

# Frontiers in photovoltaic materials and devices

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A growing number of semiconductor materials and devices are emerging as strong contenders for photovoltaic applications, but silicon still dominates the market. Ultrahigh-efficiency solar cells fabricated from gallium arsenide and its ternary alloys are finding immediate applications in space exploration. Various thin film technologies, such as hydrogenated amorphous silicon, copper indium diselenide, and cadmium telluride, hold promise for significant cost reduction. Some exciting possibilities exist for new materials and devices.

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## Abbreviations

<b>Cz</b>	Czochralski
<b>CIGS</b>	copper indium gallium diselenide
<b>FZ</b>	float-zone
<b>MC-Si</b>	multicrystalline-silicon
<b>PERL</b>	passivated emitter rear localized
<b>PV</b>	photovoltaic

## Introduction

Just as semiconductor materials and devices are the core of many electronic systems (e.g. transistors, integrated circuits, and other solid state devices), so too are they the central constituents of some of the energy-related applications in areas such as photovoltaics (PVs). For the electronics industry, and particularly for microelectronics, silicon is the key semiconductor material; similarly, for the budding PV industry, Si is the workhorse for the present and immediate future. However, a growing number of semiconductor materials and devices based on III-V- and II-VI-compound semiconductors and their alloys are emerging as strong contenders for PV applications. Some of the ultrahigh-efficiency solar cells are fabricated from gallium arsenide (GaAs) and its alloys, for example gallium aluminum arsenide (GaAlAs) and gallium indium diphosphide (GaInP<sub>2</sub>).

Enormous progress has also been made on various thin film solar cell technologies, which offers the promise for substantially reducing the cost of PV systems. Some of the leading contenders are amorphous and polycrystalline silicon (a-Si and p-Si), compound semiconductor thin films such as copper indium diselenide (CuInSe<sub>2</sub>) based alloys, and cadmium telluride (CdTe) thin films. Some of these thin film materials (e.g. a-Si-based thin film transistors) are finding applications for advanced flat-panel display technologies.

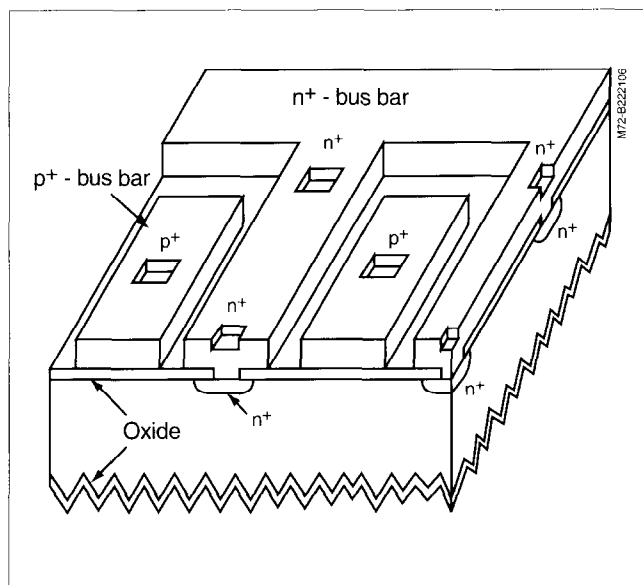
Exciting new developments are also happening in the use of ultrasmall-particle semiconductor materials in the domain of the quantum-size effect for various energy conversion devices. The technology is making a major thrust in the commercial arena with the worldwide production of PV modules reaching over 100 MW in 1996 and growing at the rate of 20–25% per year. In this review, an attempt will be made to capture the highlights of the major developments in this technology during the past two years.

## Silicon solar cells

Si has many desirable attributes, such as material abundance, high conversion efficiency (24%), a near-optimum energy gap (1.12 eV), excellent stability, silicon dioxide (SiO<sub>2</sub>) passivation, and low material cost, and it is also environmentally benign, all of which make it the most desirable material for PV technology. Moreover, the technology development effort in PV-Si has benefited enormously from the Si-based microelectronics industry. One of the major weaknesses of Si has been its relatively weak absorbance of solar radiation, because of its indirect energy gap. However, this disadvantage can be offset by various light-trapping schemes that are being developed in an effort to reduce the material use and to enhance the conversion efficiency. With the introduction of Si as a forerunner of PV technology for terrestrial power, the cost factor has become a major driving force. Consequently, during the past two decades, and more so in recent years, the major emphasis on technology development has been directed towards the reduction of cost and consequent improvement of conversion efficiency.

