 600\). Indeed, the maximum concentration factor is \(4\pi\) divided by the solid angle of the sun, which is when the exposed surface of the cell can see the sun in all directions. This can also be understood from another point of view: at higher concentration factors, the focal point would have a higher radiation temperature than the source, which is thermodynamically impossible: the image of an object cannot be hotter than the object itself. Otherwise, one could reversibly transport heat from a cold body toward a hot body, something forbidden by the second law of thermodynamics.

\[
\eta_{\text{Carnot}} = \frac{W}{E_s} = 1 - \frac{T}{T_s}
\]

![Solar Radiation Spectrum](image)

Figure 2.3 Solar spectrum at the top of the atmosphere and at sea level.
Figure 2.4 Systems for calculating various thermodynamic limits (a) for the Carnot efficiency, (b) for the Landsberg efficiency and (c) for the endoreversible efficiency. \( T_s \) is the source temperature and \( T \) is the sink temperature. Energy exchanges are represented with light gray arrows and entropy exchanges (or creation: \( S_i \)) with dark gray arrows. \( E \) is radiant power, \( Q \) is heat flux, and \( W \) is work.

2.2.2 Classical Thermodynamics Analysis of Solar Energy Conversion

The first step in computing thermodynamic efficiencies is to define the inputs and outputs, that is to define the conversion system.

A first such system is composed of the sun’s surface and the conversion engine (Figure 2.4a). The surface of the sun receives energy and entropy fluxes from the sun’s interior...
where nuclear reactions take place. Energy and entropy are then transferred radiatively to the device that rejects heat and work at ambient temperature \( T \). Classically (see Green 2003 for a recent discussion), the limiting efficiency of such a process is obtained when the internal entropy generation is negligible and given by:

\[
\eta_{\text{Carnot}} = 1 - \frac{T}{T_s}
\]  

(2.4)

This is the Carnot efficiency of the process, with a value of 95%. Of course, such an efficiency does not count as a loss of the fraction of power radiated by the cell to the sun, but this is not the point (the latter is a very small quantity). The main issue is that to have negligible internal entropy generation, the converter and the sun’s surface should have almost the same temperature, otherwise the radiative transfer between the two would result in finite entropy generation. But then, the amount of work produced is infinitesimally small: most of the sun’s power is recycled, which misses the purpose.

A more exact calculation taking into account the entropy of radiation to the sun, first done by Landsberg, gives:

\[
\eta_{\text{Landsberg}} = 1 + \frac{1}{3} \left( \frac{T}{T_s} \right)^4 - \frac{4}{3} \frac{T}{T_s}
\]  

(2.5)

that is, an efficiency of 93.3%. This corresponds (Figure 2.4b), as above, to a vanishingly small power extracted, as above, as the solar cell should be near open-circuit voltage for near-zero-entropy generation, except in the case where the system are nonreciprocal, as discussed by Ries and later by Green. Normally, optical systems are reciprocal, that is symmetric by time inversion, and this implies that if a solar cell gets light from the sun from a solid angle \( \Omega_s \), the light it emits (and we will see that solar cells must emit light in operation) should also reach the sun with a probability proportional to \( \Omega_s \). Yet systems exist that are nonreciprocal [Ries, 1983, Green, 2003], and in principle the light they emit could be sent to another device to be converted. In this way, a process can be conceptually conceived where the conversion is reversible, and the conversion device only emits thermal radiation (at ambient temperature) back to the sun. Although this seems to be an academic exercise, the Landsberg limit is effectively the highest possible limit for power extraction achievable, at least in principle. The Landsberg limit is achieved under maximal concentration, and calculation for various illumination have also been made [Brown, 2003] and give for instance a value of 73.2% for AM 1.5.

Figure 2.4c proposes yet another way for solar energy conversion using a Carnot engine using a reciprocal system. The sun heats up a blackbody absorber to a temperature \( T_a \), and a Carnot engine extracts work while heat is dumped in the heat sink at temperature \( T \). The thermodynamic analysis of this endoreversible system (De Vos, 1992) led to the formula:

\[
\eta_{\text{Endo}} = \left( 1 - \frac{T}{T_a} \right) \left( 1 - \frac{C}{C_m} \frac{T_a^4}{T_s^4} \right)
\]  

(2.6)

where \( C \) is the solar concentration and \( C_m \) is the maximal possible solar concentration (\( C_m = 46 \, 200 \)).
Maximal power is extracted at maximal concentration for an optimal temperature of $T_a = 2480$ K. The efficiency is then 85.4%. The endoreversible efficiency is quite dependent on the concentration ratio as illustrated in Figure 2.4.

The efficiency can be marginally increased to 86.8% if the light is split into quasi-monochromatic beams (e.g. using dichroic mirrors), each of them being converted by an endoreversible system such as the one above. The gain comes from the fact that the blackbody absorbers emit broad band light that can be partially recycled (Green, 2003).

Do we know of Carnot-like engines for the conversion of light into electricity? Actually yes: as we will see later, solar cells (somewhat idealised of course) are good approximate realisations of such engines when they are illuminated by a monochromatic light. We will also discuss another type of Carnot-like engine: the hot-carrier solar cell.

All the above description has been done using only one thermodynamic variable (temperature), but can be generalised to cases where other variables change and need to be taken into account. This would be the case for photochemical conversion, including a special case: that of photovoltaic conversion (De Vos, 1992).

2.3 LIMITATIONS OF CLASSICAL DEVICES

Beyond the general limits set by thermodynamics and optics that were reviewed above, there should be more specific bounds on practical devices. The most important of them is the first that has been developed: the semiconductor diode. It was first made as a Schottky diode (Se diodes [Palz, 2010] and later as a planar silicon p/n homojunction [Schockley and Queisser, 1961], followed by planar heterojunctions (GaAs), convoluted heterojunctions (Cu$_2$S), p-i-n structures (a-Si:H) and more recently interpenetrated (dye solar cells) or bulk heterojunctions (polymeric cells). They all share a common feature that limits their performance: absorption of light, generally done in one single material, results in only one type of excitation of the absorber that can be converted. This excitation, whose energy is close to the low-energy edge of the optical absorption threshold (the bandgap, $E_g$), is converted after significant relaxation in the absorber has occurred. This material parameter, the bandgap, is central to the understanding of the fundamental losses in PV conversion by solar cells. Essentially, these losses originate from the fact that one is trying to convert a broadband spectrum (blackbody radiation) with a system having a single characteristic energy ($E_g$): one is bound to find the best compromise.

To avoid being too specific on the system of conversion, some approximations are generally used when evaluating various approaches. A real device will be nonideal in many ways:

- Charge transport always entails ohmic losses, but these can be made negligible if the carrier mobility is high enough (so that the total ohmic drop is less than $kT/q$).
- Photon transport entails optical losses such as reflection or parasitic absorption. These can be made very small in practice with careful design and use of antireflection coatings.
- Heat-transport issues: because of power dissipation in the above losses and others (e.g. carriers thermalisation), photovoltaic devices become warmer under operation, and this is detrimental to the conversion efficiency. Yet, in principle, the device could be efficiently coupled to a thermostat and its temperature uniform and fixed at a given value (for instance the standard 25 °C value), so variations in temperature are ignored.