Thin-Film Solar Cells: An Overview

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Thin film solar cells (TFSC) are a promising approach for terrestrial and space photovoltaics and offer a wide variety of choices in terms of the device design and fabrication. A variety of substrates (flexible or rigid, metal or insulator) can be used for deposition of different layers (contact, buffer, absorber, reflector, etc.) using different techniques (PVD, CVD, ECD, plasma-based, hybrid, etc.). Such versatility allows tailoring and engineering of the layers in order to improve device performance. For large-area devices required for realistic applications, thin-film device fabrication becomes complex and requires proper control over the entire process sequence. Proper understanding of thin-film deposition processes can help in achieving high-efficiency devices over large areas, as has been demonstrated commercially for different cells. Research and development in new, exotic and simple materials and devices, and innovative, but simple manufacturing processes need to be pursued in a focussed manner. Which cell(s) and which technologies will ultimately succeed commercially continue to be anybody’s guess, but it would surely be determined by the simplicity of manufacturability and the cost per reliable watt. Cheap and moderately efficient TFSC are expected to receive a due commercial place under the sun. Copyright © 2004 John Wiley & Sons, Ltd.

KEY WORDS: thin-film solar cells; thin films; maturity index; review

INTRODUCTION

The modern era of photovoltaic device technology reached its Golden Jubilee year in 2003.¹ Since the discovery of a p–n junction Si photovoltaic (PV) device² reported in 1954, the science and technology of PV devices (solar cells) and systems have undergone revolutionary developments. Today, the best single crystal Si solar cells have reached an efficiency of 24.7%, compared with the theoretical maximum value of 30%. Large-scale production of solar cells during the year 2002 worldwide³ stood above 500 MWp, consisting ~40% of single crystal Si and ~51% multicrystalline Si cells and about 8% based on thin-film amorphous Si solar cells. Cumulatively, about 2 GW of solar cells are being used worldwide in a variety of applications, ranging from several MW of stand-alone / grid connected power stations to several MW of low-power electronic devices. A large number of countries, developing and developed, are seriously involved in creating and nurturing the PV industries. Human life-style being a matter of power is a well-documented fact and the poor and developing countries (ironically blessed with copious sun power) with limited conventional power sources,
particularly in remote areas, are increasingly turning to PV power for enhancing their development index. That the sunrise PV industry worldwide is already a billion dollar industry leaves no doubt that it has matured fast to be reckoned with economically in the world arena. However, its growth is limited largely by the ultimate cost of the PV power. Despite tremendous progress in all aspects of production of Si-based solar cells and the rapid decrease of production cost from $4.2/Wp in 1992 to $1.7/Wp in 2002, large-scale household applications are not commercially viable as yet. With respect to single crystal Si technology, the single most important factor in determining the cost of production is the cost of the 250–300 μm-thick Si wafer used for the fabrication of solar cells. Unless a much thinner wafer, and thus less amount of Si, is used and the production process is made cheaper and simpler, any further decrease in Si cells cost will be only by small increments.

The problem of high cost of Si was recognized right from the beginning. And it has also been recognized that cheaper solar cells can be produced only if cheaper and more sparsely used materials and lower cost technologies are utilized. The first thin/thick-film Cu₂S/CdS cell was based on rather simple and cheap technology known as the ‘Clevite process’, in which several μm-thick CdS film was deposited on to a metal or metallized plastic substrate, then an acid etch of the CdS film followed by immersion in hot cuprous chlorides solution for few seconds to topotaxially convert the CdS surface to Cu₂S. Small-area cell efficiencies as high as 10% were reported and produced commercially by several companies in USA and France. However, the rapidly rising stabilized efficiency of cells based on the better-understood Si technology, compared with lower and questionable stability of Cu₂S/CdS cell, led to premature death of the latter. Nevertheless, extensive basic research on the Cu₂S/CdS PV devices has proved very useful for later developments in thin-film solar cells (TFSC).

The chance discovery of the possibility of doping amorphous hydrogenated Si (a-Si:H) films created a lot of excitement in the PV industry. As a result of an enormous amount of basic and applied research by a very large number of scientists and engineers worldwide, a major PV industry on megawatt scale, based on a-Si:H thin films, grew rapidly in several countries. However, after several years of significant development and production activities, a-Si:H has failed to challenge the supremacy of crystalline silicon, largely because of little cost advantage, lower efficiency and relatively poor stability compared with crystalline Si cells.

The number of possible and viable thin/thick-film materials for solar cells is quite large. Some of the most attractive candidates, based on a-Si:H, CdTe and CuInSe₂ materials have been the subject of intense R&D and exploration of manufacturing technologies for the last three decades. Despite all these efforts, which cell material and which production technology will ultimately succeed in the commercially competitive field is still anybody’s guess. Several reviews on the physics, materials aspects, device characterization, performance and manufacturing technologies of TFSC have been published in the recent past. Instead of focusing on these issues, this review seeks to highlight the weaknesses in different thin-film solar cell devices and production technologies so that a comparative analysis can be made.

**STATUS OF DIFFERENT PHOTOVOLTAIC TECHNOLOGIES**

To provide a commercial view of the current photovoltaic technologies, it is useful to compare the manufacturing cost and the energy payback time. Figure 1 shows the average module manufacturing cost, average cost per watt weighed by the production capacity, of thin-film modules in comparison with non-thin-film modules based on data available in 2001. There has been a steady and rapid decline in the cost and one expects the cost comparison of thin-film cells to become increasingly favorable. The average cost of thin-film module manufacturing is reduced by 64% compared to 51% for non-thin-film modules. Clearly, thin-film solar cell technologies have the potential for producing cheaper devices on a large scale.

Another major consideration in comparing different PV technologies is the energy payback period, which refers to the number of years in which the electrical energy generated by the devices will be equal to the energy required for production of these devices. Figure 2 shows a comparison for different types of solar cells and other system components required for different applications. The figure gives two estimates for multicrystalline modules to avoid the uncertainty related to the variation in the energy consumption estimates. The low estimate is based on the lower end value for silicon purification and does not consider the primary crystallization step, while the high estimates assume the high-energy end value for silicon that includes energy intensive primary
Figure 1. Manufacturing cost and production capacity projections for thin-film and non-thin-film modules based on the data available in year 2001 (data from Reference 5).

Figure 2. Energy payback time for different PV technologies: A multicrystalline Si 1997 low; B multicrystalline Si 1997 high; C thin-film 1997; D multicrystalline Si 2007; E thin-film 2007, for different applications. Other system components are also shown for comparison (data from Reference 13).
crystallization process. For grid-connected rooftop and array fields, the TFSC technology fare much better. On the other hand, the multicrystalline estimates based on lower end value fare well for solar home systems because of the higher balance of system (BOS) cost.

**WHY THIN/THICK-FILM MATERIALS?**

In order to appreciate this query, it is essential to understand what a thin-film is. A thin film is a material created *ab initio* by the random nucleation and growth processes of individually condensing/reacting atomic/ionic/molecular species on a substrate. The structural, chemical, metallurgical and physical properties of such a material are strongly dependent on a large number of deposition parameters and may also be thickness dependent. Thin-films may encompass a considerable thickness range, varying from a few nanometers to tens of micrometers and thus are best defined in terms of the birth processes rather than by thickness. One may obtain a thin material (not a thin-film) by a number of other methods (normally called thick-film techniques) such as by thinning a bulk material, or by depositing clusters of microscopic species in such processes as screen-printing, electrophoresis, slurry spray, plasma gun, ablation, etc. A thick film can indeed be very thin, limited by the size of the depositing clusters, and its properties may also be sensitive to the various deposition parameters. Being simpler, cheaper and having relatively much larger throughput or rate of deposition, thick-film techniques are of considerable interest for viable TFSC technologies.

The atomistic, random nucleation and growth processes bestow new and exotic properties to thin-film materials. These properties can be controlled and reproduced, provided a range of deposition parameters are monitored and controlled precisely. Those who do not bother to understand the fundamentals of thin-film materials often regrettfully conclude that thin-films are a ‘fifth state of matter’—a state so named in the early history of thin-film technology to indicate highly variable properties.

