

Inorganic photovoltaic cells

The inorganic semiconductor materials used to make photovoltaic cells include crystalline, multicrystalline, amorphous, and microcrystalline Si, the III-V compounds and alloys, CdTe, and the chalcopyrite compound, copper indium gallium diselenide (CIGS). We show the structure of the different devices that have been developed, discuss the main methods of manufacture, and review the achievements of the different technologies.

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Some applications of photovoltaic cells that have been well established over the past 50 years include¹:

1. Supplying power in remote locations, e.g. for communications and weather monitoring systems and the lighting and water pumping systems used in developing countries;
2. Supplying power for consumer products, e.g. for electronic calculators and garden lights; and
3. Supplying power for applications in space, e.g. for satellites and space vehicles.

Most photovoltaic cells produced are currently deployed for large-scale power generation either in centralized power stations or in the form of 'building integrated photovoltaics' (BIPV). BIPV is receiving much attention, as using photovoltaic cells in this way minimizes land use and offsets the high cost of manufacture by the cells (or panels of cells) acting as building materials. Although crystalline Si solar cells were the dominant cell type used through most of the latter half of the last century, other cell types have been developed that compete either in terms of reduced cost of production (solar cells based on the use of multicrystalline Si or Si ribbon, and the thin-film cells based

on the use of amorphous Si, CdTe, or CIGS) or in terms of improved efficiencies (solar cells based on the use of the III-V compounds). All of these semiconductors have energy bandgaps within the range 1.1-1.7 eV, that is they are near to the optimum energy bandgap (1.5 eV) for photovoltaic solar energy conversion by a single junction solar cell¹. The best efficiencies obtained with each cell type are given in Table 1 and the market share of the different cell types during 2006 are given in Fig. 1¹⁷. Although the use of crystalline Si cells has continued to increase rapidly, the most successful technology at present is that based on the use of multicrystalline Si, which has expanded even faster. The key aim of all the technologies is to reduce production costs to 1 \$/peak Watt (1 \$/Wp) to compete on cost with other forms of power generation. Cells based on the use of crystalline and multicrystalline Si cost more than four times this amount. It is generally accepted that this target is most likely to be reached using thin-film fabrication technologies when expanded for large scale production. The technologies also need to have acceptable energy payback times – this is the time taken for a device to generate as much energy as was needed to fabricate the device. Crystalline

Table 1 Best efficiencies reported for different solar cells and modules.

Type of solar cell	Highest reported small area cell efficiency			Highest reported module efficiency		
	Efficiency (%)	Area (cm ²)	Reference	Efficiency (%)	Area (cm ²)	Reference
Crystalline Si	24.7	4.0	UNSW ⁱ , PERL ^{ii,2}	22.7	778	UNSW/Gochermann ³
Multicrystalline Si	20.3	1.0	FhG-ISE ^{iii,4}	15.3	1017	Sandia/HEM ⁵
Amorphous (and nanocrystalline) Si	10.1	1.2	Kaneka, single junction ⁶	10.4	905	USSC ^{iv} , triple junction ⁷
μc-Si/αSi:H micro-morph cell	11.7	14.2	Kaneka, minimodule ⁸	11.7	14.2	Kaneka, minimodule ⁸
HIT ^v cell	21.8	100.4	Sanyo Corporation ⁹	17.3	11 000	Sanyo Corporation ⁹
GaAs cell	25.8	3.9	Kopin Corporation ¹⁰	Not relevant	Not relevant	
InP cell	21.9	4.0	Spire Corporation ¹¹	Not relevant	Not relevant	
GaInP ₂ /GaAs/Ge multijunction cell	39.3*	0.4	Spectrolab, concentrator ¹²	Not relevant	Not relevant	
CdTe	16.5	1.0	NREL ^{vi,13}	10.7	4874	BP Solarex ¹⁴
CIGS ^{vii}	19.5	0.4	NREL ¹⁵	13.4	3459	Showa Shell ¹⁶

ⁱ UNSW, University of New South Wales.

ⁱⁱ PERL, passivated emitter rear locally diffused.

ⁱⁱⁱ FhG-ISE, Fraunhofer Institute for Solar Energy Systems.

^{iv} USSC, United Solar Systems Corporation.

^v HIT, heterojunction with intrinsic thin layer.

^{vi} NREL, National Renewable Energy Laboratory.

^{vii} CIGS, copper indium gallium diselenide.