The material and device technologies for Si solar cells in recent years have proceeded along three directions: firstly, single crystals or polycrystalline ingots; secondly, self-supporting ribbons; and thirdly, polycrystalline thin films. The key development of Si-based PV technology during the past four decades has been reviewed in a recent article by Wenham and Green [1\*\*]. The process for fabrication of ingots involves the following approaches: Si feedstock → Si → crystal growth by Czochralski (Cz), float-zone (FZ), or various casting or directional-solidification techniques (mainly for multicrystalline ingots). A Cz-grown single-crystal Si is widely used for solar cells. Considerable progress has been made in recent years on Cz-crystal growth to maximize the size (~200 mm diameter), throughput, and yield. The main drawbacks of the Cz process are the contamination caused by contacts with the crucibles and the replacement of crucibles and the graphite susceptor. FZ growth eliminates the crucible cost and the contact problem and allows higher growth speed. It is a technologically more complex process and produces relatively smaller-ingot diameter (~150 mm). However, the FZ process generally leads to better material quality because of lower impurity content and consequently higher minority carrier lifetime

Figure 1



Rear point contact solar cell. Reproduced with permission from [1\*\*].

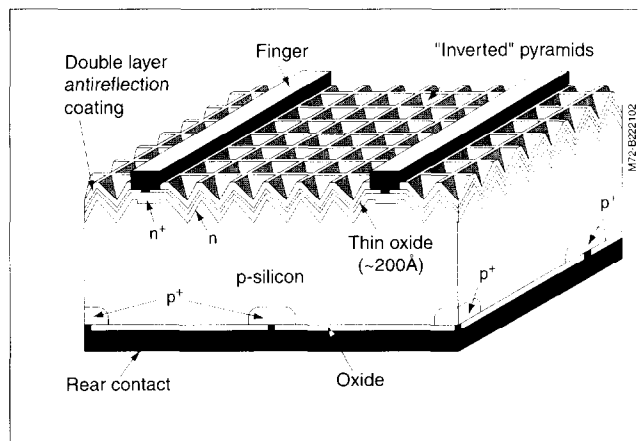
(~20 msec). This is an important consideration, particularly for the design of very high efficiency solar cells (~24%).

### Single crystal silicon solar cell

Extraordinary progress has been made in recent years in achieving record-level efficiencies of 22% and 24% in Cz- and FZ-grown single-crystal Si materials. Two of the device structures that incorporate many improved design features that led to such high efficiencies are: first, the point-contact solar cells developed by the Stanford University group (Figure 1); and second, the passivated emitter rear localized (PERL) cell developed by the University of New South Wales (UNSW) group (Figure 2). A modified version of the PERL cell, the laser-grooved buried-contact solar cell, is under intense development at UNSW. However, the processing techniques used for the fabrication of these laboratory-scale, high-efficiency solar cells are very complex for cost-effective production of terrestrial solar cells. Most of the solar cell manufacturers do not regard photolithography as a viable option. Hence, recent research and development efforts have been directed toward simplified processing schemes. One such processing scheme involves a random pyramid passivated emitter and a rear cell (RP-PERL), which provides a significant advantage over the modified PERL process [2\*]. The process has led to a new record value of 22% efficiency for a Cz-Si. Dramatic reduction of surface recombination velocity down to 10 cm/s has been achieved by exposing the material to corona discharge.

Another successful approach has been the combined use of high-throughput, screen-printed aluminum (Al) rapid thermal processing (RTP), simultaneous diffusion of a phosphine-doped emitter and back-surface field (BSF),

Figure 2



Structure of the PERL cell. Reproduced with permission from [1\*\*].

and low-temperature deposition of a surface-passivating layer, which has led to a device efficiency of 19%–20% [3\*\*,4]. Applying this process to a high-throughput, industrial-type sequence has resulted in a 17.5%-efficient device. A novel approach involving simultaneous diffusion of B and P in Si from a spin on solid source and growth of an *in situ* passivating oxide in a single-step process has been successfully used to achieve 20.1% and 10.1% efficiency in FZ- and Cz-grown Si, respectively [5\*]. Record-level efficiencies of 19.4% and 16.5% under 1-sun front and rear illumination have been demonstrated in an FZ-Si bifacial solar cell [6\*]. Properly installed bifacial solar cells can generate up to 50% more power with higher power-to-weight ratios.

