Advanced Inorganic Materials for Photovoltaics

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Guest Editors

Abstract

By 2050, world annual energy consumption is predicted to grow from the present 13 terawatt-years (TWyr) to nearly 30 TWyr. Although all energy sources must be considered in meeting this challenge, solar energy may arguably be the only carbon-free source capable of supplying a significant fraction of energy at these levels. This issue of *MRS Bulletin* reviews the status and future development of solar photovoltaic technologies based on inorganic materials. The discussion begins with materials and cell designs for second-generation photovoltaics based on thin films [a-Si:H, Si, Cu(In,Ga)(Se,S)$_2$, CdTe]. Recent advances in tandem cells and concentrators are also reported, along with photovoltaic approaches involving nanoscale materials such as quantum dot arrays. Finally, work on transparent conducting oxides that are critical to nearly all cell designs are discussed.

Photovoltaic Market

World annual energy consumption is predicted to grow from the current 13 terawatt-years (TWyr) to as much as 30 TWyr by 2050.[1] As we struggle to meet this huge demand, the global energy sector will also face two pressing issues: declining fossil reserves and climate change caused by artificially produced greenhouse gas emissions.

Nuclear power is considered a leading candidate for reduced-carbon-emission electricity production. There is, however, uncertainty about the size of nuclear fuel reserves, the efficiency of nuclear reactors when using lower-grade uranium ores, and the likelihood of finding satisfactory solutions for nuclear waste disposal. Estimates by the International Atomic Energy Agency indicate that nuclear power growth will flatten in coming years.[2]

In terms of renewable sources, hydroelectric power is one of the dominant technologies today, but supply expansion is limited.

Wind power is approaching competitiveness with conventional power production and must be considered as an important source in meeting future energy needs. Some estimates, however, place the total usable wind energy production in the 2–4 TWyr range, much less than the 30 TWyr level.[1]

With roughly 125,000 TW of solar power striking the earth at any time, solar may be the only renewable energy source with the capacity to meet a large fraction of future needs.

There are many different approaches for capturing solar energy.[1] Photosynthetic solar conversion for biofuel production is under active investigation. Solar thermal systems convert the sun's radiation into thermal energy for heating applications or, in conjunction with solar concentration, into electricity.

This article deals with photovoltaic (PV) electricity generation, and the key issue is cost. Assuming a 20-yr system lifetime, the present cost of PV-generated electricity is in the range of $0.25–$0.65/kWh, as compared with the cost of coal-based electricity, which is closer to $0.04/kWh.[3]

Generating a significant fraction of future energy requirements from PVs is a major challenge, particularly because present PV production is almost insignificant relative to fossil-fuel–based generation. In 2003 in the United States, solar energy produced ~0.1% of the electricity generated by fossil fuels. At the same time, PV costs have reached a range where demand is very elastic, with small decreases in price causing large increases in sales. As a consequence, PV manufacturing is growing exponentially at approximately 30% per year, and this rate is, if anything, increasing (Figure 1). In 2005, the PV market exceeded $10 billion.[4] This growth has been driven by government policies (subsidies or feed-in tariffs), mainly in Japan and in Germany.[5] PV production will be further stimulated by the PV goals for Europe of supplying 12% of total energy and 22% of electricity from renewable sources in 2010.[6,7] Similarly, the Solar America Initiative in the United States calls for investments to make PV power competitive with other forms of renewable energy by 2015,[8] and more than 15 U.S. states have mandated renewable energy standards.

This market growth will drive price reductions. The historic learning curve for PV module manufacturing shows a 20% price reduction for every doubling of accumulated sales through about 2003 (see Figure 2). The price of standard PV modules, typically expressed in units of cost divided by the power produced under peak solar illumination (in watts), is currently around $3–$4/Wp. Taking into account PV system costs that are not related to the solar panel raises the price to about $6–$8/Wp, which converts to roughly the $0.25–$0.65/kWh range given earlier. Assuming a 25%–30% per year market growth, the learning curve yields a factor of two drop in cost every 8–10 years. Reaching a competitive cost with current coal-produced electricity would take 30–40 years. Although this extrapolation is strongly dependent on market growth and learning curve assumptions, as well as future prices of conventional electricity, most estimates give similar time frames. If these estimates prove true, PVs will have a limited ability to make significant contributions to 2050 energy needs.