The following features of thin-film processes have been shown to be of interest for solar cell technologies.

1. A variety of physical, chemical, electrochemical, plasma based and hybrid techniques are available for depositing thin-films of the same material.
2. Microstructure of the films of most materials can be varied from one extreme of amorphous/nanocrystalline to highly oriented and/or epitaxial growth, depending on the technique, deposition parameters and substrate.
3. A wide choice of shapes, sizes, areas and substrates are available.
4. Because of relaxed solubility conditions and a relaxed phase diagram, doping and alloying with compatible as also, in many cases, incompatible materials can be obtained.
5. Surface and grain boundaries can be passivated with suitable materials.
6. Different types of electronic junctions, single and tandem junctions, are feasible.
7. Graded bandgap, graded composition, graded lattice constants, etc., can be obtained to meet the requirements for a designer solar cell.
8. In case of multicomponent materials, composition, and hence bandgap and other optoelectronic properties, can be graded in desired manner.
9. Surfaces and interfaces can be modified to provide an interlayer diffusion barrier and surface electric field.
10. Surfaces can be modified to achieve desired optical reflectance/transmission characteristics, haze and optical trapping effects.
11. Integration of unit processes for manufacturing solar cells and integration of individual solar cells can be easily accomplished.
12. Besides conservation of energy and materials, thin-film processes are in general eco-friendly and are thus ‘Green’ processes.

But, keeping in mind that all good things come for a price, the ability to tailor numerous properties of thin-films required for an efficient solar cell demands good understanding of the material so produced with the help of a range of monitoring and analytic facilities. One also has to keep in mind that the high sensitivity of film properties to deposition parameters can produce a multitude of undesired results; thus thin-film materials must thus be treated with due respect and understanding.
PV materials

Conventionally, photovoltaic materials are inorganic semiconductors, which form suitable junctions with other materials and exhibit a PV effect when exposed to light. A large number of semiconductor materials show a PV effect, but only a few of them are of sufficient commercial interest because they must satisfy the constraints for minimizing thickness and wide availability. Ideally, the absorber material of an efficient terrestrial solar cell should be a direct bandgap semiconductor with a bandgap of \( \sim 1.5 \) eV with a high solar optical absorption \( (\sim 10^5/cm) \), high quantum efficiency of excited carriers, long diffusion length, low recombination velocity, and should be able to form a good electronic junction (homo/hetero/Schottky) with suitably compatible materials. With high optical absorption, the optimum thickness of an absorber in a solar cell is of the order of the inverse of the optical absorption coefficient and thus it must be a thin-film.

From the point of view of processing and manufacturing, elemental materials are the simplest. However, there are no suitable elemental semiconductor materials available with direct bandgap close to 1.5 eV. Silicon being an indirect bandgap material with a gap \( \sim 1.1 \) eV is by no means an ideal material. For effective solar absorption, Si wafers have to be at least 50 \( \mu m \) thick unless optical enhancement techniques are used to improve the effective absorption. A recent addition to the list of elemental materials is the boron-doped diamond-like carbon \(^{15}\) and fullerene films\(^{16,17}\) which have been investigated for photovoltaic applications with promising results.

A much wider choice of materials exists with two-component alloy/compound films. A metastable alloy film of a-Si:H, with a large tailorable bandgap, easy dopability and high optical absorption coefficient has emerged as an attractive material, and was discovered somewhat serendipitously. Indeed, in the 1980s, a-Si:H based thin-film solar cell technology challenged the supremacy of crystalline Si cells. Besides this metastable a-Si:H alloy, other two-component (binary) materials, which are attractive for thin-film solar cells are: GaAs, CdTe, Cu_xS, Cu_2O, InP, Zn_xP_y, etc. Of these, GaAs, InP and their derived alloys and compounds are ideal for photovoltaic applications, but are far too expensive for large-scale commercial applications. With increasing number of components, the number of possible materials increases in geometrical proportion. For example, alloys and compounds of I–III–VI ternaries and related quaternaries can form a host of suitable photovoltaic materials.\(^{18}\)

However, it must be emphasized here that with increasing number of components, the phase diagram of these materials in bulk form is quite complex. In the form of thin microcrystalline films, the phase diagram is fuzzy and more complicated, if at all definable. Indeed, it is sufficiently relaxed to allow the formation and coexistence of all possible crystal structures and too heterogeneously distributed.

An interesting alternative to inorganic semiconductor absorbers are organic semiconductors, which combine some interesting optoelectronic properties with the excellent mechanical and processing properties of polymeric/plastic materials. In organic semiconductors, absorption of photons leads to the creation of bound electron–hole pairs (excitons) with a binding energy of \( \sim 0.5 \) eV rather than free charges. The excitons carry energy, but no net charge, and have to diffuse to dissociation sites where their charges can be separated and transported to the contacts. In most organic semiconductors, only a small portion (\( \sim 30\% \)) of the incident light is absorbed because the majority of semiconducting polymers have bandgaps higher than 2.0 eV. The typically low charge-carrier and exciton mobility require active absorber layer thickness to be less than 100 nm. This thickness is sufficient to absorb most of the incident solar photons if light trapping is used. More importantly, organic semiconductors can be processed from solutions at or near room temperature on flexible substrates using simple, cheap and low-energy deposition methods such as spin or blade coating thereby yielding cheaper devices. Even though the efficiency of these devices is poor at present, they may find immediate applications for disposable solar cell based small power applications. Among the major issues to be addressed before reasonable market penetration of the organic devices takes place are the improvement of the stability of conjugate polymers, and the matching of the bandgap of the organic materials with the solar spectrum for higher conversion efficiency by using blended/composite polymers and suitable dyes.

Thin-film solar cell devices

In principle, a solar cell is a junction device obtained by placing two electronically dissimilar materials together with a thin electronic barrier in between to separate charge. However, efficient devices must ensure high conversion efficiency of solar photons and high collection efficiency of excited charge carriers. A variety of
Figure 3. Typical TFSC structures for single-junction: (a) substrate Cu(InGa)Se$_2$; (b) superstrate CdTe; and (c) tandem a-Si triple-junction devices
junctions such as Schottky barrier, homojunction and heterojunction have been studied. Junctions can be abrupt, graded, buried, heteroface, etc., involving materials of different conductivity/ type of conductivity. Typical examples of the cross-section of various junctions, Cu(InGa)Se₂, CdTe/CdS, triple junction p-i-n a-Si:H are shown in Figure 3.

Different junction devices with appropriately graded bandgap can be placed in tandem, or can be integrated to form a multijunction device. Theoretically, if all solar photons can be converted to electricity, one may approach thermodynamic Carnot cycle efficiencies. Theoretical analysis shows that 53% efficiency can be achieved with four junction devices and as the number of junctions goes to infinity, the efficiency can reach as high as 68%. In view of the difficulty and complexity of fabricating such optoelectronically matched junctions, commercial devices with up to only three junctions have been in production for a-Si:H and GaAs–based devices. This is made possible by the fact that in these cases bandgap tailoring with additives/dopants is conveniently achieved. By using multijunction device structure in a:Si-H tandem solar cells, relatively more stable and higher-efficiency devices with a minimized Staebler–Wronsky degradation effect are fabricated.

Innovative device structures that employ mesoporous TiO₂ films change the concept of two distinctive p and n layers conventionally used to form p–n junction devices. Extremely thin absorber (ETA) solar cells use TiO₂ mesoporous films embedded with organic and inorganic absorber materials. These device structures are designed to improve the effective charge carrier separation within the absorber materials and to enhance the light absorption due to its scattering abilities. Plastic/organic solar cell devices employ blend cell structure
in addition to the conventional layered structure. In a blend cell, the molecule mixing occurs on a scale that allows good contact between molecules. This increases the interface area of charge percolation and allows most excitons to reach the donor/acceptor interface. Typical structures of an ETA and blended plastic solar cells are shown in Figure 4. Several blend structures have been proposed that include polymer-blend,27 TiO2-blend,28 C60-blend29 and nanorod-blend.30 However, an ideal device structure suitable for high-efficiency devices is yet to be identified.

