Thin-film solar cells: review of materials, technologies and commercial status

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Abstract The recent boom in the demand for photovoltaic modules has created a silicon supply shortage, providing an opportunity for thin-film photovoltaic modules to enter the market in significant quantities. Thin-films have the potential to revolutionise the present cost structure of photovoltaics by eliminating the use of the expensive silicon wafers that alone account for above 50% of total module manufacturing cost. The strengths and weaknesses of the contending thin-film photovoltaic technologies and the current state of commercial activity with each are briefly reviewed.

1 Introduction

Over recent years, the photovoltaics market has been booming, with sales almost completely dominated by product based on the use of silicon wafers, similar to those used in microelectronics. Wafer costs account for over 50% of the total module cost. One way of eliminating this major cost component is by replacing wafers by thin-films of semiconductors deposited onto a supporting substrate (or, more commonly, a glass superstrate). The sustained boom (10 years of 40%/annum compounded growth) is causing demand for silicon wafers to outstrip the capacity to supply, creating a market entry opportunity for a number of competing thin-film technologies. These fall into two main classes; one based on silicon in amorphous, nanocrystalline

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and polycrystalline phases and on polycrystalline chalcogenide (Group six) semiconducting compounds. A third class of emerging technologies is based on organometallic dyes and polymers.

2 Present thin-film product

Figure 1 summarises the performance of thin-film modules available on the market in early 2006. Energy conversion efficiency at the module level based on manufacturers' nominal ratings ranges from about 4% to above 10%, compared to the 10–16% range which is typical for wafer-based product. Present thin-film modules are based on amorphous silicon, either in a single junction or multiple junction configurations, as well as on the chalcogenide compounds CdTe or CIS (copper indium diselenide or disulphide). Thin-film modules based on polycrystalline silicon have been a more recent market entrant.

As apparent from Table 1, showing the production volume for different manufacturers of these thin-film technologies over the past 3 years, rapidly-growing production volumes are dominated by the amorphous silicon and cadmium telluride approaches. However, since the volumes associated with the wafer-based approaches are also increasing rapidly, the thin-film technologies have to grow quickly just to maintain their present market share (total combined share is less than 10%). There is a higher barrier for market entry for thin-film technologies, due to higher capital costs per unit output for thin-film manufacturing facilities. The manufacturing of the conventional wafer-based modules is commonly broken down into four separately-financed operations: silicon purification, crystal growth and wafering, cell processing, and cell encapsulation.
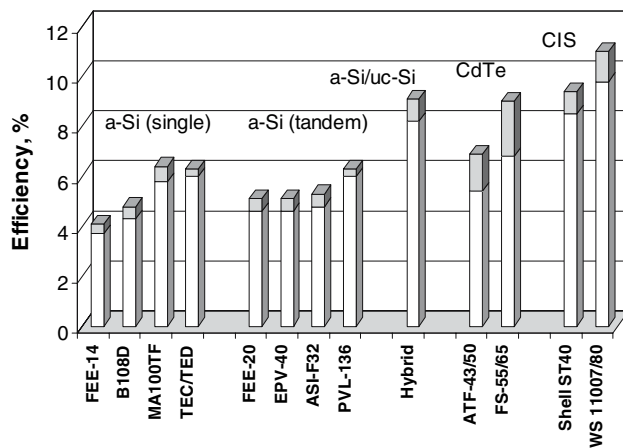
Fig. 1 Nominal energy conversion efficiency range of various 2006 thin-film modules (data from [1]; darker top region indicates range for product meeting specifications)

However, in a thin-film operation, all these operations effectively are bundled into the one facility.

The rapidly escalating demand for silicon wafers is creating a supply shortage that will moderate the growth of the wafer-based output over at least the coming 2 years. This gives a thin-film product an opportunity to increase market share and to establish its credentials on a market previously not all that interested, at least partly due to the undeniably superb reliability and durability demonstrated by the wafer-based approach.

3 Thin-film technologies

3.1 Silicon-based

3.1.1 Single-junction amorphous silicon

Amorphous silicon solar cells have been used in consumer products such as calculators and digital watches since the

early 1980s. Although attempts have been made to launch outdoor power modules onto the market since the mid-1980s, it is only recently that several companies, notably Kaneka and Mitsubishi of Japan, have supplied single-junction a-Si power modules in appreciable quantities (Table 1) [2]. The amorphous silicon is deposited at low temperature in a way that allows about 10% (atomic) hydrogen to be incorporated, the secret to this technology's success [3]. The hydrogen greatly improves the quality of the material. A p-i-n junction structure is used with the n- and p-type regions creating a field in the i-layer due to their work-function difference [3]. Individual cells deposited onto a glass sheet are laterally connected in series by an approach such as shown in Fig. 2b. Since the amorphous silicon is not very conductive, a key feature of the technology is the use of a transparent conductive tin oxide layer between the silicon and the glass.