Recently, there has been a revival of interest in metal-insulator-semiconductor inversion layer (MIS-IL)-type devices because they offer an inherent cost advantage compared to the p-n junction device [7,8]. An 18.5% efficiency has been achieved in the second generation of MIS-IL solar cells by the minimization of recombination losses at the front-grid contact and reduction of surface-recombination velocity. The feasibility of this approach has been demonstrated in a pilot-scale production process. Further design improvements can lead to 20% efficiency.

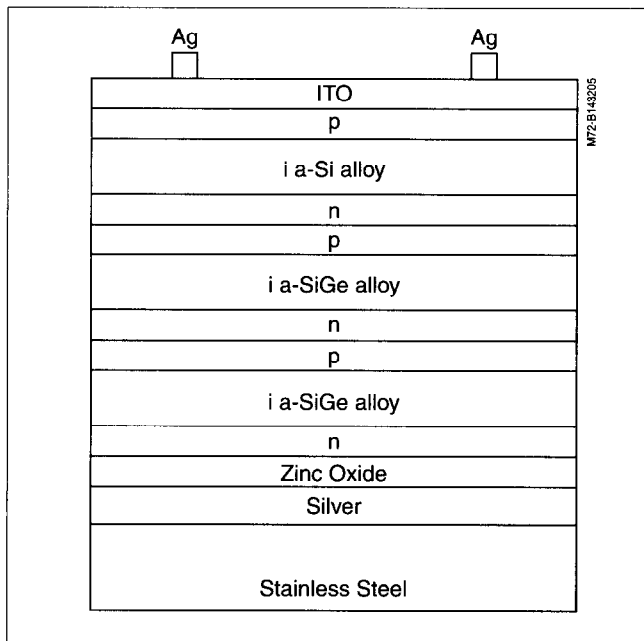
### Multicrystalline silicon solar cells

Presently, cast multicrystalline silicon (MC-Si), accounting for nearly 50% of the Si-based solar cells manufactured worldwide, is a dominant PV technology. Several techniques are used to produce MC-Si ingots. Among these, casting- and Bridgman-type directional solidification are the most widely used growth techniques. Both of these methods generally produce multicrystalline ingots. Recent advances in these processes have resulted in block-shaped ingots up to 150 kg in weight. The presence of grain boundaries and point defects such as vacancies, interstitials, transition metal impurities, oxygen, carbon, and their

complexes degrade the quality of MC-Si. High-efficiency processing techniques developed for single-crystal Si are generally not applicable to these materials because of the expected degradation of carrier lifetime resulting from high processing temperature (1000°C or higher).

For the first time, solar cell efficiencies of 18.2% have been achieved in large-grained MC-Si ingots, by using a processing temperature not exceeding 900°C [9•]. The minority-carrier lifetime in the finished device actually increased from 12  $\mu$ s to 135  $\mu$ s, and the surface recombination velocity (SRV) resulting from Al-BSF was  $10^4$  cm/s. Further improvement in cell efficiency to 18.6% has been achieved by decreasing the rear surface recombination velocity to  $2 \times 10^3$  cm/s with deeper penetration of Al alloys [10••]. Subsequently, the UNSW group has achieved 18.2% efficiency in an MC-Si grown by the heat exchange method (HEM) by using their standard PERL process with processing temperatures exceeding 1050°C [11•]. Because the MC-Si contains a high concentration of defects and impurities, the main challenge in device processing is to include various defect-engineering approaches like gettering, hydrogen passivation [12], and low-temperature optical processing [13] without increasing the cost.

**Figure 3**



Schematic diagram of a triple-junction structure. Reproduced with permission from [23••].