**TFSC MATERIALS REVIEW**

The TFSC consists of several layers of different materials in thin-film form. In general the solar cell consists of substrate, TCO, window layer (p or n-type), absorber layer (i or p-type) and metal contact layer. Each of the component materials has different physical and chemical properties and each affects the overall performance of the device in some form or the other. A critical understanding of the behavior of these individual components is essential for designing a device. Also important are the various interfaces between the different layers. Since each layer has different crystal structure, microstructure, lattice constant, electron affinity/work function, thermal expansion coefficient, diffusion coefficient, chemical affinity and mobility, mechanical adhesion and mobility, etc., the interfaces can cause stresses, defect and interface states, surface recombination centers, photon reflection/transmission/scattering, interdiffusion and chemical changes with attendant electro-optical changes.

![Figure 4. Innovative TFSC structures: (a) mesoporous device structures for ETA solar cells (adopted from Reference 26), (b) organic blend cells. MDMO-PPV (poly)[2-methyl, 5-(3*, 7** dimethyl-octyloxy)]-p-phenylene vinylene; PCBM ([6,6]-phenyl C61 butyric acid methyl ester)](image-url)
A brief review of the current understanding of different TFSC components and interface chemistry is given in the following sections. The discussion of these components is primarily limited to the major TFSC technologies based on CIGS, CdTe, a-Si:H and futuristic organic materials.

**Substrate**

Thin-film solar cells devices are configured in either substrate or a superstrate structure. For superstrate configuration, the substrate is transparent and the contact is made by a conducting oxide coating on the substrate. For substrate configuration, the substrate is metal or metallic coating on a glass/polymer substrate which also acts as the contact. Substrate is a passive component in the device and is required to be mechanically stable, matching thermal expansion coefficient with deposited layers and inert during the device fabrication. Suitable substrates are selected for different processes on the basis of these criteria. Flexible substrates, stainless steel foils/polymer films, are suitable for roll-to-roll deposition enabling a compact deposition system design as well as flexibility in device handling. Electrically conductive substrate enables the fabrication of front and rear-side conduction cells, whereas insulating substrate enables fabrication of monolithically interconnected cells for modules. Deposition involving high-temperature processes generally requires expensive and rigid substrates such as high-temperature glass or ceramics. A low-temperature process enables usage of less expensive flexible substrate. It should be noted that, in TFSC technology, the substrate could be a major expense.

Both superstrate and substrate device structures are currently being pursued for CIGS device fabrication. The film growth and interdiffusion and hence the device properties are dependent on the device structure. The CIGS solar cells based on superstrate structure is inferior to substrate structure because of the interdiffusion of CdS during high-temperature CIGS film growth. The best device efficiency of 10.2% was reported on superstrate...
device configuration having a ZnO buffer layer.\textsuperscript{31} On the other hand, a substrate configuration with CdS buffer layer resulted in a 19.2\% efficiency device.\textsuperscript{32} The substrate appears to play an active role in improving the photovoltaic performance of the CIGS absorber materials. The Na in the soda-lime glass substrate has been considered as a key prerequisite for efficient CIGS device fabrication. Na diffuses from the substrate into CIGS absorber and improves the grain growth and cell performance.\textsuperscript{33} Sodium is inherently present in soda-lime glass (SLG) and in the case of Na free substrate Na precursors (Na$_2$Se, Na$_2$S, NaF) are intentionally incorporated in the device fabrication.

CdTe devices are fabricated preferably in superstrate configuration because the CdTe surface is exposed for contacting. In addition, the benign feature of CdS diffusion during the processing reduces the lattice mismatch between CdTe and CdS. CdTe solar cells use borosilicate glass for high-temperature deposition (600°C) and soda-lime glass for low-temperature deposition (60–500°C). CdTe has also been deposited on thin metallic foils such as stainless steel, Mo, Ni and Cu. Mo is best suited for CdTe deposition, owing to better thermal matching. For deposition at high temperatures the possibility of oxide layer formation on the metallic substrate exists, which can create a barrier for electrical conduction.\textsuperscript{34}

Amorphous and nanocrystalline Si solar cells can also be prepared on a variety of metallic and non-metallic substrates. For example, $p-i-n$ cells are usually fabricated with glass substrate (superstrate configuration) while, $n-i-p$ cells are commonly grown on metallic substrates (substrate configuration). Structural properties of the microstalline Si cells are found to be dependent on the substrate properties.\textsuperscript{35} Large substrate area deposition techniques have clearly demonstrated the capabilities of thin-film deposition techniques in this regard. Roll-to-roll deposition on stainless steel and glass-in-module-out technologies for a-Si solar cells are already in production.

\textit{Transparent conducting oxide (TCO)}

Transparent conducting oxides in general are $n$-type degenerate semiconductors with good electrical conductivity and high transparency in the visible spectrum. Thus, a low-resistance contact to the device and transmission of most of the incident light to the absorber layer is ensured. The conductivity of a TCO depends on the carrier concentration and mobility. An increase in the carrier concentration may result in enhanced free carrier absorption, which reduces the transparency of the TCO in the higher-wavelength region. Hence increasing the mobility by improving crystalline properties is considered to be the pathway for a good TCO.\textsuperscript{36} Besides these optoelectronic properties, the mechanical, thermal, chemical, and plasma-exposure stability and passivity\textsuperscript{37} of TCOs are important considerations. Studies have shown\textsuperscript{38} that only ZnO-based TCOs can withstand H-bearing plasma and are also stable up to 800K. Therefore, ZnO-based materials are being increasingly used in TFSC technologies. A number of reviews on TCOs have appeared in literature.\textsuperscript{36,39–41} Table I lists typical values of resistivity and transmission in the visible region for various TCOs of interest for photovoltaic application.\textsuperscript{41,42}

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<tr>
<th>Material</th>
<th>Resistivity ($\Omega$ cm)</th>
<th>Transparency (%)</th>
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<tbody>
<tr>
<td>SnO$_2$</td>
<td>$8 \times 10^{-4}$</td>
<td>80</td>
</tr>
<tr>
<td>In$_2$O$_3$:Sn (ITO)</td>
<td>$2 \times 10^{-4}$</td>
<td>$&gt;80$</td>
</tr>
<tr>
<td>In$_2$O$_3$:Ga (IGO)</td>
<td>$2 \times 10^{-4}$</td>
<td>85</td>
</tr>
<tr>
<td>In$_2$O$_3$:F</td>
<td>$2.5 \times 10^{-4}$</td>
<td>85</td>
</tr>
<tr>
<td>Cd$_2$SnO$_4$ (CTO)</td>
<td>$2 \times 10^{-4}$</td>
<td>85</td>
</tr>
<tr>
<td>Zn$_2$SnO$_4$ (ZTO)</td>
<td>$10^{-2}$</td>
<td>90</td>
</tr>
<tr>
<td>ZnO:In</td>
<td>$8 \times 10^{-4}$</td>
<td>85</td>
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It is possible to take advantage of differing properties of two TCOs by forming a bilayer. High-efficiency CIGS and CdTe devices are generally fabricated with such bilayer structures, consisting of a highly conducting layer for low-resistance contact and lateral current collection and a much thinner high-resistivity layer (called HR layer by CdTe groups and buffer layer by CIGS groups) of a suitable material, to minimize forward current.

\begin{footnotesize}
\begin{center}
Table I. Typical resistivity and transmission (in the visible) for various TCO materials investigated for TFSC application (data from References 41 and 42)
\end{center}
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through pinholes in the window layer. By incorporating a 50-nm-thick resistive SnO₂, In₂O₃, ZnO, or Zn₂SnO₄ layer, the CdS layer thickness can be reduced to <20 nm, which significantly improves the blue response of the CdTe devices. The presence of the smoother high-resistive layer also improves the CdS film morphology by providing large grains during chemical bath deposition. Bilayer ZnO is used in CIS solar cells on the front side for substrate configuration.