*Boeing-Spectrolab (Sylmar, CA) announced a 40.7% efficient cell under 240x concentrated light in December 2006 (unpublished).

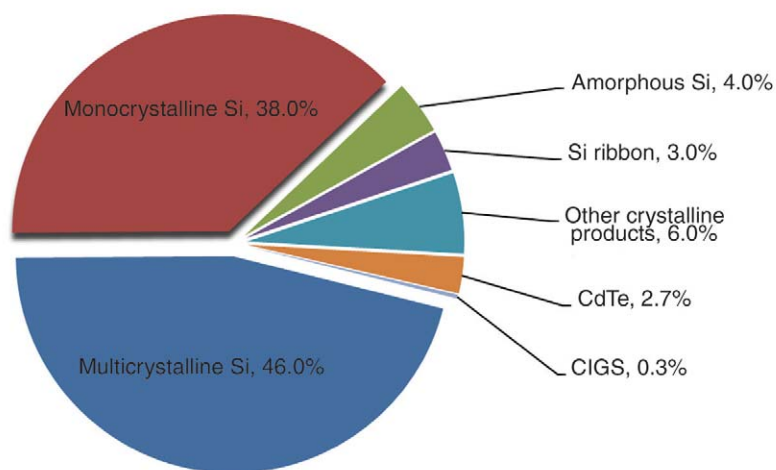


Fig. 1 Market share of solar cell types sold during 2006.

and multicrystalline devices typically have energy payback times of 3–4 years and the thin-film technologies, 12–18 months. Fig. 2 shows two examples of BIPV, the first using crystalline Si solar cells, the second using CIGS thin-film solar cells.

Si-based cells

Crystalline Si solar cells

A cross-sectional view of the Si solar cell structure that has been used in production up to the present is given in Fig. 3a¹⁸. For crystalline Si devices, a boule of B-doped *p*-type Si is grown using the Czochralski

method and wafers are sawn from the boule. Crystalline (and multicrystalline) Si have an indirect energy bandgap resulting in a low optical absorption coefficient, with the consequence that the wafers need to be greater than 200 μm thick to absorb most of the incident light. The wafer surfaces are 'textured' by dipping into a solution of NaOH and isopropyl alcohol to minimize reflection losses and to refract light entering the Si to high angles of refraction and enhance the optical path length in the Si. A *p*-*n* junction is formed by diffusing phosphorus into the wafer as an impurity dopant. Screen-printed Ag contact fingers are used on the *n*-type surface to make electrical



Fig. 2 (a) The 40 kWp facade of the Northumberland building at Northumbria University, UK, which uses the crystalline Si solar modules manufactured by BP Solar (Saturn modules). (b) The 85 kWp facade of the Technium OptIC (Opto-electronics Technology and Incubation Centre) in St Asaph, Wales, which is covered with CIGS modules manufactured by Shell Solar.

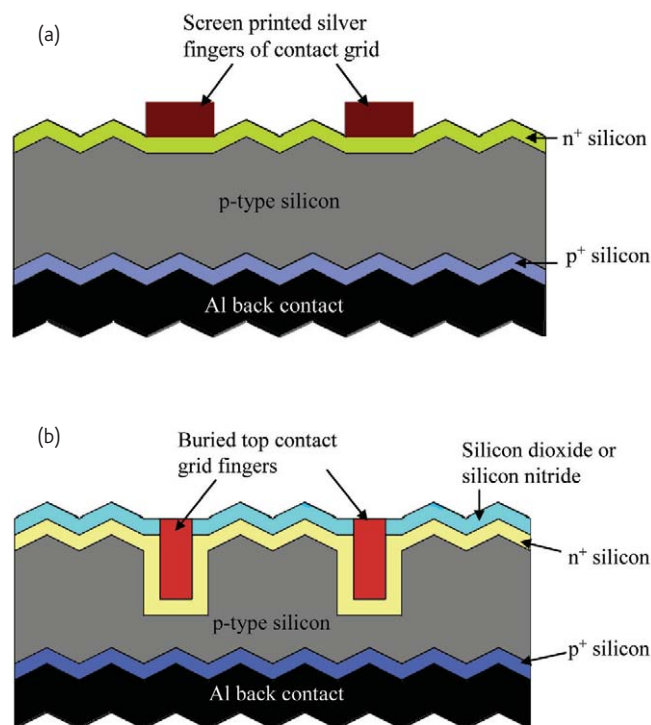


Fig. 3 Cross-sectional view of (a) a Si solar cell produced with screen-printed contacts, (b) a UNSW solar cell with buried contacts.

contact while also allowing light to be transmitted to the junction region. Al paste is used to make contact at the back *p*-type surface. This is annealed to introduce a *p*⁺ doped region at the back of the cell to lower the contact resistance and supply a back surface field that reflects minority carriers back toward the junction¹⁹. An antireflection (A/R) coating (usually TiO₂ or silicon nitride) is deposited over the top surface to complete the device.