### Thin film silicon solar cell

Thin film Si offers an exciting opportunity for the development of efficient low-cost solar cells. There has been a resurgence of interest in this technology in recent years, particularly in view of the possibility of light trapping

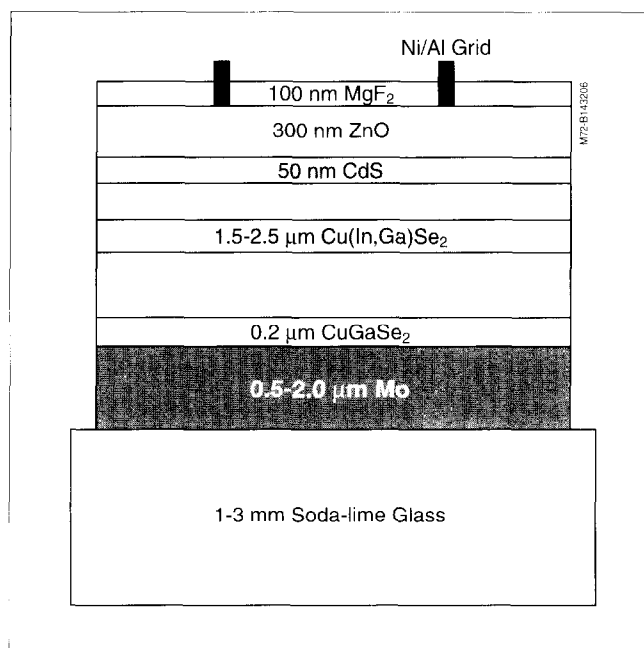
within Si. From the PV point of view, thin film Si has some advantages because of less stringent requirements on material quality. Recent theoretical calculations [14•] show that it is possible to attain 17% efficiency in a 2  $\mu$  thick Si film if the grain size is bigger than 10  $\mu$  and the dislocation density is less than  $10^6$  cm<sup>-2</sup>. This is further reinforced by the demonstration of 21.5% efficiency in a chemically thinned 47  $\mu$  epitaxial Si-film grown on an insulating substrate [15]. The most exciting new development is the achievement of 9.8% efficiency in a 3.5  $\mu$  film and 9.3% in a 1.5  $\mu$  poly-Si film [16••,17••]. The structure of these cells is glass/back reflector/n-i-p p-Si/ITO/Ag grid, and it has been named the 'STAR' cell (surface textured-enhanced absorption with a back reflector). The cell is fabricated on a glass substrate by a low-temperature plasma chemical vapor deposition (CVD) process [18]. It shows no degradation after up to 600 hours of light exposure. In addition to the above, several deposition technologies are currently being explored, including liquid phase epitaxy (LPE) [19,20], electron cyclotron resonance CVD (ECR CVD) [21], and electrodeposition [22].

### Amorphous and microcrystalline silicon thin film solar cells

Among the thin film PV technologies, hydrogenated-amorphous silicon (a-Si:H) holds one of the most promising options for low-cost solar cells. It is by far the most mature and commercially viable technology. The technology of a-Si:H for PV is based on two types of device design: a single-junction and multi-junction p-i-n structure. Although major progress has been made in recent years in improving the deposition processes, material quality, device design and manufacturing processes, the improvement of cell efficiency appeared to hit a bottleneck. It is generally recognized that any significant increase in efficiency can only be achieved by using multi-junction devices. It is indeed the case as shown by the achievement of a world record stable efficiency of 13% (initial efficiency of 14.6%) in a triple-junction structure, [23••] as shown in Figure 3. The previous best stable efficiency was 11.8%. This was accomplished by optimization of factors such as, hydrogen dilution for film growth, bandgap profiling, current matching, and a microcrystalline tunnel junction. Similarly, a new record in stabilized efficiency of 9.5% for 1200 cm<sup>2</sup> a-Si:H/a-SiGe:H has recently been reported [24]. This was possible by low-temperature (180°C) deposition of an a-SiGe:H film while maintaining good opto-electronic properties.

One of the vexing problems in a-Si:H technology has been the photo-induced degradation of the cell performance due to the Staebler-Wronski (SW) effect. Extensive studies culminating in limited success have been made over the last two decades to understand the origin of this metastability and to minimize its impact. The status of our understanding of the mechanism of degradation behavior up to 1995 has been recently reviewed [25]. In recent years, a great deal of attention has been paid to the possi-

Figure 4



Schematic of CIGS-based solar cell. Reproduced with permission from [30\*\*].

ble involvement of hydrogen with the SW effect, energetics, and transport in a-Si [26\*]. A new model has been proposed linking hydrogen motion to a metastable defect formation [27\*]. In this model, two mobile hydrogen atoms, created by optical excitation, collide and form a metastable, immobile complex containing two Si-H bonds. The microscopic nature and the feasibility of such defect complexes have been investigated by using a molecular dynamics simulation [28\*]. The model appears to satisfactorily explain the kinetics of defect creation and annealing, including the saturation behavior.