The learning curve derives primarily from wafer-based crystalline silicon (monocrystalline or single-crystal, multicrystalline, and some ribbon silicon) modules that dominate the PV market, comprising more than 90% of shipments in 2005 (Figure 3). This is typically referred to as the first generation of photovoltaics. The dominance of crystalline silicon stems from its wide availability and reliability, as well as from knowledge and technology borrowed from the microelectronics industry and resulting from more than two decades of terrestrial PV research with substantial government funding. The price reductions already achieved with silicon are significant (Figure 2). Although the shortage in silicon

feedstock that is currently influencing the learning curve (Figure 2) is likely to be resolved in the near future, there are still questions about whether the present curve can be maintained with silicon.[9] The movement toward thinner silicon wafers and the future development of higher-efficiency cells will certainly help. Even if this trend is maintained, a discontinuity in the learning curve is needed for the 30–40-year time frame discussed here to be reduced.

It is a common belief that lowering PV costs to a level competitive with conventional power sources will require significant reductions in manufacturing costs, which may be realized in thin films, and/or new architectures that lead to dramatic improvements in efficiency.[10] Indeed, once in large-volume production, second-generation cells based on thin films will offer the potential for appreciably lower areal manufacturing costs with reasonable efficiencies.

On the other hand, third-generation concepts attempt to exploit a much larger fraction of the solar spectrum to achieve very high efficiencies while also lowering costs.

Second- and third-generation inorganic PV technologies are the principal subject of this issue of *MRS Bulletin*. Although not discussed in detail here, organic solar cells also have significant potential for low-cost energy production, and the interested reader is referred to the January 2005 *MRS Bulletin* for an in-depth review of these technologies.[11]

Photovoltaic Devices

A solar cell is a semiconductor device that converts photons from the sun into electricity. Figure 4 shows the generic structure and operation of a single-junction inorganic solar cell. The highest efficiency devices (e.g., single-crystal Si) are made on crystalline substrates. This is an important contributor to system costs, which second-generation approaches seek to reduce through thin-film techniques compatible with low-cost substrates like glass. At the heart of the cell is the light-absorbing material that converts photons into carriers (electrons and holes) via the photovoltaic effect. The different PV technologies discussed in this issue are identified by the composition of the absorbing material. After
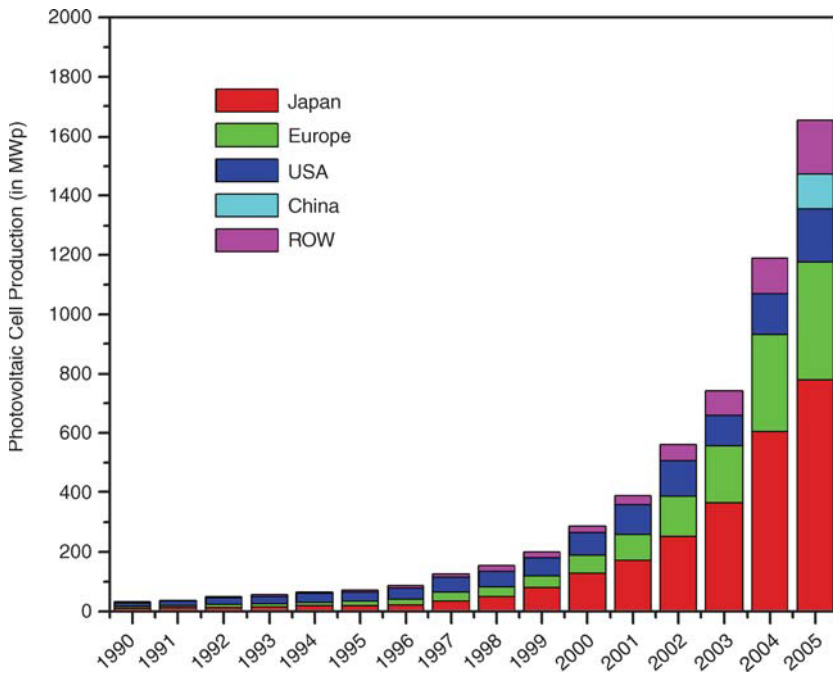