By controlling the microstructure, textured single- and double-layer TCOs can be deposited and are used in a-Si solar cells to enhance the scattering-assisted light absorption. The texture angle has a major impact on light trapping and internal reflections. Increasing the angle causes better internal trapping in the i-layer, but also higher SnO₂/a-Si reflection losses, as well as SnO₂ and metal absorption losses. Similar optical enhancement has also been reported to be useful for very thin (1 μm) CdTe solar cells.

Window layer

The primary function of a window layer in a heterojunction is to form a junction with the absorber layer while admitting a maximum amount of light to the junction region and absorber layer; no photocurrent generation occurs in the window layer. For high optical throughput with minimal resistive loss the bandgap of the window layer should be as high as possible and as thin as possible to maintain low series resistance. It is also important that any potential ‘spike’ in the conduction band at the heterojunction be minimized for optimal minority carrier transport. Lattice mismatch (and consequent effects) at the junction is important for consideration for epitaxial or highly oriented layers. In the case of microcrystalline layers, mismatch varies spatially and thus the complicated effect, if any, averages out.

The CIGS solar cells typically use a CdS window layer, which is deposited by a chemical bath deposition (CBD) technique, which provides a superior device performance compared with that deposited by a physical vapour deposition (PVD) technique. This is partly due to the improvement in the interface chemistry between CIGS and CdS during the chemical process. The chemical bath removes the natural oxides from the CIGS film surface and also allows Cd to diffuse into the Cu-poor surface layer of the CIGS films. In addition, it is possible to use thinner layers of CdS because CBD deposition provides good surface coverage of the rough polycrystalline CIGS surface, even at a film thickness of 10 nm. Similar device performance has been reported when the CdS films are PVD deposited after CIGS films dipped in the chemical bath without thiourea.

Between CdTe (111) and CdS (001) the lattice mismatch is ~9.7%, compared to near perfect lattice match between CIGS (112) and CdS (001). In spite of the large lattice mismatch, CdS remains the best heterojunction partner for CdTe, probably because high-efficiency devices with reduced lattice mismatch can be fabricated by forming an interfacial CdSₓ₋₁Teₓ alloy layer and also because the role of mismatch in a submicrometer-grained polycrystalline films may not be significant. The relatively low bandgap of CdS as a window layer reduces blue response, but the effect is mitigated in both CdTe and CIGS devices by utilizing thinner CdS films. To maximize the blue response in CdTe devices, it is necessary to utilize the thinnest possible CdS layer in conjunction with a bilayer TCO to ensure uniformly low dark current. In an alternative approach, improved optical transmission is obtained by using a wide-bandgap semiconductor alloy such as Cd₁₋ₓZnₓS of higher resistivity as window layer. By changing the chemical precursors used for CBD film deposition one can change x continuously from CdS to ZnS. Thus, the optical transmission, thickness and film resistivity can be optimized to improve the device output.

For devices based on I–III–VI films such as CIGS, there are several alternative window layers currently being investigated to replace CdS because of the concern about the toxicity of Cd, and also to improve the blue response in devices. Table II lists alternative window layers investigated by different groups. Efforts are also being made to replace the CBD process by a PVD process so as to be able to integrate the heterojunction formation into in-line fabrication process.

For a-Si solar cells, depending on device configuration, the n- or p-layer is very thin and acts like a window layer that allows all the photons to be transmitted to the i-region. Given the very high absorbance of these films, a very thin doped layer (~10 nm) is required. Alloy films such as a-SiC:H having excellent optical transparency and good photoconductivity have been used as the window layers.
Absorber

Copper indium gallium diselenide (CIGS)

The I–III–VI chalcopyrite materials have some very desirable properties for photovoltaic application. CuInS$_2$, having a bandgap of 1.03 eV is considered an ideal material for photovoltaic application. The difficulties in controlling the sulfur during deposition and the relatively rapid diffusion of metals and impurity species, even at low temperatures, slow down the development of this material. However, devices with efficiency 11.4% have been reported. On the other hand, CuInSe$_2$, with bandgap of 1 eV, has proved to be a leading candidate for photovoltaic applications. It is one of the most absorbing semiconductor materials (absorption coefficient of $3 \times 10^5$/cm) and also makes an excellent junction and a solar cell. CuInSe$_2$ and other chalcopyrites appear to tolerate wide range of anion-to-cation off-stoichiometry. Unlike the II–VI analogue, CuInSe$_2$ can be doped n- and p-type to a low-resistivity level merely via introduction of native defects. The most benevolent feature of polycrystalline CuInSe$_2$ lies in the electrically benign nature of its numerous structural defects and hence polycrystalline CuInSe$_2$ films are as good an electronic material as its single-crystal counterpart. This makes CuInSe$_2$ based solar cells less sensitive to the impurities, grain size and crystalline defects. Devices with active area efficiency of 15.4% have been fabricated from CuInSe$_2$. Superior device performance is achieved when the junction is matched to the solar spectrum by increasing the bandgap. The resultant increase in $V_{oc}$ also benefits to the manufacturing process and device properties by: (a) reducing the number of scribes for the monolithic integration of the cells into module; (b) reducing the top and bottom electrode thickness; (c) lowering the temperature coefficient at maximum power point; and (d) making it less sensitive to light intensity fluctuations. Alloying with Ga$^{64}$, Al$^{65}$ or S$^{66}$ increases the bandgap of CuInSe$_2$ so as to make it more suitable for high-efficiency single-junction and multijunction devices. An increase in the bandgap and improved process conditions resulted in the fabrication of high-performance solar cells with efficiencies of 19.2% for small-area$^{32}$ and 13.1% for a large area ($90 \times 60 \text{ cm}^2$). Even though the efficiency and stability of the device are very promising, there are several factors that are less favorable for large-scale production of such devices. The increasing number of alloy components makes the multiple processes extremely complex and thus intelligent processes are required for precise control of the composition during deposition. The use of expensive and rare metals such as In and Ga adds to the cost of manufacturing.

Cadmium telluride (CdTe)

Owing to its optoelectronic and chemical properties, CdTe is an ideal absorber material for high-efficiency, low-cost thin film polycrystalline solar cells. CdTe is a direct bandgap material with an energy gap of 1.5 eV, and an absorption coefficient $\sim 10^7$/cm in the visible region, which means that a layer thickness of a few micrometers is sufficient to absorb $\sim 90\%$ of the incident photons. Owing to the high temperature of deposition in most cases, the films are deposited with Cd deficiency, giving rise to p-type conductivity. Because of the high ionicity (72%) of CdTe, the crystallite formed are well-passivated and strong chemical bonding (5.75 eV) results in high chemical and thermal stability. CdTe solar cell devices have proven to be remarkably tolerant to the deposition methods, and devices with efficiency $>10\%$ have been fabricated by several deposition techniques. Some of