Green and coworkers²⁰ from the University of New South Wales (UNSW) have pointed out that there is a high penalty for using screen-printed contacts. High shading losses, the high resistivity of the screen-printed Ag grids compared with pure Ag (three times as high), a high contact resistance between the grid and Si, and poor aspect ratio reduce device efficiencies to approximately 14%. This has led the researchers to develop solar cells in which the contacts are defined either using photolithography or laser scribing^{21,22}. A typical 'UNSW cell structure' is shown in Fig. 3b. For the design shown, the surface of the Si has been oxidized to passivate the front surface of the cell and grooves for contacting cut using laser scribing. In this 'buried contact' design, the contact metals, Ni, Cu, and then Ag, are deposited using electroless methods. The improved design permits shallower *p*-doping at the surface of the device without degrading the open circuit voltage, improving the short wavelength response of the cell. The higher doping concentration of this *n*⁺ region also reduces the contact resistance at the grid contact. This type of cell is used in the high efficiency Saturn modules produced by BP Solar^{23,24}. A photograph of a cell is given in Fig. 4a.

The highest efficiency Si solar cell produced in the laboratory is the 'passivated emitter rear locally diffused' (PERL) solar cell, which has an efficiency of 24.7%². The high efficiency is achieved by improving the surface texturing and by the inclusion of a SiO₂ layer at the back of the device to passivate the back surface of the device².

There is worldwide effort to minimize Si usage and design devices that incorporate 'light trapping' features such that thinner layers of Si can be used²⁵. One strategy is to deploy Si solar cells in 'concentrator systems'. In these systems, a large area lens focuses the incident sunlight onto a cell with smaller area²⁶. However, with such systems, there is a need to track the sun, and concentrator systems can only be used in parts of the world where there is unimpeded sunlight. A schematic of such a system is given in Fig. 5.

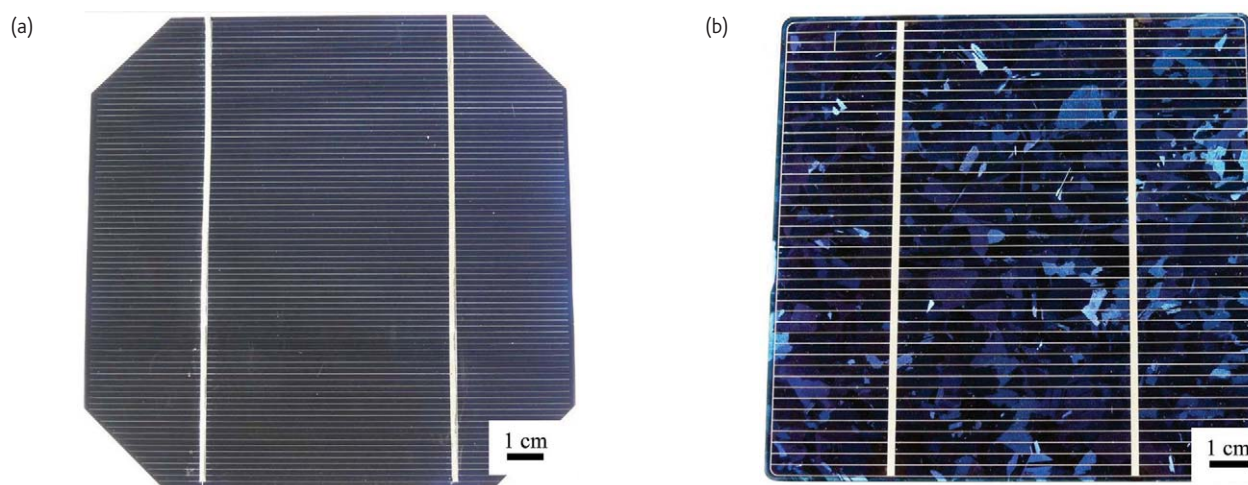


Fig. 4 Photographs of (a) crystalline Si, and (b) multicrystalline Si solar cells.