Figure 1. Photovoltaic cell production in peak megawatts (MWp) as reported by the PV industry. Shipments for Japan, Europe, the United States, China, and the rest of the world (ROW) are shown. (Source: *PV News, Photon International,* and the IEA Photovoltaic Power Systems Program.)
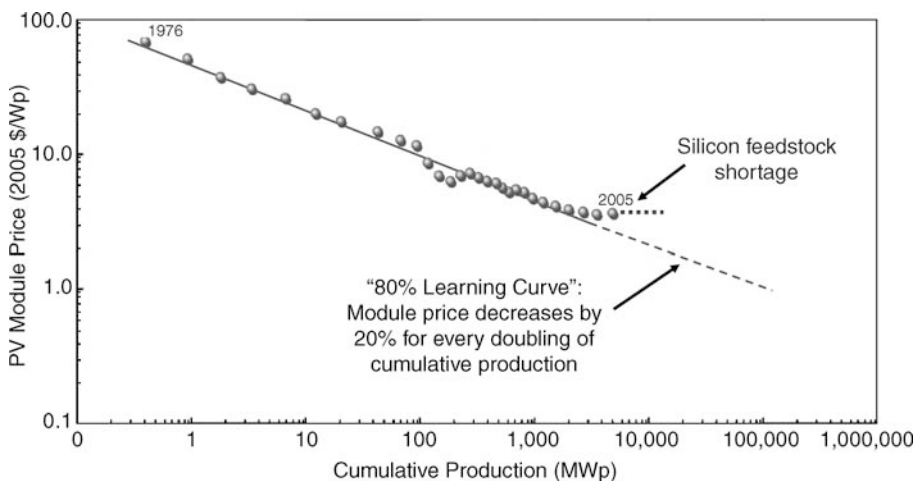

Figure 2. Photovoltaic module prices per peak watt (Wp) against cumulative production in peak megawatts (MWp). (After T. Surek, National Renewable Energy Laboratory, 2007).
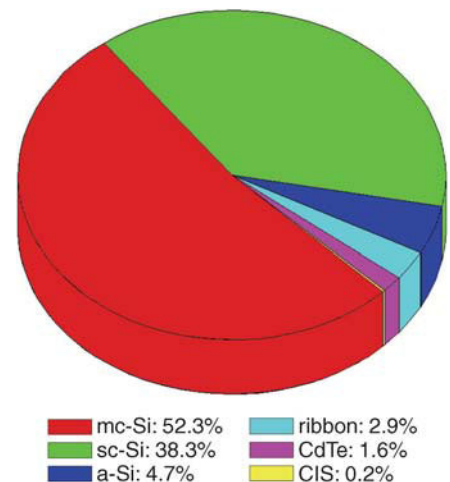