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<th>Alternate buffer</th>
<th>Material</th>
<th>Deposition technique</th>
<th>Reference</th>
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<tr>
<td>In$_x$Se$_y$</td>
<td>In$_2$Se$_3$</td>
<td>Co-evaporation</td>
<td>51</td>
</tr>
<tr>
<td>Ga$_x$Se$_y$, Ga$_2$S$_3$, Ga$_2$Se$_3$</td>
<td></td>
<td></td>
<td>51</td>
</tr>
<tr>
<td>In(OH)$_2$S$_y$, In(OH)$_3$</td>
<td></td>
<td>CBD</td>
<td>52</td>
</tr>
<tr>
<td>ZnIn$_x$Se$_y$</td>
<td></td>
<td>ALD</td>
<td>53</td>
</tr>
<tr>
<td>Sn(S,O)$_2$</td>
<td></td>
<td>Spray</td>
<td>54</td>
</tr>
<tr>
<td>ZrO$_2$</td>
<td></td>
<td>CBD, PLD</td>
<td>55</td>
</tr>
<tr>
<td>ZnO, GaZnO, ZnO:B</td>
<td></td>
<td>RF/DC/DC sputtering</td>
<td>56</td>
</tr>
<tr>
<td>ZnSe, ZnS</td>
<td></td>
<td>Sputter, co-evaporation</td>
<td>57</td>
</tr>
<tr>
<td>(ZnCd)$_2$S</td>
<td></td>
<td>Spray, PVD, CBD</td>
<td>58</td>
</tr>
<tr>
<td>a-CdS:O</td>
<td></td>
<td>Sputtering</td>
<td>59</td>
</tr>
</tbody>
</table>
these techniques, close-spaced sublimation (CSS), PVD, electrodeposition and screen-printing have been scaled to yield large area modules. The solar cells based on CdS/CdTe junction have achieved an efficiency 16-5% in small areas compared with the theoretical maximum efficiency\(^2\) of 29%. For the past ten years the efficiency has only changed from 15-8%\(^3\) to 16-5%.\(^6\) The reason for such slow progress appears to be a lack of R&D efforts on such issues as the requirement of activation treatment that changes the bulk, interfacial and grain boundary properties, and the difficulty of forming an ohmic contact without degrading the device. The issue related to the environmental problem of Cd raised primarily by European nations (despite their abundant use of Cd in batteries) needs to be resolved and is addressed in the literature.\(^7\)

**Amorphous, micro/nanocrystalline and polycrystalline silicon**

Amorphous silicon is widely accepted as a thin-film solar cell material because: (a) it is abundant and non-toxic; (b) it requires low process temperature, enabling module production on flexible and low cost substrates; (c) the technological capability for large-area deposition exists; and (d) material requirements are low, 1–2 \(\mu\)m, due to the inherent high absorption coefficient compared with crystalline silicon. The high absorption of light results from the inherent high disorder, dangling bonds of the order of \(10^{19}/cm^3\), in the material so that all optical transitions are allowed. On the other hand, the disorder acts as recombination centers that severely reduce the carrier lifetime and pin the Fermi energy level so that the material cannot be doped either \(n\)- or \(p\)-type. Incorporation of 10% hydrogen in the film during deposition greatly reduces the density of the defects to \(10^{16}/cm^3\), yielding a new and exotic material, a-Si:H which has a well-defined optical threshold (mobility gap) at \(1.75\) eV compared with the crystalline Si indirect bandgap at \(1.1\) eV. The reduction in the defect density makes the a-Si:H material suitable for doping and alloying with a range of materials and for junction device fabrication. However, the properties of the material and the junction device are severely affected by the light-induced creation of metastable defects, known as the Staebler–Wronski effect. Light-induced degradation of a-Si:H devices is partially tackled by reducing the a-Si:H layer thickness so that the photogenerated carriers need to move only a short distance before they reach the electrode. However, thinning down also results in lower light absorption and thus optical confinement techniques employing diffusely reflecting front and back contacts are required to increase effective layer thickness in order to absorb the photons. Over a period of time, extensive research and development work on deposition technique and device structure have resulted in development of single-junction and multijunction devices with high efficiency and moderately good stability.

The a-Si alloy materials are no longer strictly classical amorphous materials with short-range order (<1 nm). Under suitable deposition conditions and strong hydrogen dilution, nanocrystalline and microcrystalline materials\(^8\) are obtained. The existence of very small Si crystallites dispersed in amorphous matrix deposited by plasma enhanced chemical vapor deposition (PECVD) under high-H dilution was confirmed with infrared absorption and XRD measurements.\(^9\) While the crystallite size and volume fraction are very small, these crystallites catalyze the crystallization of the remainder of the amorphous matrix upon annealing. Microcrystalline materials deposited by this method is found to have less defect density and are more stable against light degradation compared with a-Si. Recently developed improved efficiency materials consist of this heterogeneous mixture of the amorphous and an intermediate range order microcrystalline material. The laser\(^10\) and rapid thermal annealing, and optically assisted metal-induced crystallization techniques\(^11\) were also used to obtain a microcrystalline film from an amorphous film and to increase the grain size.

New high-rate deposition technologies for polycrystalline Si films and innovative solar cell designs are being evolved to make reasonably efficient cells with thickness less than 25 \(\mu\)m at an acceptably high throughput. For example, crystalline silicon on glass (CSG) technology combines the low manufacturing cost of thin-film technology with the established strengths of silicon wafer technology.\(^12\) Owing to the high conductivity of the silicon, no TCO was required for the current collection. With the assistance of light trapping technique, efficient modules (as high as 7%) have been fabricated on 2-\(\mu\)m-thick silicon films.\(^13\) High rate deposition of polycrystalline silicon films can also be obtained by hot-wire CVD techniques.\(^14\) Large-grain, 5–20 \(\mu\)m, polycrystalline silicon layers have been deposited at rates as high as 3 \(\mu\)m/min, using iodine vapour transport at atmospheric pressure.\(^15\) Deposition of polyc-Si for solar cell applications has been reviewed extensively in the literature.\(^16,17\)

Microcrystalline and polycrystalline silicon films have lower optical absorption in contrast to the high optical absorption in a-Si. Thus, in the former case, light trapping is necessary to extract the photon energy efficiently.
In addition, since the electronic transport properties (in particular the lifetime of the carriers) depend on the
grain size, the active film thickness in the cell has to be small to minimize the loss of photogenerated carriers,
unless the grain surfaces are passivated. Effective passivation of grain boundaries can be achieved by hydro-
genation.80 The low growth rate with high hydrogen dilution may be a problem for manufacturing.

**Organic semiconductors**

Organic semiconductors can be classified into three categories, depending on their chemical properties, as inso-
luble, soluble and liquid crystalline. They can be further classified as monomers, such as dyes, pigments and
polymers.81 Doping of organic semiconductors can be done by introducing foreign atoms or molecules, or by
electrochemical oxidation/reduction processes. Some dopants for \( p \)-type materials are: \( \text{Cl}_2, \text{Br}_2, \text{I}_2, \text{NO}_2, \)
organic molecules such as \( \omega \)-chloranil, and 2,4,7-trinitrofluorenone, TCNQ, or high-electron-affinity semicon-
ductors such as \( \text{C}_6\text{O}_6, \text{CN-PPV} \) or perylene diamides. Some dopants for \( n \)-type materials are: alkali metals, phe-
nothiazines or semiconductors with low ionization potential. The mobile charge concentration can also be
changed by trapping of stray electrons in the conduction band (material becoming a better hole conductor than
electron conductor by shifting the Fermi level close to the volume bond due to the reduction of free electron
concentration), making the material a doped \( p \)-type conductor. Since there is no net increase in the charge car-
rrier concentration, the conductivity does not increase unless the mobility is affected.

Organic solar cells have the advantage of using chemically tailored materials with the desired properties and
can potentially be manufactured by inexpensive technologies. In order to be attractive from the manufacturing
point of view, the organic solar cell device efficiency has to be improved from the current <3% efficiency.82
Also, organic solar cells have a stability problem common to conjugated polymers.83 However, these may not be
very serious problems and may be overcome in the near future.

**Back contact**

For polycrystalline CdTe and CIGS devices, the back contact is applied to the \( p \)-type semiconductor in both
superstrate and substrate configurations. In order to form an ohmic contact, the metal used for contact should
have a work function higher than that of the \( p \)-type semiconductor. This aligns the metal Fermi level with the
upper valence band edge. In the substrate configuration of CIGS solar cells, Mo is used as the contacting mate-
rial because of its relatively inert nature during the highly corrosive CIGS deposition conditions. Mo forms an
ohmic contact via the formation of a thin intermediate MoSe\(_2\) layer formed during the CIGS deposition.84 Sev-
eral alternative contact materials are also investigated for CIGS devices.85 The adhesion of Mo films to the
substrate and the sheet resistivity is highly dependent on the sputter deposition conditions. The relationship
between the microstructure and stress of Mo films under different sputtering conditions are well established.86
In general the Mo films sputter-deposited at low process pressure tend to be dense, having low resistivity and
compressive stress. As the Ar process gas pressure increases, the film stress switches from being compressive to
tensile. Interestingly, Mo does not form an ohmic contact to CIGS in the superstrate configuration, probably
because of the absence of MoSe\(_2\) and Pt and Ti films are used instead.