In an effort to improve the efficiency, stability, and structural properties of a-Si:H thin films, a new class of material, hydrogenated microcrystalline silicon ( $\mu\text{c-Si:H}$ ), is emerging as a contender for PV applications. Recent work has demonstrated that  $\mu\text{c-Si:H}$ , as deposited by a very high frequency (70–140 MHz) glow-discharge technique at relatively low substrate temperature ( $< 250^\circ\text{C}$ ), can be used to fabricate p-i-n solar cells with reasonable efficiency ( $\eta = 7.7\%$ ) and with no photodegradation. The current collection in such a device is caused by a combination of both drift and diffusion. It has also been shown that a combination of amorphous and microcrystalline material can be used to fabricate a tandem structure called the 'micro-morph' cell. The material and device parameters have been improved to the extent that 12.0% stable efficiency has been demonstrated [29\*\*]. A number of other techniques such as  $\text{H}_2$ -dilution in plasma-enhanced CVD (PECVD) and hot wire CVD (HWCVD), are being pursued to grow microcrystalline thin films for solar cell applications.

### Thin-film copper indium gallium diselenide (CIGS) solar cells

$\text{Cu}(\text{In,Ga})\text{Se}_2$  (CIGS) (Figure 4) is by far the most promising material for thin film PV devices. Recently, a record efficiency of 17.7% has been achieved in a typical device structure consisting of glass/Mo/CIGS/CdS/ZnO fabricated by a physical vapor deposition (PVD) technique [30\*\*]. This remarkable achievement was possible by optimization of the optical, electrical, and structural properties of the CIGS absorber layer and appropriate design and control of the component layers and their interfaces, under different growth conditions. The deposition of a high-quality CIGS absorber layer is the crucial processing step and thus far, the PVD technique appears to be the preferred method [31,32].

Although PVD is the preferred method for high-efficiency cell fabrication, recent results suggest that a wide variety of techniques, such as sputtering, spray pyrolysis, closed-space sublimation (CSS), molecular-beam epitaxy (MBE), and electrodeposition are currently being pursued. Among these, electrodeposition offers a low-cost option for fabricating CIGS absorbers, and recently 13.7% efficiency has been achieved in CIGS-based devices [33\*].

In all of these processes, tailoring of the bandgap of the CIGS absorber layer toward the optimum range of 1.3–1.5 eV and adjusting the Ga/(Ga+In) ratio to 0.4–0.75, respectively, is crucial. The optimum ratio for high-efficiency cells thus far has been approximately 0.27. The effort to increase the Ga content generally results in a decrease of cell efficiency, which is largely due to compositional nonuniformity, phase separation, film morphology, and spatial distribution of Ga caused by diffusion [34]. The spatial nonuniformity is sometimes tailored into the device structure to optimize cell efficiency. Defects and impurities in the absorber layer, and in heterojunction interfaces play a dominant role in controlling the optical, electrical, and structural properties as well as the performance of thin film solar cells. Deviation from stoichiometry is used to control the p- and n-type behavior of these materials.

Clearly, the defects in chalcopyrite materials are very complex, but despite the presence of a high density of defects in polycrystalline copper indium diselenide (CIS) and CIGS thin films, it is still possible to fabricate very high efficiency solar cells. Therefore, understanding the physics and chemistry of the defects remains a major challenge in optimizing the transport properties of these materials. Deep-level transient spectroscopy (DLTS), admittance spectroscopy-modulated photocurrent techniques [35], and radiative-recombination [36] studies have been extensively used to characterize the distribution of defects throughout the bandgap. A high degree of defect tolerance in a CIS-type material has been studied theoretically [37\*]. First-principle calculations show that the defect pair  $(2\text{V}_{\text{Cu}}^- + \text{In}_{\text{Cu}}^{2+})^\circ$  in CIS has an extremely low formation

energy. The ease of formation of such an electrically inactive defect pair may explain why CIS-type compounds are so insensitive to the presence of a large concentration of native defects. Significant attractive interactions between defect pairs can lead to the formation of defect compounds such as  $\text{CuIn}_5\text{Se}_8$ ,  $\text{CuIn}_3\text{Se}_5$ , and so on, as separate phases in the bulk material.