Figure 3. Distribution of photovoltaic cell production by technology in 2006: multicrystalline Si (mc-Si), single-crystal Si (sc-Si), amorphous Si (a-Si), ribbon Si, CdTe, and copper indium diselenide (CIS). [Source: *Photon International* (March 2006).]
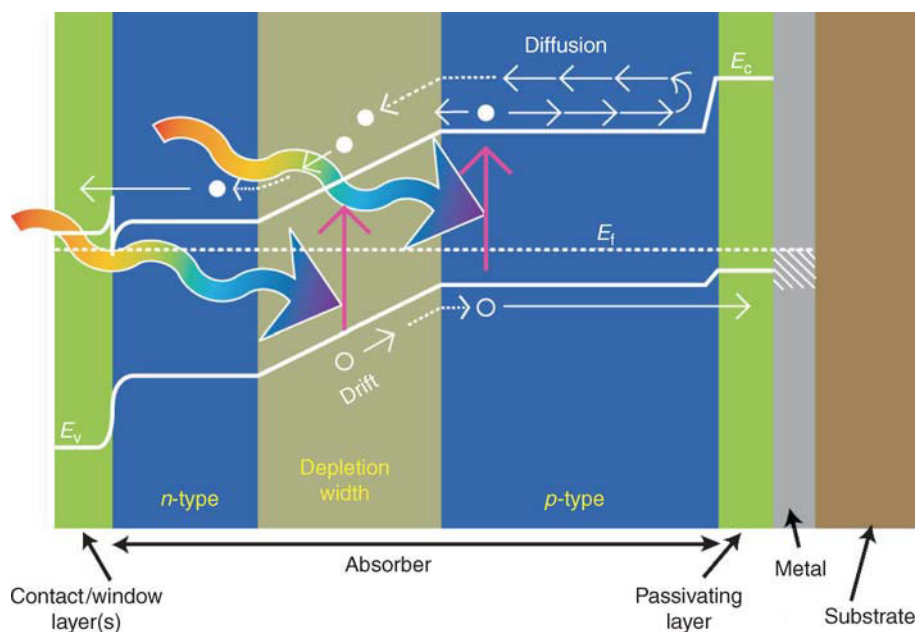
Figure 4. Schematic illustration of a *p–n* junction solar cell, showing the structure, carrier generation, and separation. Wavy arrows represent photons. E_v is the valence-band energy, E_f is the Fermi level, and E_c is the conduction-band energy. (Courtesy of S. Kurtz.)

Figure 5. Current–voltage (*J–V*) characteristic of a solar cell with and without illumination. The open-circuit voltage (V_{oc}), short-circuit current (J_{sc}), and fill factor are identified.

carrier generation, the electrons and holes separate and are collected at the contacts. There are two main modes for charge carrier separation: drift of carriers, driven by the built-in electrostatic field of a *p–n* junction, and diffusion of carriers from zones of high to low carrier concentration following an electrochemical potential gradient. These are illustrated in Figure 4. When drift is important, the structure of the cell (e.g., the depletion width) can be used to compensate for poor diffusion. When diffusion is dominant, optimizing materials quality becomes more important. Drift is typical of inorganic cells, which are normally *p–n* junction devices. The highest-efficiency devices, however, rely on diffusion to transport carriers to the junction for collection. Diffusion is the dominant transport mechanism for dye or organic solar cells.

The properties of the contacts and window layers are also critical to device performance. At least one contact must be electrically conducting and transparent to photons in the spectral range where the absorber creates carriers. Transparent conducting oxides are the material of choice for this purpose. It is also important to point out that the simple structure and the division into well-defined layers with specific functions shown in Figure 4 are not adequate to describe many solar cells. In a number of designs, light enters through the substrate, and contacts can be quite complicated, fabricated from several layers

with significant interdiffusion at metallurgical junctions.

Photovoltaic Figures of Merit

Some of the basic metrics for characterizing PV devices will appear in the articles in this issue. Figure 5 shows a typical current–voltage characteristic of a solar cell in the dark and under illumination. Power is generated when the cell operates in the fourth quadrant of the graph where voltage is positive and current is negative. The fill factor is the power produced at the maximum power point on the illuminated *J–V* curve divided by the product of the open-circuit voltage (V_{oc}) and short-circuit current (J_{sc}). Think of it as a measure of how rectangular the *J–V* characteristic is in the fourth quadrant. Another useful measure, quantum efficiency (QE), is the ratio of the number of charge carriers collected by the solar cell to the number of photons at a given illuminating energy. Ideally, it is a step function at the bandgap of the absorber. In real devices, however, the absorption threshold is less abrupt[12]—the step is sloped instead of vertical—and there is also a roll-off at higher energies.