There are no low-cost metals available with appropriate higher work function (>4.5 eV) to form ohmic con-
tact on CdTe and Au has been used in most cases. Ni-based contacts have also shown promising results.87,88 In
an alternative approach pseudo-ohmic contact was developed for CdTe devices. Here, a highly doped semi-
cductor is first deposited/formed on a CdTe surface followed by the application of a metal film contact. Semi-
cconductors such as \( \text{HgTe}, \text{ZnTe}:\text{Cu}, \text{Cu}_x\text{Te}, \) and \( \text{Te} \) can be deposited between CdTe and contact metal to achieve
a good ohmic contact. Cu-doped graphite paste and antimony telluride have also been tried, with mixed success.
Etching of CdTe films using Br–methanol, NP solution, etc., creates a Te-rich \( p^+ \), which can be useful in making
a pseudo-ohmic contact with Cu/Au layer, since the use of elemental Cu leads to \( p^+ \) \( \text{Cu}_2\text{Te} \) formation. The
modification of the CdTe surface allows the use of many different contact materials for lateral current collec-
tion. Wet contacting methods and all-vapor contacting methods are actively being investigated for commercial
development.

For amorphous silicon devices, the back contacts are formed on \( n \)-type semiconductor (and hence higher
work function metals are not required) using Ag or Al. However the use of Ag or Al directly on \( n \)-type
semiconductor will result in optical losses in the long-wavelength region. The long-wavelength response of the device will be improved if the $n$/metal interface reflects the long-wavelength radiation back to the cell. Thus the back contact for both $p-i-n$ and $n-i-p$ configuration is often formed with double-layer back reflector consisting of ZnO and Ag or Al. The low index ZnO layer will effectively increase the total internal reflection from the $n$-ZnO interface. The optical and electrical properties of the ZnO layer play a significant role in improving the back reflection properties and also the device performance.\(^8^9\)

Whereas the work function of the electrode materials does not exert a strong effect on polycrystalline TFSC, because of the interface layer between the semiconductor and metal, it is very important for organic-based solar cells since it determines, together with the low unoccupied molecular orbits (LUMO)/high occupied molecular orbits (HOMO) and Fermi level of the semiconductor, whether the electrode forms an ohmic or a blocking contact for the respective charge carrier. Moreover a large difference in work function of the electrode materials can increase the $V_{oc}$ considerably. Low-work function metals such as Al, Ca, In, Ag are the common electrode materials for the electron-collecting contact. On the other hand, high-work function materials such as Au are preferred for the hole-collecting contact. One contact has to be at least partly transparent which requires a thin metallic layer. However, this may increase the series resistance significantly. ITO is therefore often used in place of Au for contact.

Interfaces

TFSC are comprised of several layers of different semiconductors and metals, and thus the device has a large number of interfaces. Besides these surfaces/interfaces, submicrometer grain-size polycrystalline films have a high concentration of grain boundaries acting as internal interfaces. As far as possible, photovoltaic materials are selected to match lattice constant, electron affinity/work function and thermal expansion coefficient between the adjacent layers. However, the interface properties also get modified during device processing as a result of growth process involving the sequential deposition of multilayers at different deposition conditions. In addition, post-deposition treatments involving high-temperature annealing can alter the interface and intergrain properties. Interfacial defect states and chemical and metallurgical changes affect the optoelectronic transport properties of the device. As a result, the device parameters such as open-circuit voltage, current and fill factor can be modified significantly. Extensive scanning tunneling microscopy studies of interfaces and intergranular regions show clearly that they are not only active, but are also significantly different electronically from the bulk of the grains. On the other hand, manipulation of the interfacial structure, chemistry and metallurgy provides a powerful tool to tailor/e engineer the Fermi level, bandgap, electric field and their gradients to improve the overall device performance. Both activation and passivation of grain boundaries have been effectively used in some devices.

In most of the heterojunction devices, the $p-n$ interface properties significantly affect the solar cell performance. Studies on CIGS devices show that the electrical properties are strongly affected by the CIGS/CdS interface properties. XPS studies show the presence of a CuIn$_3$Se$_5$ phase on CIGS films, which reduces the conduction band offset from 1 eV (CIGS/CdS) to 0.3 eV (CuIn$_3$Se$_5$/CdS) and results in better device performance.\(^9^0\) DLTS measurements show that the surface of the CIGS films is type-converted.\(^9^1\)

Studies on CdTe/CdS devices shows that CdS/ITO interface is not an efficiency limiting one. There is slight roughening that takes place during high-temperature processing at the ITO/CdS interface and that is considered to be beneficial in reducing the reflection loss.\(^9^2\) On the other hand, CdS/CdTe interface properties can significantly affect the device properties. For example, under certain processing conditions, CdTe diffusion into CdS can reduce CdS bandgap and decreases the window transmission. On the other side of the device, CdS diffusion into CdTe narrows the CdTe bandgap, resulting in increased long-wavelength quantum efficiency.\(^9^3\) The CdTe–CdS interdiffusion may reduce the lattice mismatch, by forming a CdTe$_x$S$_{1-x}$ interfacial layer, and also the interface state density and ideality factor, as reported.\(^9^4\)

Amorphous Si solar cells contain a number of interfaces, particularly the $p/i$ and $n/i$ interfaces in the $p-i-n$ cell structure. According to the defect pool model,\(^9^5\) there is a higher defect density near the interfaces compared with the bulk of the $i$-region. This results in recombination processes being dependent on the position in the $i$-region. Improvements in the device properties by annealing under reverse bias can be explained by the movement of hydrogen to the interface and consequent reduction in the interface states.\(^9^6,^9^7\) The presence of
interface states also causes open-circuit voltage limitation, particularly for the p/i interface. In fact, modifying this interface by using a buffer layer increases $V_{oc}$. Since textured substrates are used in order to enhance the optical absorption, this affects the topography of all the layers, depending on deposition conditions, and causes interfacial roughness. The resultant optical scattering for different wavelengths can cause improvements in the photoresponse of the devices.

**MANUFACTURING**

Manufacturing of photovoltaic modules involves the sequential deposition of different thin-films on a large-area substrate. A typical polycrystalline superstrate module manufacturing process begins with cleaning of the glass substrate followed by the TCO deposition, window layer and absorber layer formation. Generally three laser or mechanical scribing steps are employed to define, interconnect and isolate the cells. Metallization after the second scribe interconnects the cells defined by the first scribe. The interconnection schemes vary from one module manufactures to the other. Modules are then completed by lamination, followed by attaching the current leads. Figure 5 shows the cross-section of a typical photovoltaic module with a few cells for clarity. The actual process, device structure and materials may vary for different manufacturers. Most process steps are proprietary. The schematic diagram reveals the advantage of TFSC technology in allowing monolithic integration of the cells in the module manufacturing process with minimum area losses in the module.

There are several key issues such as yield, material cost and capital cost that critically affect the manufacturing of large-area photovoltaic modules. The production yield depends on many factors, especially on the uniformity of the deposition process and laser scribing process used to isolate and interconnect the individual cells. Device uniformity over a large area is very critical because a faulty device can severely affect the performance of the entire module. Similarly nonuniform scribe and also debris from laser or mechanical scribing severely affect the module performance. Apart from these there are several materials-related issues that critically affect the successful commercialization of TFSC. For CIGS, the complex inline deposition process used for the CIGS films, incorporation of Na and the use of expensive material such as In are some of the major concerns. Back-contact-related stability issues have slowed down the successful commercialization of CdTe photovoltaic manufacturing.