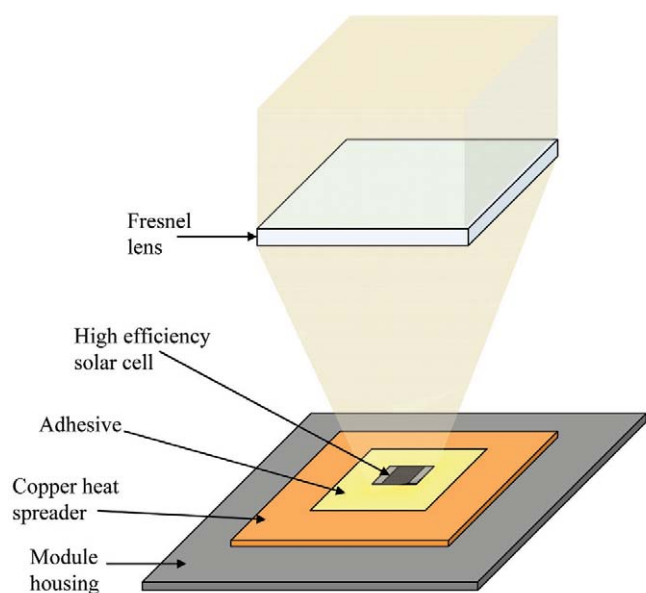


Fig. 5 Schematic view of a concentrator system. The Fresnel lens focuses light onto the high efficiency cell which may be composed of Si or III-V compounds.

Multicrystalline Si solar cells

Here, molten Si is poured into a container and then allowed to cool, resulting in Si ingots with large columnar grains (typically 0.3 mm diameter) growing from the bottom of the container upwards²⁷. The grains are so large that they extend through the wafers cut from the solidified block. The incorporation of hydrogen during device processing plays an important role in passivating the grain boundaries in the devices formed. This is most conveniently introduced by using plasma-enhanced chemical vapor deposition (PECVD) to deposit silicon nitride as the top insulating layer, rather than SiO₂, as hydrogen is used in this process. Otherwise, cell processing is similar to that used for crystalline

devices. A photograph of a multicrystalline cell is shown in Fig. 4b. Advantages of using multicrystalline growth over the Czochralski method include lower capital costs, higher throughput, less sensitivity to the quality of the Si feedstock used, and higher packing density of cells to make a module because of the square or rectangular shape of the cells. The best modules made using multicrystalline Si generally have efficiencies 2–3% less than those of crystalline Si, and cost approximately 80% of crystalline Si cells to produce.

It is also possible to pull multicrystalline Si in the form of thin sheets or 'Si ribbon' from a Si melt, and the sheets then processed to make solar cells²⁸. The need for sawing wafers can be avoided using this method. However, because resulting cells generally have lower efficiencies than those made from the cast blocks and the casting method is simpler, the casting method is preferred by most manufacturers.

Amorphous Si solar cells

Thin films of amorphous Si are usually produced using PECVD of gases containing silane (SiH₄)²⁹. The layers may be deposited onto both rigid substrates (e.g. glass) and flexible substrates (e.g. thin metallic sheets and plastics), allowing for continuous production and diversity of use. The material used in solar cells is actually hydrogenated amorphous Si (α -Si:H), an alloy of Si and hydrogen (5–20 at. % H), in which the hydrogen plays the important role of passivating the dangling bonds that result from the random arrangement of the Si atoms. The hydrogenated amorphous Si is found to have a direct optical energy bandgap of 1.7 eV and an optical absorption coefficient, α , greater than 10⁵ cm⁻¹ for photons with energies greater than the energy bandgap. This means that only a few microns of material are needed to absorb most of the incident light, reducing materials usage and hence cost. Most devices produced have the *p-i-n* structure shown in Fig. 6a. A major problem with modules made using single *p-i-n* junctions is that

the efficiency degrades under illumination to less than 5% because of a phenomenon known as the Staebler-Wronski effect²⁹.