The most fundamental measure of performance is, of course, the energy conversion efficiency—the percentage of power converted from sunlight to electrical energy. Two decades ago, Shockley and Queisser[13] used a detailed-balance approach to estimate the thermodynamic efficiency limit for solar cells with a single absorbing
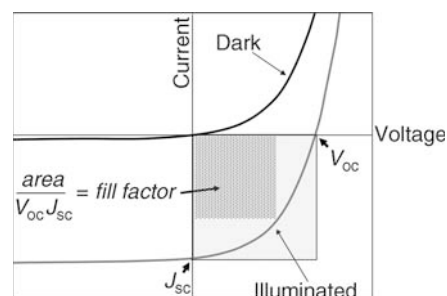
material (single junction). Their approach balanced the radiative transfer between the sun, modeled as a black body at 6000 K, and the solar cell, assumed to be a 300 K black body, which absorbs photons with energy above an energy threshold (the bandgap). They varied the bandgap of the absorber and the solid angle from which the solar cell can collect the sun's radiation (concentration). As the bandgap of the absorber is increased, the open-circuit voltage increases, but because only photons with energy above the bandgap are converted into carriers, the short-circuit current decreases. This tradeoff between voltage and current leads to a maximum in efficiency as a function of bandgap. For unconcentrated solar irradiance (one sun), a maximum efficiency limit of ~31% at a gap near 1.3 eV was found. For full solar concentration (46,300 suns), maximum efficiency was ~41% for a 1.1 eV material.

Improving the Cost Performance of PV Devices

The record unconcentrated efficiencies for single-crystal Si (sc-Si) cells and modules are 24.7% and 22.7%, respectively. For multicrystalline Si (mc-Si), the best efficiencies are 20.3% and 15.3%, respectively.[14] These values are far enough below the theoretical limit that there is still room for efficiency improvements; hence, laboratory and industrial-scale efforts focus on improving cell efficiencies and also on implementing innovative and low-cost fabrication processes. Whereas wafer-based Si solar cells dominate the market and are likely to maintain this dominance in the near future, approaches with the potential for much more significant solar electricity cost reductions are needed if PVs are to contribute substantially to future energy needs. In this issue of *MRS Bulletin*, we have chosen to focus on second- and third-generation approaches with the potential for achieving significant cost reductions.

For a review of the status of crystalline and mc-Si photovoltaic technology, interested readers are referred to Reference 15.

In the simplest view, the cost of PV-generated electricity is set by a tradeoff between manufacturing cost, system lifetime, and solar conversion efficiency. Second-generation approaches focus on reduced manufacturing cost using thin-film techniques to lower substrate costs, materials usage, and processing expense. The first two articles in this issue, by Schropp et al. and Beach and McCandless, describe recent activities in polycrystalline/amorphous silicon solar cells and in chalcogenide-based thin-film PVs. Despite the remarkable progress these technologies have made in the last years, the actual market share of thin-film technologies is very modest (<7% total for CIS, CdTe, and a-Si; see Figure 3). In part, this is because processes and equipment for manufacturing thin-film modules are less mature than for crystalline silicon. There is considerable room for materials, energy utilization, and process optimization. This drives a strong need for basic materials research, especially as it relates to lower manufacturing costs with improved reliability and module efficiency.

Third-generation technologies attempt to "leapfrog" to a cost-efficiency performance competitive with conventional electricity production. They are sometimes defined as approaches that do not rely on conventional *p–n* junctions. Organic and dye-sensitized solar cells are examples. A more formal definition involves cells capable of higher efficiency then the single-junction Shockley–Queisser limit. Using this definition, the next two articles, by Dimroth and Kurtz and by Luque et al., discuss third-generation PV approaches, such as multijunction and quantum dot solar cells. Returning to the efficiency discussion, from a purely thermodynamic argument, the maximum solar conversion efficiency for the sun at 6000 K and a solar conversion device at 300 K follows from the Carnot efficiency and is about 95%. The much lower single-junction Shockley–Queisser limit of roughly ~30% arises from two fundamental loss mechanisms: transmission loss of photons with energies below the bandgap, and thermal relaxation of hot carriers created by photons with energies greater than the bandgap.