![Figure 5. Schematic cross-sectional diagram of a thin-film photovoltaic module (adopted from Reference 10)](image)
COMPARATIVE ANALYSIS OF TFSC TECHNOLOGIES

Table III A, B shows the best cell and module efficiencies, achieved so far with various TFSC. On the basis of efficiencies relative to the theoretically expected value, GaAs is the best, followed by CIGS, but, on the basis of cost per peak watt, GaAs is the most expensive. A detailed analysis of the cost of various TFSC has been carried out in the literature. It turns out that whatever the production /deposition technology, and whatever be the TFSC material, the total cost per watt is primarily determined by the cost of the substrate, and one or two most expensive materials (such as Ge, Te, Ga, In, etc.) used in the particular technology. Table IV lists the estimated cost of one of the most expensive materials in each technology to underscore the point that all thin-film

<table>
<thead>
<tr>
<th>Small area</th>
<th>Efficiency (%)</th>
<th>Area (cm²)</th>
<th>V_{oc} (V)</th>
<th>J_{sc} (mA/cm²)</th>
<th>Fill factor (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaAs</td>
<td>23.3 ± 0.7</td>
<td>4.00</td>
<td>1.011</td>
<td>27.6</td>
<td>83.8</td>
</tr>
<tr>
<td>a-Si</td>
<td>12.7 ± 0.4</td>
<td>1.00</td>
<td>0.887</td>
<td>19.4</td>
<td>74.1</td>
</tr>
<tr>
<td>Si (thin film transfer)</td>
<td>16 ± 0.4</td>
<td>4.017</td>
<td>0.645</td>
<td>32.8</td>
<td>78.2</td>
</tr>
<tr>
<td>Si (nanocrystalline)</td>
<td>10 ± 0.2</td>
<td>1.199</td>
<td>0.539</td>
<td>24.4</td>
<td>76.6</td>
</tr>
<tr>
<td>CuInS₂</td>
<td>11 ± 0.4</td>
<td>0.511</td>
<td>0.729</td>
<td>21.83</td>
<td>71.7</td>
</tr>
<tr>
<td>CuInSe₂</td>
<td>15 ± 0.4</td>
<td>0.515</td>
<td>0.712</td>
<td>41.2</td>
<td>72.6</td>
</tr>
<tr>
<td>CuInGaSe₂</td>
<td>19 ± 2</td>
<td>0.408</td>
<td>0.689</td>
<td>35.71</td>
<td>78.12</td>
</tr>
<tr>
<td>CdTe</td>
<td>16 ± 9</td>
<td>0.47</td>
<td>0.621</td>
<td>36.0</td>
<td>75.5</td>
</tr>
<tr>
<td>GaInP/GaAs</td>
<td>30 ± 3</td>
<td>4.00</td>
<td>2.488</td>
<td>14.22</td>
<td>85.6</td>
</tr>
<tr>
<td>a-Si/CIGS</td>
<td>25.8 ± 1.3</td>
<td>4.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a-Si/a-SiGe/a-SiGe</td>
<td>14 ± 0.7</td>
<td>2.4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CIGS</td>
<td>13 ± 4</td>
<td>3.549</td>
<td>31.2</td>
<td>2.16</td>
<td>68.9</td>
</tr>
<tr>
<td>CdTe</td>
<td>16 ± 5</td>
<td>1.032</td>
<td>0.845</td>
<td>25.9</td>
<td>75.5</td>
</tr>
<tr>
<td>GalnP/GaAs</td>
<td>30 ± 1.5</td>
<td>0.2496</td>
<td>2.548</td>
<td>14.11</td>
<td>86.2</td>
</tr>
<tr>
<td>a-Si/a-SiGe/a-SiGe</td>
<td>10 ± 0.5</td>
<td>2.375</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table III B. Best performance of various film modules

<table>
<thead>
<tr>
<th>Module</th>
<th>Efficiency (%)</th>
<th>Area (cm²)</th>
<th>V_{oc} (V)</th>
<th>I_{sc} (A)</th>
<th>Fill factor (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a-Si (submodule)</td>
<td>12.0 ± 0.4</td>
<td>100</td>
<td>12.5</td>
<td>1.3</td>
<td>73.5</td>
</tr>
<tr>
<td>Poly-Si</td>
<td>8.2 ± 0.2</td>
<td>661</td>
<td>25.0</td>
<td>0.318</td>
<td>68.0</td>
</tr>
<tr>
<td>CIGS</td>
<td>13.4 ± 0.7</td>
<td>3459</td>
<td>31.2</td>
<td>2.16</td>
<td>68.9</td>
</tr>
<tr>
<td>CdTe</td>
<td>10.7 ± 0.5</td>
<td>4874</td>
<td>26.21</td>
<td>3.205</td>
<td>62.3</td>
</tr>
<tr>
<td>a-Si/a-SiGe/a-SiGe</td>
<td>10.4 ± 0.5</td>
<td>905</td>
<td>4.353</td>
<td>3.285</td>
<td>66.0</td>
</tr>
</tbody>
</table>

Table IV. Estimated cost of expensive material used in the module fabrication. Calculation uses the approximation of 10% module efficiency; the expected PV feedstock price of $20, 70% crystal growth utilization and 64% wafer utilization (data from references 104 and 105)

<table>
<thead>
<tr>
<th>Process</th>
<th>Material</th>
<th>Utilization rate (%)</th>
<th>Cost ($/kg)</th>
<th>Thickness (µm)</th>
<th>Cost ($/W)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdTe sublimation (commercial)</td>
<td>CdTe</td>
<td>75</td>
<td>170</td>
<td>4</td>
<td>0.05</td>
</tr>
<tr>
<td>CdTe electrodeposition (pilot line)</td>
<td>Te</td>
<td>95</td>
<td>250</td>
<td>2</td>
<td>0.02</td>
</tr>
<tr>
<td>In-line a-Si GD (commercial)</td>
<td>Ge</td>
<td>10</td>
<td>3000</td>
<td>1</td>
<td>0.12</td>
</tr>
<tr>
<td>Box carrier (batch) a-Si (commercial)</td>
<td>Ge</td>
<td>25</td>
<td>3000</td>
<td>1</td>
<td>0.05</td>
</tr>
<tr>
<td>High-rate a-Si (experimental)</td>
<td>Ge</td>
<td>10</td>
<td>3000</td>
<td>1</td>
<td>0.12</td>
</tr>
<tr>
<td>High-rate CIGS evaporation (experimental)</td>
<td>In</td>
<td>50</td>
<td>400</td>
<td>2</td>
<td>0.03</td>
</tr>
<tr>
<td>Sputtering CIGS (experimental)</td>
<td>In target</td>
<td>75</td>
<td>800</td>
<td>2</td>
<td>0.043</td>
</tr>
<tr>
<td>Silicon film™ (experimental)</td>
<td>Si</td>
<td>75</td>
<td>20</td>
<td>50</td>
<td>0.03</td>
</tr>
<tr>
<td>Single crystal silicon</td>
<td>Si (feedstock)</td>
<td>45</td>
<td>20</td>
<td>320</td>
<td>0.32</td>
</tr>
</tbody>
</table>
technologies are comparable in cost and all are of course, material-wise much cheaper than crystalline Si.\textsuperscript{104,105} Also to be noted is the fact the energy payback period for all TFSC is significantly smaller than that for crystalline Si.

Anticipating clear advantages of TFSC and based on considerable R&D on the materials and devices concerned, a number of industries for production of Cu\textsubscript{2}S/CdS,\textsuperscript{106} CdTe/CdS, CIGS/CdS, a-Si:H cells have been established worldwide. In some cases, large-scale production facilities as high as 10–30 MW\textsubscript{p} per year have been planned.\textsuperscript{107,108} Table V shows the world cell/module production\textsuperscript{109} based on different TFSC for the year 2001. Also shown is the crystalline, multicrystalline and ribbon Si module production for comparison. Most unfortunately, however, c-Si based PV industry continues to overwhelm TFSC industries which has in fact led to the closure of most of them; a-Si:H-based industries continue the valiant battle, albeit a losing one.