It is possible to absorb the solar spectrum more efficiently and to improve cell stability by using multiple *p-i-n* structures with different energy bandgap *i*-layers to produce 'double junction' or 'triple junction'

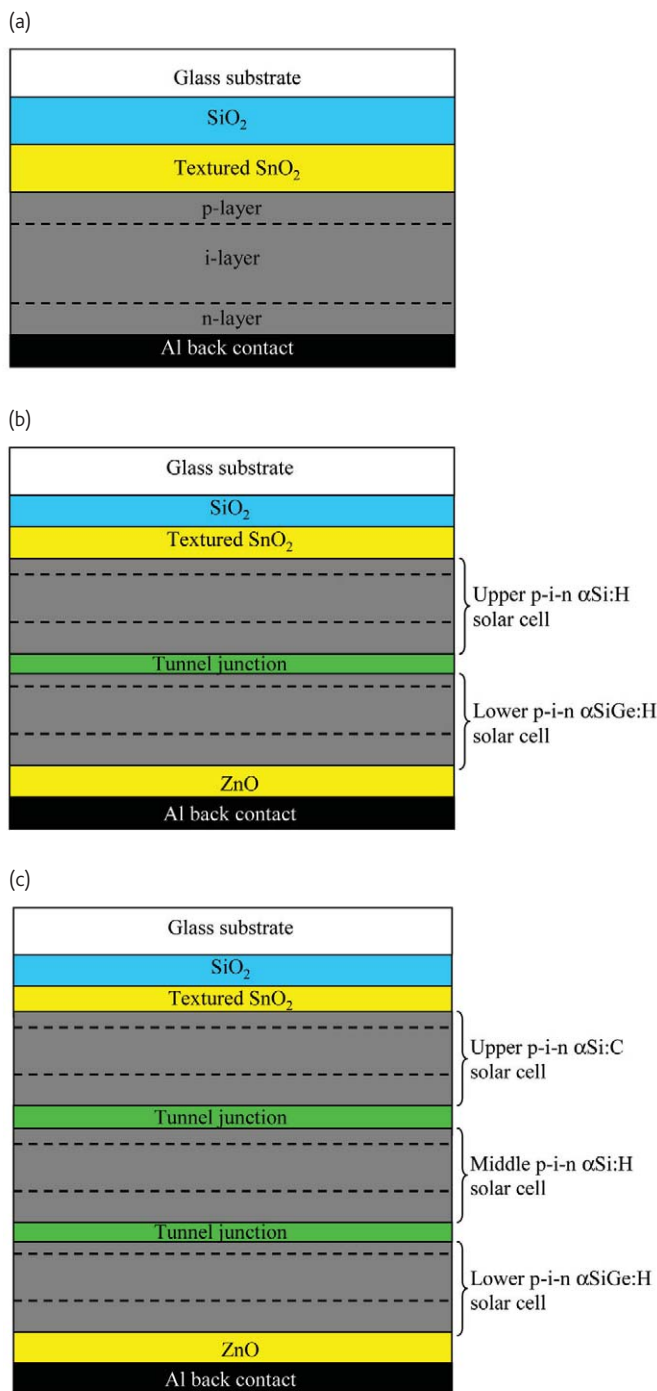


Fig. 6 A cross-sectional view of (a) a single junction, (b) a double junction, and (c) a triple junction amorphous Si solar cell.

structures as shown in Figs. 6b and 6c. Narrower energy bandgap layers are produced by alloying the Si with Ge and wider energy bandgap layers are produced by alloying the Si with carbon. The highest reported stabilized efficiency of a double-junction is greater than 9.5%, and for a triple-junction module it is greater than 10%²⁹.

If the gases used for deposition of amorphous Si are diluted in hydrogen, the deposit consists of regions of crystalline Si immersed in an amorphous matrix³⁰. This two phase material is known as 'microcrystalline Si' or sometimes as 'nanocrystalline Si'. The physical properties of the material resemble those of crystalline/multicrystalline Si rather than amorphous Si, especially with regard to stability under intense illumination. Work is currently underway to develop hybrid amorphous Si/microcrystalline Si tandem solar cells and modules (referred to in the literature as 'micro-morph devices'). Trials indicate that these hybrid devices and modules rival triple-junction amorphous Si in terms of efficiency and stability³¹.

HIT solar cells

A novel device developed by Sanyo is the 'heterojunction with intrinsic thin layer' (HIT) solar cell⁹. In this device, layers of amorphous Si are deposited onto both faces of a textured wafer of single-crystal Si. This results in 10 cm x 10 cm multijunction devices with efficiencies greater than 21% and 80 cm x 120 cm modules with efficiencies up to 17.3%⁹. The advantages of this structure include the potential for high efficiency, very good surface passivation, low-temperature processing (all steps are carried out at less than 200°C, except for substrate production), reduced energy payback time, and reduced cost relative to conventional Si devices.