It has been shown recently that incorporation of Na (~7%) in CIGS leads to the formation of p-Cu(In,Ga) $_3$ Se $_5$  as the predominant phase, and a solar cell with 12% efficiency could be made using this as the absorber [38\*]. The effect has been investigated by X-ray diffraction, X-ray photoelectron spectroscopy, and Hall Effect measurements. The hole concentration in CIGS increases dramatically to  $10^{16}$ – $10^{17}$  for a wide range of Cu/(In+Ga) ratios (0.4–0.8), and this leads to improved cell efficiency. This also explains why the highest-efficiency (17.7%) solar cells are obtained when CIGS is deposited on Mo-coated soda lime glass, presumably because of the out diffusion of Na from the substrate to the CIGS layer. A comparative study of different substrates, with and without Na, shows a positive effect of Na on the junction properties and device performance [39]. A quantitative study shows that the ideal range of Na concentrations in CIS and CIGS solar cells is between 0.05 and 0.5 at% [40].

The highest-efficiency CIGS solar cells use chemical-bath deposited (CBD) CdS as the heterojunction partner. Owing to the environmental sensitivity of Cd, an extensive effort is underway to find a noncadmium-containing material as the window material. Several materials have been shown to work, although not as efficiently as CdS [41]. One of the major strengths of this technology is the remarkable stability shown by these devices. The major challenge presented to those active in this area is how to close the gap in efficiency between small-area laboratory devices and large-area commercial modules?

### Cadmium telluride thin film solar cell

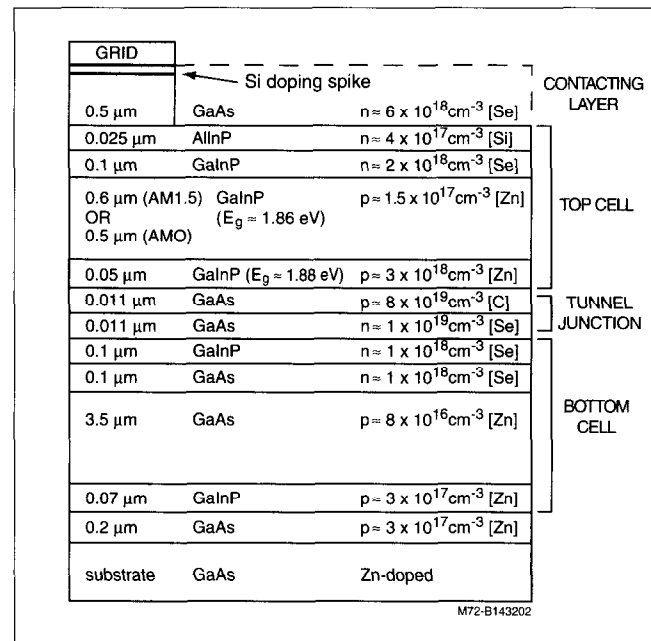
Enormous progress has been made in recent years on CdTe/CdS thin film solar cells in which CdTe is the p-type absorber material. The optimum bandgap (1.44 eV) and high absorption coefficient due to direct optical transition make it an ideal PV material with a theoretical efficiency of 30%. One of the major advantages of CdTe/CdS thin film solar cells is the low-cost fabrication options. A number of relatively simple, low-cost methods have been used to fabricate solar cells with efficiencies in the range 10%–16%. Some of the low-cost deposition methods that show promise include: firstly, closed-space sublimation; secondly, spray deposition; thirdly, electrodeposition; fourthly, screen printing, and fifthly, sputtering. All of these techniques are being considered for large-scale manufacturing by several industries.

Most recently, a record 16% efficiency has been reported in a CdS(0.4  $\mu$ )/CdTe (3.5  $\mu$ ) thin film solar cell in which

CdS and CdTe films are deposited by metalorganic CVD deposition (MOCVD) and CSS techniques, respectively [42]. Most of the high-efficiency solar cells use a superstrate device configuration in which CdTe is deposited on the CdS window layer. A typical device structure consists of glass/CdS/CdTe/Cu-C/Ag. In most cases, the post-deposition heat treatment of the CdTe layer in the presence of  $\text{CdCl}_2$  is essential for the optimization of device performance [43\*]. This critical processing step leads to enhanced grain growth, and increased minority-carrier lifetime, probably resulting from the elimination of deep levels within the bandgap of CdTe [44]. A photoluminescence measurement at low temperature shows a broad band of 1.42 eV, which most likely results from the formation of a  $V_{\text{Cd}}\text{-Cl}$  defect complex [45]. It also leads to interdiffusion of sulfur at the interface between CdS and CdTe forming an S-rich  $\text{CdTe}_{1-x}\text{S}_x$  region.