The main reasons for the failure of the TFSC industries to make significant impact on the PV market are related to the cell stability, cell cost and the prevailing complexities of the manufacturing process. Module manufacturing issues are different from the small area device fabrication that receives much attention by achieving record efficiencies. Key issues such as average efficiency, yield, materials cost and capital cost critically affect the manufacturing of large-area photovoltaic modules. Unfortunately in the past, scaling-up issues were considered an engineering problem and much attention has been focused on improving the device efficiency rather than attempting to make a reasonably efficient device that can be easily manufactured. The severity of this problem would be clearer when we realize that the thin-film industry needs to design its own unique process equipment, unlike the case of silicon technology which significantly benefited from the matured electronic manufacturing industry. The recent demonstration 13.6% CIGS efficient devices using a simple ink-based non-vacuum process may be considered as a positive step towards addressing the manufacturing issues.\textsuperscript{110} It is thus clear that, despite the clear advantages in the thin-film technology and impressive progress in the small-area device efficiencies, all TFSC technologies have failed the commercial viability test which is the fundamental criterion for success of any technology/product in a free-market globalized economy.

**WHAT IS THE FUTURE OF TFSC TECHNOLOGY?**

Surely, the emphasis on R&D on TFSC is to understand the science of devices better, to enhance their efficiencies and to develop economically viable manufacturing processes. As long as the cost per watt and reliability of long life are dominant factors, c-Si-based PV technology will continue to prevail over the TFSC technologies in coming years. But if simpler and cheaper manufacturing process can be developed to produce any moderate (7–10%) efficiency cells, even of limited life of a few years, at a cost lower than that of c-Si cells, the TFSC industry will get a stimulus to a bright future, at least in developing countries.

TFSC technologies have witnessed a lot of developments and also commercial turmoil. It would be appropriate to take a holistic view of the commercial maturity of the technologies. Such a maturity index\textsuperscript{111} should take into account the cost of materials, production process, throughput, energy input, efficiency, stability, life

<table>
<thead>
<tr>
<th>Technology</th>
<th>US (MW)</th>
<th>Japan (MW)</th>
<th>Europe (MW)</th>
<th>ROW (MW)</th>
<th>Total (MW)</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single crystal Si</td>
<td>63.3</td>
<td>24.88</td>
<td>34.88</td>
<td>14.33</td>
<td>136.78</td>
<td>35.02</td>
</tr>
<tr>
<td>Multicrystalline Si</td>
<td>18.53</td>
<td>116.12</td>
<td>35.8</td>
<td>14.4</td>
<td>184.85</td>
<td>47.33</td>
</tr>
<tr>
<td>Ribbon Si</td>
<td>5.4</td>
<td>8.2</td>
<td>13.6</td>
<td>3.48</td>
<td>33.3</td>
<td></td>
</tr>
<tr>
<td>Total non-thin-film</td>
<td>87.23</td>
<td>141.0</td>
<td>78.88</td>
<td>28.73</td>
<td>335.23</td>
<td>85.83</td>
</tr>
<tr>
<td>a-Si (terrestrial)</td>
<td>10.66</td>
<td>11.02</td>
<td>8</td>
<td>4</td>
<td>33.68</td>
<td>8.62</td>
</tr>
<tr>
<td>a-Si (indoor)</td>
<td>5.0</td>
<td>3</td>
<td>8</td>
<td>2.05</td>
<td>18.0</td>
<td></td>
</tr>
<tr>
<td>CdTe (terrestrial)</td>
<td>0.33</td>
<td>0.33</td>
<td>0.8</td>
<td>0.31</td>
<td>0.18</td>
<td></td>
</tr>
<tr>
<td>CdTe (Indoor)</td>
<td>1.2</td>
<td>1.2</td>
<td>1.2</td>
<td>0.18</td>
<td>0.18</td>
<td></td>
</tr>
<tr>
<td>CIGS</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
<td>0.18</td>
<td>0.7</td>
<td></td>
</tr>
<tr>
<td>Total thin-film</td>
<td>11.69</td>
<td>17.22</td>
<td>8</td>
<td>7</td>
<td>43.91</td>
<td>11.24</td>
</tr>
</tbody>
</table>
and utility effectiveness. The development of such an index is obviously a difficult job at present, but, an empirical analysis can still be made even though such an analysis would be rather subjective. Nevertheless, our effort in this direction shows that the maturity index of a-Si:H technology has nearly saturated and those of CdTe- and CIS-based technologies are now moving slowly towards saturation. The maturity index of thin-film poly/nano Si technology is, however, rising rapidly and has the possibility of surpassing all other TFSC technologies. The newly emerging materials such as organics, carbon nanotubes and fullerenes are also very promising as low-cost, low-efficiency, disposable cells await the development of production technologies as simple as casting and screen-printing.

Although Cu₂S thin-film cells were developed at about the same time as c-Si cells, the latter is seen by some as the first-generation and the TFSC as the second-generation technology. As mentioned earlier, TFSC technology has not yet fulfilled the major objective of lower-cost cells. Nevertheless, many new concepts in the science and technology of TFSC have emerged. These concepts form the basis of the so-called third-generation PV technology of multiple and tandem junctions. In principle, by stacking a large number of suitably tailored and designed cells, efficiencies as high as 68% are possible theoretically. And, in principle, thin-film multicomponent materials allowing such tailoring to be done. However, manufacturability of such cells at a reasonable cost is a tough challenge for the future.

CONCLUSION

Based on the preceding review, we may conclude the following.

1. TFSCs are attractive devices, which offer the possibility of reducing the active material requirement significantly. Even if expensive and/or not available in abundance, a number of semiconductors are well suited in thin-film form for reasonably efficient solar cell devices to be manufactured on a large scale.

2. The performance of all thin-film solar cells being studied presently is improving steadily, owing to increasingly better understanding of the unique and wide range of structural, chemical and optoelectronic characteristics of thin-film materials, and effective exploitation of some properties for such functions as passivation, activation, photon scattering/recycling, generation of surface electric fields, graded bandgaps, etc. Further progress is expected in closing the gap between the achieved efficiencies and the theoretically expected ones, with more detailed understanding of the electronic role of interfaces in the layered structure of the devices and with more precisely audited account of photons and excited carriers in the device.

3. Of the various thin-film solar cells, the a-Si:H-based cell may continue to be manufactured on a megawatt scale for specialized applications. Despite low production throughput, low efficiency, stability problems and cost being comparable to crystalline Si cells, the cell technology has the advantage of a simple and standardized manufacturing process for integrated modules on hard and flexible substrates. But, even with enhanced efficiency and stability in its more complicated multijunction avatar, the cell will continue to lose ground to the more stable, more efficient and comparably priced c-Si cell.

4. Despite major industrial ventures to produce CdTe and CIS-based cells on a megawatt scale, progress has been slow because of the problems of reliability with the manufacturing processes and the ultimate cost of the device. A simple and cheaper manufacturing process such as screen-printing, spray pyrolysis, electroplating, or chemical solution deposition onto cheaper and flexible substrates, albeit with lower efficiencies, could revive the commercial fortunes of these cells.

5. Economic viability of a cell will remain the single most important criterion for commercial scale production. For a whole range of low- and medium-power applications in energy-starved developing countries, watts/m² may be compromised as long as the dollars/watt figure is reasonably acceptable. This implies that, although R&D to achieve higher efficiency goals must continue as an important scientific objective, a lot more R&D effort is required to develop simpler and cheaper manufacturing processes for acceptable (5–10%) device efficiencies.

6. Single-element and possibly stable organic semiconductor films are best suited for device manufacturing. Compared with the high maturity of c-Si cell, the maturity level of poly/micro/nanocrystalline Si thin films
is much lower at present. However, the rapid rate of growth of the maturity of these emerging materials suggests that these devices may overtake other thin-film solar cells in the near future. Other attractive materials such as semiconducting forms of carbon nanotubes and some organic materials are also opening up new vistas, adding to the bewildering saga of TFSC.

7. Solar cells that may combine the features of solid-state junctions with those of photoelectrochemical liquid cells in a nanomaterial gel base and with efficient n- and p-type dyes appear to be feasible at proof-of-the-concept stage and call for serious R&D efforts in this exotic area.

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REFERENCES