III-V solar cells

Single junction III-V solar cells

The III-V compounds, such as GaAs, InP, and GaSb, have direct energy bandgaps, high optical absorption coefficients, and good values of minority carrier lifetimes and mobilities (in highly pure, single-crystalline material). This makes them excellent materials for high-efficiency solar cells³². The III-V materials used most widely for making single-junction solar cells are GaAs and InP, as both have near optimum energy bandgaps of 1.4 eV. Originally, devices were formed by the diffusion of *n*-type dopants into wafers from single crystals produced using either the liquid-encapsulated Czochralski (LEC) method or a Bridgmann method³³. However, the highest conversion efficiencies confirmed under standard conditions are 25.8% for GaAs and 21.9% for InP single-junction cells, and were obtained with epitaxially grown homojunction structures produced in the US by the Kopin (Bedford, MA)¹⁰ and Spire (Westboro, MA)¹¹ Corporations, respectively.

The disadvantage of using III-V compounds in photovoltaic devices is the very high cost of producing device-quality substrates or epitaxial layers of these compounds. Crystal imperfections, including unwanted impurities, severely reduce device efficiencies and alternative, lower

cost deposition methods cannot be used. These materials are also easily cleaved and are significantly mechanically weaker than Si. The high density of the materials is also a disadvantage, in terms of weight, unless very thin cells can be produced to take advantage of their high absorption coefficients. These drawbacks have led to III-V compounds not being considered as promising materials for single-junction, terrestrial solar cells. The development of III-V based devices has been undertaken primarily because of their potential for space applications. There, the potential for high conversion efficiencies together with radiation resistance in the demanding environment of space power generation mitigates against the high materials cost³⁴. The high cost of cell manufacture can also be offset for terrestrial applications by using the high efficiency III-V cells in concentrator systems³⁵. These devices are of course subject to the requirements for direct sunlight and tracking as mentioned on page 22.

A recent development is that of quantum well (QW) cells made using GaAs and III-V alloys. A strain balanced, 50 QW solar cell has a higher efficiency than a *p-n*-GaAs control cell. This device was grown by metal-organic chemical vapor deposition (MOCVD)³⁶.

III-V multijunction devices

In a single-junction Si solar cell, 56% of the available energy is lost because photons with energies less than the bandgap are not absorbed, and photons with energies greater than the bandgap 'thermalize', such that the excess energy over the bandgap is lost as heat³⁷. A range of studies have shown that using multijunction solar cells (sometimes referred to as tandem solar cells), such losses can be minimized leading to much higher efficiency devices^{38–40}. A landmark achievement demonstrating this concept was the development in 1990 of a GaAs/GaSb stacked cell with an efficiency greater than 30%⁴¹. Much work since then has been on the development of stacked cells grown by MOCVD onto GaAs, InP, and more recently Ge substrates⁴⁰. The most efficient stacked cell devices are now produced by Spectrolab in Sylmar, California^{12,42}. A cross-sectional view of a device with an efficiency >39% is given in Fig. 7.

Thin-film solar cells based on compound semiconductors

Solar cells based on CdTe

With a direct optical energy bandgap of 1.5 eV and high optical absorption coefficient for photons with energies greater than 1.5 eV, only a few microns of CdTe are needed to absorb most of the incident light. Because only thin layers are needed, material costs are minimized, and because a short minority diffusion length (a few microns) is adequate, expensive materials processing can be avoided.

A cross-sectional view of a typical CdS/CdTe solar cell is shown in Fig. 8a.

A front contact is provided by depositing a transparent conductive oxide (TCO) onto the glass substrate. The TCO layer has a high optical

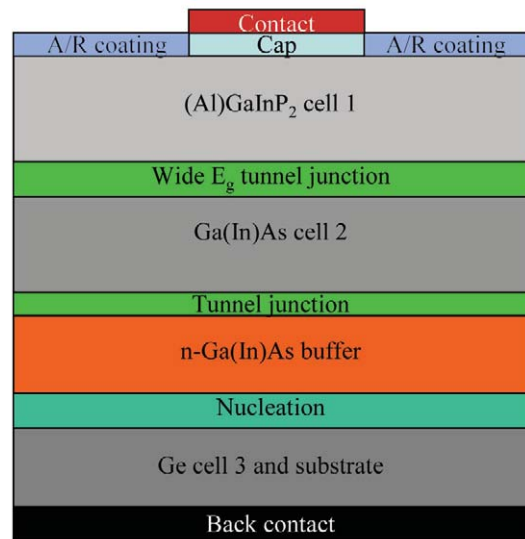


Fig. 7 Cross-sectional view of a III-V multijunction device grown on a Ge substrate with 39.3% efficiency.