Tandem or multijunction approaches are discussed first by Dimroth and Kurtz. They integrate multiple absorbers with different bandgaps into the same cell. A broader portion of the solar spectrum is absorbed while minimizing thermal relaxation losses. Tandem solar cells based on III–V compound semiconductors are a relatively mature technology used extensively in space power applications where the power-to-weight ratio is the key figure of merit. They have the highest reported efficiencies but are fabricated on single-crystal substrates using epitaxial deposition techniques and, hence, are relatively expensive to manufacture. Generating low-cost electricity with these devices requires solar concentration to reduce the required cell area. Research and development in this field is focused on increasing the efficiency from 40% to 50% and on reducing manufacturing cost while optimizing the cells for specific applications.

In their article, Luque et al. discuss a more speculative approach toward very high efficiencies based on nanotechnology. Quantum-dot–based cells have a theoretical thermodynamic conversion efficiency of up to ~66% under high concentration, similar to that of a three-junction cell. In particular, approaches based on multiple exciton generation (two or three excitons generated per incident photon) mitigate the losses associated with thermalization of carriers created by above-bandgap absorption, whereas intermediate-band solar cells focus on capturing energy from sub-bandgap photons.

The final article, by Fortunato et al., is devoted to an important class of inorganic materials found in nearly every thin-film PV device, namely, transparent conducting oxides (TCOs). TCOs function simultaneously as a window layer, enabling light to reach the active absorbing material, and as an ohmic contact, transporting photogenerated charge carriers away from the absorber. Indium-oxide–based films are presently the dominant TCO. The high cost of In, coupled with the growing realization that the properties required of TCOs are dependent on the PV technology under consideration, is driving research into alternative materials and processes tailored to specific applications. The article reviews TCOs in current use, the requirements that present and future PV technologies place on TCOs, and research directions designed to meet these needs.

Summary

Photovoltaic technology holds the promise of an almost inexhaustible energy source with minimal environmental impact. Significant reductions in the cost of PV-produced power are required to realize this potential, and the inorganic PV technologies reviewed in this issue are focused on meeting this challenge. In the simplest view, all PV devices perform the same two functions: conversion of photons into carriers and collection of those carriers. In addition, the research directions pursued in each technology have the same ultimate goals of reduced manufacturing cost and increased conversion efficiency. In reality, the rich set of materials issues that must be resolved to achieve these goals vary significantly from one materials system to the next. The ability of researchers in this field to identify and overcome the challenges associated with each technology will determine which are successful in making it to the marketplace and ultimately whether PVs are successful in realizing their promise.

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Luque received the Torres Quevedo National Prize for Technology in 1989, the Alexander-Edmond Becquerel Prize in PV research in 1992, the William Cherry Prize for PV research in 2006, the King James I Award for environmental research in 1999, and the National Juan de la Cierva Award for technology transfer. He belongs to the Academies of Engineering of Spain, Russia, and Belarus, is *doctor honoris causa* at the Universities of Jaén and Carlos III of Madrid, and is an honorary member of the Ioffe Institute in St. Petersburg. He has published more than 250 scientific papers and several books, and he holds 13 patents.

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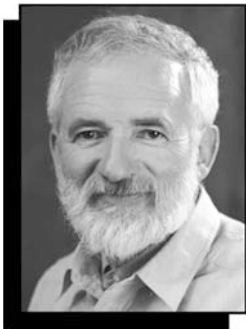
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He has authored or co-authored more than 300 papers and was a symposium organizer for the MRS Spring Meeting (1996–1999), the ICANS-21, the 3rd and 4th International Conferences on Hot Wire CVD (Cat-CVD) Process, and the 2005 and 2006 Plastic Electronics Conferences.

Schropp can be reached at Utrecht University, Faculty of Science, Surfaces, Interfaces and Devices, PO Box 80.000, 3508 TA Utrecht, the Netherlands; tel. 31-30-2533170, fax 31-30-2543165, and e-mail R.E.I.Schropp@ phys.uu.nl. 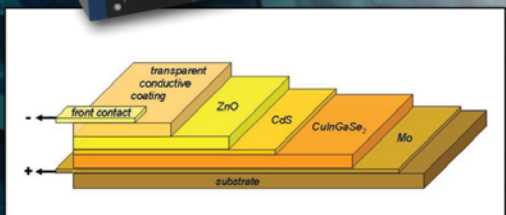   □