The strength of a-Si technology is its simplicity combined with the use of benign and abundant silicon. The technology also is able to capitalise on equipment development in the active matrix display area, where similar deposition equipment is used. One factor that explains the relatively slow uptake of a-Si technology, given its early potential, is the light-induced degradation of material quality. Manufacturers now rate product in terms of ''stabilised'' performance, which is obtained after a month or two of field exposure. However, stabilised module efficiency is quite low, generally in the 4–6% range as apparent from Fig. 1.

3.1.2 Multiple junction amorphous silicon devices

One way of accommodating the decreased material quality under light exposure is to use thinner layers of amorphous silicon. This is possible if two or more cells are stacked on top of one another, as in Fig. 3. If the bandgaps of the

Table 1 Production volume and plans of the larger thin-film manufacturers (2003–2006) [2]

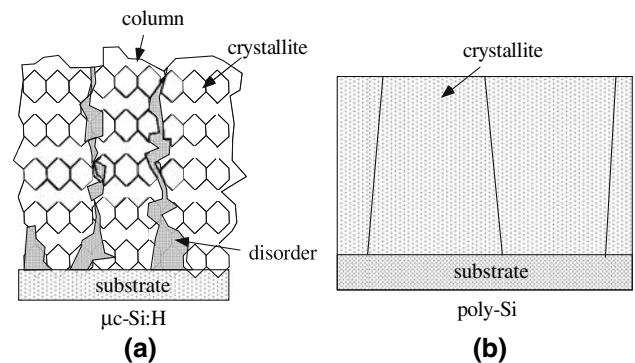| Company	Type	Efficiency	2003 (Actual)	2004 (Actual)	2005 (Actual)	2006 (Planned)
Kaneka	a-Si	6.0–6.3%	13.5 MW	17.MW	20.8 MW	29 MW
United Solar	a-Si	6.0–6.3%	7 MW	14 MW	22 MW	30 MW
Mitsubishi	a-Si	6.1–6.4%	3 MW	8 MW	9 MW	11 MW
RWE Schott	a-Si	4.8–5.3%	2 MW	3 MW	3 MW	3 MW
Bangkok Solar	a-Si	4.3–4.8%	0.1 MW	2 MW	6 MW	13 MW
CSG Solar	p-Si	7.3%	–	–	–	10 MW
Antec	CdTe	5.4–6.9%	5 MW	7.5 MW	8 MW	8 MW
First Solar	CdTe	6.8–9.0%	3 MW	6 MW	21 MW	40 MW
Shell Solar	CIS	8.5–9.4%	3 MW	2 MW	2 MW	–
Wuerth Solar	CIS	9.8–11.0%	0.42 MW	1.2 MW	1.5 MW	1.3 MW
Sulphurcell	CIS	6.0–6.7%	–	–	–	1.5 MW
TOTAL INDUSTRY			47 MW	74 MW	118 MW	–

Fig. 2 (**a**) Single-junction amorphous silicon solar cell; (**b**) Individual cells deposited onto a glass sheet are laterally connected in series by the approach shown
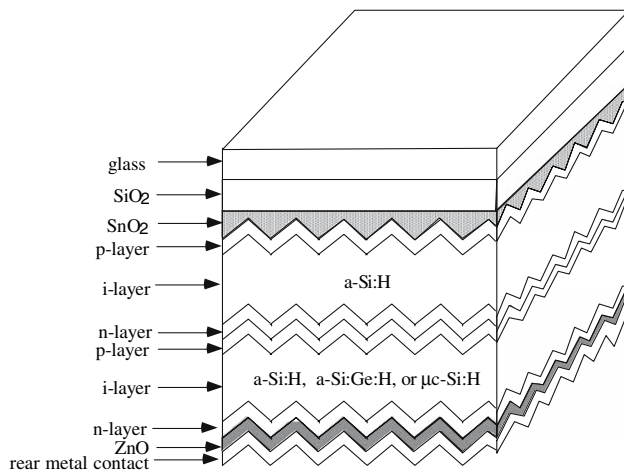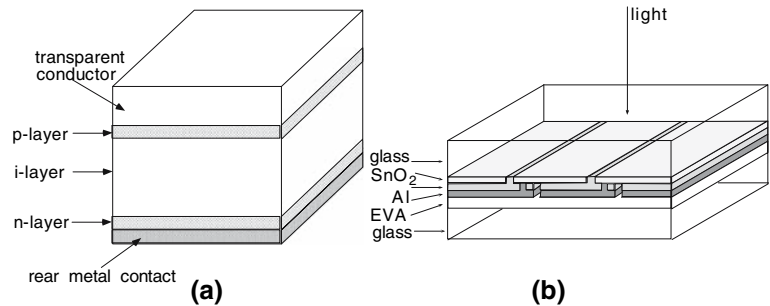
Fig. 3 Multiple-junction stacked or tandem solar cells where two or more current-matched cells are stacked on top of one another