transparency in the visible and near-infrared regions and high *n*-type conductivity. This is followed by the deposition of a CdS window layer, the CdTe absorber layer, and finally the back contact. For commercial devices, the CdS layer is usually deposited using either closed-space sublimation (CSS)⁴³ or chemical bath deposition¹³, although other methods have been used to investigate the fundamental properties of devices in the research laboratory^{44,45}. The CdTe *p*-type absorber layer, 3–10 μm thick, can be deposited using a variety of techniques including physical vapor deposition (PVD)⁴⁶, CSS¹³, electrodeposition⁴⁷, and spray pyrolysis⁴⁸. To produce the most efficient devices, an activation process is required in the presence of CdCl₂ regardless of the deposition technique. This treatment is known to recrystallize the CdTe layer⁴⁹, passivate grain boundaries⁵⁰, and promote interdiffusion of the CdS and CdTe at the interface⁵¹. Forming an ohmic contact to CdTe is difficult because the work function of CdTe is higher than all metals. This can be overcome by creating a thin *p*⁺ layer by etching the surface in bromine methanol or HNO₃/H₃PO₄ acid solution and depositing Cu-Au alloy or ZnTe:Cu⁵². This creates a thin, highly doped region that carriers can tunnel through. However, Cu is a strong diffuser in CdTe and causes the performances to degrade with time. Another approach is to use a very low bandgap material, e.g. Sb₂Te₃, followed by Mo or W⁵³. This technique does not require a surface etch and the device performance does not degrade with time.

The most efficient CdTe/CdS solar cells (efficiencies up to 16.5%¹³) have been produced using a slightly different design to that shown in Fig. 8a. The improved efficiency is a result of the use of a Cd₂SnO₄ TCO layer which is more transmissive and conductive than the classical SnO₂-based TCOs, and the inclusion of a Zn₂SnO₄ buffer layer which improves the quality of the device interface. Two companies currently manufacture CdTe-based modules: First Solar and Antec Solar. Both use

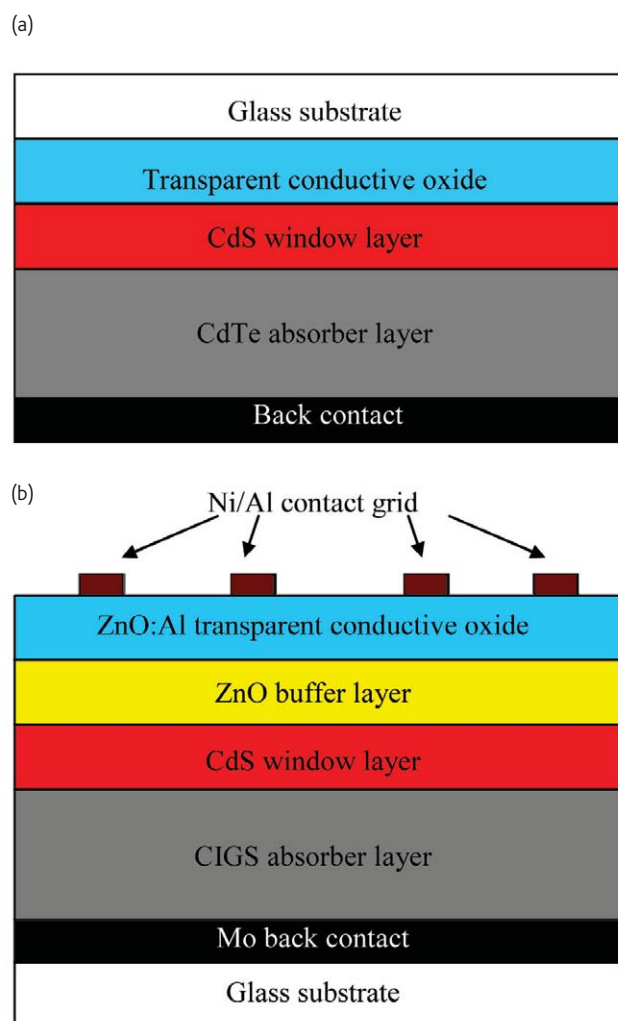


Fig. 8 Cross-sectional views of thin-film solar cells based on the use of compound semiconductors. (a) A CdS/CdTe thin-film solar cell. (b) A CdS/CIGS thin-film solar cell.