Very recently, synchrotron-radiation techniques of grazing-incidence X-ray scattering and angular dependence of X-ray fluorescence have been used to investigate the interface morphology of the CdTe/CdS heterojunction (YL Soo,

Figure 5



GaInP/GaAs tandem cell. Reproduced with permission from [46].

Y Koo and AD Compagn, personal communication). The results show heat treatment can cause significant mixing of Te between CdS and CdTe layers. The interfacial mixing increases the cell efficiency, probably by reducing the density of recombination centers.

Another key issue that has received considerable attention is the formation of a stable, low-resistance contact to p-type CdTe. The process of making such a contact is fairly com-

plex and poorly understood. The processes that are generally used consist of either the deposition of a p<sup>+</sup> layer of Te-Cu on a freshly etched CdTe surface, or by diffusion of p-type dopants such as Cu prior to contact metalization. Overall, the process of fabricating CdTe/CdS is relatively simple and amenable to large-scale production. Like CIGS technology, the manufacturing processes for this technology need to be developed further. However, several companies worldwide are setting up large-scale production facilities.

### III-V solar cells

GaAs is one of the III-V semiconductor materials that has a direct bandgap of 1.43 eV and therefore, is optimally suited for the fabrication of high efficiency PV devices. Photovoltaic conversion efficiency over 25% has been achieved on single-junction solar cells fabricated in epitaxially grown GaAs on a single-crystal substrate. The bandgap and the lattice parameters of GaAs-based semiconductors can be systematically changed by alloying with other III-V elements such as Al, In, P, and Sb, and this forms the basis of multi-junction devices that have a potential (depending on the number of such junctions that are used in a tandem structure) of achieving extremely high efficiencies.

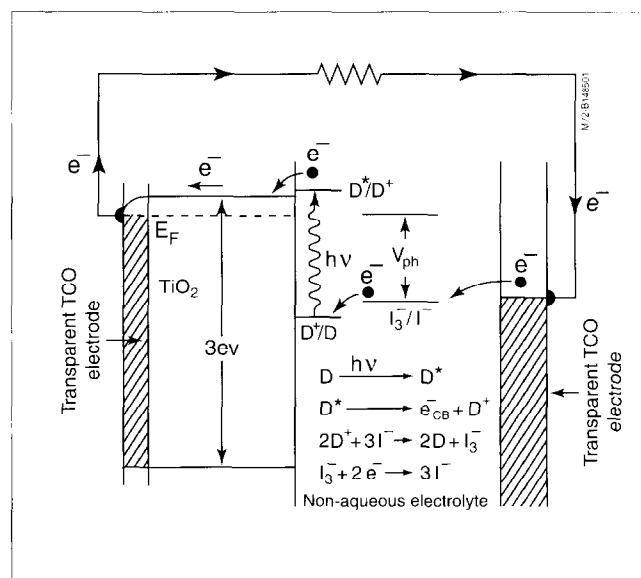
In designing tandem cell structures, two different approaches are generally taken: firstly, individual cells are grown separately and then mechanically stacked one above the other; and secondly, each cell is grown monolithically with a tunnel-junction interconnect. The tandem combination of a GaInP<sub>2</sub> ( $E_g = 1.9$  eV) and GaAs has a theoretical efficiency of ~36%. The most exciting development in recent years has been the fabricating of a high efficiency (29.5%) monolithic tandem cell consisting of GaInP<sub>2</sub> (top cell) and GaAs (bottom cell) with a low-resistivity tunnel-junction interconnect (Figure 5), invented and developed at the National Renewable Energy Laboratory [46]. Very recently, the efficiency has been further improved to 30.28% in an essentially similar structure that incorporates a GaInP<sub>2</sub> tunnel junction and AlInP diffusion barrier [47]. By virtue of its superior radiation resistance, these cells are now being produced on a large scale for space applications. A new world-record efficiency of 26.9% AM0 has recently been reported [48], which is an improvement over the previously reported efficiency of 25.7%.