thermal sublimation processes and have managed to produce modules with baseline efficiencies of 8–9%^{54,55}. First Solar current production costs are \$1.25/Wp for a 99 MWp/year manufacturing line, and projected output is 275 MWp/year for 2008 with estimated cost below the \$1/Wp barrier⁵⁶. In August 2007, CdTe modules manufactured by First Solar were installed on the roof of a logistic centre in Ramstein, Germany. The installation is capable of generating 2.5 MWp of power, i.e. it is currently the largest thin-film BIPV generation project using thin-film solar cells.

Solar cells based on chalcopyrite compounds


The first chalcopyrite solar cells developed were based on the use of CuInSe_2 (CIS). It was, however, rapidly realized that incorporating Ga to produce the solid solution Cu(In,Ga)Se_2 (CIGS), results in a widening of the energy bandgap to 1.3 eV and an improvement in

material quality, resulting in solar cells with enhanced efficiencies. CIGS has a direct energy bandgap and high optical absorption coefficient for photons with energies greater than the bandgap, such that only a few microns of material are needed to absorb most of the incident light, with consequent reductions in material and production costs. The best CIGS solar cells are grown on sodalime glass in the sequence: back contact, absorber layer, window layer, buffer layer, TCO, and then the top contact grid. A typical structure is shown in Fig. 8b. CIGS solar cells have been produced with efficiencies of 19.5%¹⁵ and modules with efficiencies of 13.4%¹⁶. The back contact is a thin film of Mo deposited by magnetron sputtering, typically 500–1000 nm thick. The CIGS absorber layer is formed mainly by (i) the coevaporation of the elements either uniformly deposited or using the so-called three-stage process⁵⁷, or (ii) the deposition of the metallic precursor layers followed by selenization and/or sulfidization. Coevaporation yields devices with the highest performance while the latter deposition process is preferred for large-scale production. Both techniques require a processing temperature $>500^\circ\text{C}$ to enhance grain growth and recrystallization. Another requirement is the presence of Na, either directly from the glass substrate or introduced chemically by evaporation of a Na compound⁵⁸. The primary effects of Na introduction are grain growth⁵⁹, passivation of grain boundaries⁶⁰, and a decrease in the absorber layer resistivity⁶¹. This usually yields an increase of 1–2% in efficiency for Na concentrations $<1\%$ ⁶². The junction is usually formed by the chemical bath deposition of a thin (50–80 nm) window layer. CdS has been found to be the best material, but alternatives such as ZnS, ZnSe, In_2S_3 , $(\text{Zn,In})\text{Se}$, Zn(O,S) ⁶³, and MgZnO ⁶⁴ can also be used. The buffer layer can be deposited by chemical bath deposition, sputtering, chemical vapor deposition, or evaporation, but the highest efficiencies have been achieved when using a wet process as a result of the presence of Cd^{2+} ions⁶⁵. A 50 nm intrinsic ZnO buffer layer is then deposited and acts as to prevent any shunts. The TCO layer is usually ZnO:Al 0.5–1.5 μm . The cell is finally completed by depositing a metal grid contact Ni/Al for current collection. The main CIGS manufacturers are Würth Solar, Avancis (formerly Shell Solar), and Global Solar. Numerous other ventures are engaged worldwide in the development of CIGS-based photovoltaic products.

Conclusions

Most commercially produced solar cells are manufactured using either crystalline or multicrystalline Si. Thin-film solar cells based on the use of Si, CdTe, and CIGS are now being mass manufactured and it is expected with economies of scale that they will achieve the cost reduction needed to compete directly with the other forms of energy production. Multijunction solar cells, so far made primarily using the III-V compounds, have clearly proven that by minimizing thermalization and transmission losses, very large improvements in efficiency can be made over those of single-junction cells. These devices find application

in generating power for space applications and are used in concentrator systems. The future development of multijunction devices using low-cost thin-film technologies is especially promising for producing more efficient and yet inexpensive devices. Cost reductions will also be

significant when the thin-film technologies are directly produced on building materials other than glass, as many materials, e.g. tiles and bricks, can be substantially cheaper than glass and have much lower energy contents. 

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