The efficiency of a two-junction tandem cell has almost reached its practical limit and any further improvement will require incorporation of a third junction consisting of a semiconductor with a bandgap in the range of 0.95–1.1 eV. Theoretical efficiency for a three-junction cell at AM1.5 is over 45% [49], which implies a practically achievable efficiency approaching 40% if a suitable combination of materials can be developed.

In spite of these remarkable achievements in fabricating high-efficiency cells with III-V semiconductors, the technology is not yet cost effective for terrestrial applications.

However, significant progress has been made in recent years in this direction by using two approaches: firstly, growth of cells on low-cost substrates; and secondly, use of an epitaxial lift-off technique. Efficiencies of 20%–21% have been achieved for a single-junction GaAs cell grown on a sub-millimeter grain-size poly-Ge substrate, which has the potential for significant cost reduction [50]. This opens up the possibility of using this process to grow high-quality GaAs on even lower-cost substrates such as glass and Mo foils. Fabrication of high-efficiency GaAs solar cells on reusable substrates through the use of a single-crystal template (CLEFT process [cleavage of lateral epitaxial film for transfer]) has been demonstrated for quite some time. Whether this technology will lead to an adequate reduction of cost still remains an issue. In the meantime, there has been substantial progress on growing thin film GaAs/GaInP solar cells on a single-crystal substrate and lifting it off by etching, followed by transfer to a glass substrate [51]. A similar approach has been used to fabricate a substrate from a GaAs solar cell on Pd-coated Si showing 20% AM1.5 efficiency [52]. The potential impact of grain size, grain-boundary passivation, intragrain defects, and impurities on the fabrication of high-efficiency polycrystalline GaAs solar cells on low-cost substrates has recently been reviewed [53].

Figure 6



Mechanism of dye-sensitized TiO<sub>2</sub> solar cell. Reproduced with permission from [56].

### Dye-sensitized titanium dioxide solar cells

The application of dye-sensitized semiconductor electrodes to a new type of PV cell has recently generated much interest. The photoelectrode of these PV cells consists of a 10–20 μm film of nanocrystalline titanium dioxide (TiO<sub>2</sub>) particles (10–30 nm in diameter) that contain a monolayer of adsorbed dye molecules; the dye-coated par-

ticles are supported on a transparent conducting glass substrate (e.g. tin oxide). The pores of the nanocrystalline  $\text{TiO}_2$  films are filled with a liquid electrolyte containing the iodide/triiodide redox couple in a nonaqueous electrolyte, such as acetonitrile. A transparent counter electrode is placed over the nanocrystalline  $\text{TiO}_2$  and the edges of the cell are sealed. The operational principle of this cell is shown in Figure 6. These cells are termed either photochemical solar cells, dye-sensitized solar cells, or Grätzel cells, the latter because of the breakthrough report [54] by Grätzel and O'Regan on the dye-sensitization of  $\text{TiO}_2$ . The standard dye presently used in cells is  $\text{Ru(11)(4,4'-dicarboxy-2,2'-bipyridine)}_2(\text{NCS})_2$  (absorption peak at 550 nm); this system shows conversion efficiencies of 7%–10% under standard solar conditions. A recent new 'black' dye (4,9,14-tricarboxy 2,2'-6,6'-terpyridyl ruthenium(11)trithiocyanate) has been discovered that produces an efficiency of nearly 11% (M Grätzel, personal communication; [55]). The kinetics of the electron transfer between the dye and  $\text{TiO}_2$  is a critical factor controlling the device efficiency. Recent ultrafast spectroscopic studies show that the electron injection in  $\text{TiO}_2$  is at least biphasic, with ~50% occurring < 150 fs and 50% in ~1.2 ps [56\*]. This ultrafast electron transfer not only ensures high energy conversion efficiency, but is also essential for long-term stability of the device.

## Conclusions

Remarkable progress has been made in the synthesis, processing, and characterization of semiconductor materials and devices, which has led to major improvements in PV conversion efficiencies and the reduction of cost. Silicon continues to dominate the PV industry. Exciting new developments are happening, particularly in polycrystalline and microcrystalline thin film solar cells. Thin film solar cells based on aSi:H, CIS-CIGS, and CdS/CdTe offer promising options for substantially reducing the cost. Very high conversion efficiencies have been achieved in multi-junction III-V semiconductors, which are presently being commercialized for space applications. Exciting new developments are happening in some relatively new materials and devices such as dye-sensitized nanocrystalline  $\text{TiO}_2$  solar cells.

## Acknowledgement

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