Fig. 4 (**a**) Mixed-phase microcrystalline/amorphous material; (**b**) single-phase polycrystalline film

lower cells are smaller than that of the upper cells, this also gives a performance boost [3].

The earliest approach to reducing the bandgap from the quite high values typical of hydrogenated amorphous silicon (1.7 eV) was by alloying with germanium. The US company, United Solar, is the most successful current proponent of this approach, marketing a module based on a 3-cell stack with the two underlying cells made from a-Si alloyed with germanium. This gives nominal module performance in the 6–7% range, comparable to the best of the single junction a-Si approaches. A more recent approach is to combine an amorphous silicon top cell with a bottom cell consisting of a two-phase mixture of amorphous and microcrystalline silicon, as shown in Fig. 4a. The bandgap of the lower cell is determined by the crystalline regions in this mixed phase, and is similar to that of wafer-based cells (1.1 eV). Apart from the use of two cells, which improves module performance to the 8–10% range, the technology otherwise resembles that of amorphous silicon, with its associated strengths and weaknesses. Although these hybrid cells are not presently manufactured in any significant commercial quantities, Japanese manufacturers, Kaneka and Sharp have announced plans to supply commercial quantities of such modules.
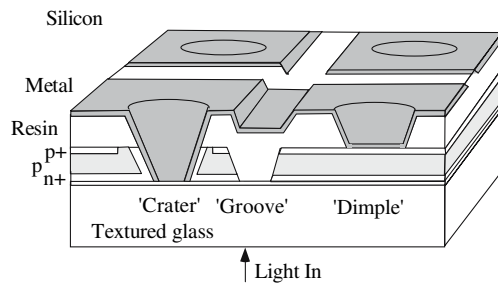
3.1.3 Crystalline silicon on glass (CSG)

The present author has been involved in developing and commercialising an alternative silicon-based technology that involves high temperature processing to convert an initially amorphous silicon layer to a polycrystalline layer, with the differences from microcrystalline material demonstrated in Fig. 4b. The resulting films have properties similar to those of the polycrystalline wafers that now dominate the commercial solar module market. The better quality of this material makes it more conductive, eliminating the need for a transparent conducting oxide together with the associated costs and other disbenefits, as well as eliminating the a-Si stability problem. The schematic cell structure is shown in Fig. 5 [4].

CSG technology includes several other features that further improve the ruggedness of the technology, including a fault tolerant metallisation approach and the use of higher grade borosilicate float glass, as compared to the soda-lime glass used in normal modules. Accelerated life-testing has shown exceptional durability potential for this approach, even as compared to the wafer-based approach [5, 6]. CSG Solar AG has completed a manufacturing facility for this technology which is making its market appearance in 2006. Module energy conversion of 7–8% is initially expected, increasing with increasing production experience to the 9–10% range.

Fig. 5 Crystalline silicon on glass (CSG) unit cell structure. The texturing of the glass is an important feature since it allows the silicon layer to be very thin (~1 micron), although not shown in this diagram

3.2 Chalcogenide-based cells

3.2.1 Cadmium sulphide

The first thin-film solar cell candidates for large-scale manufacture were based on cadmium sulphide. Attempts to commercialise this technology in the mid-1970s and early 1980s were unsuccessful, attributed to stability issues with the cells and the appearance of amorphous silicon as an apparently superior contender at that point in time. However, greater difficulties than originally anticipated in commercialising amorphous silicon provided opportunities for two related chalcogenide-based polycrystalline thin-film technologies discussed below.

3.2.2 Cadmium telluride

A device schematic for a cadmium telluride cell is shown in Fig. 6. A layer of cadmium sulphide is deposited from solution onto a glass sheet coated with a transparent conducting layer of tin oxide. This is followed by the deposition of the main cadmium telluride cell by as variety of
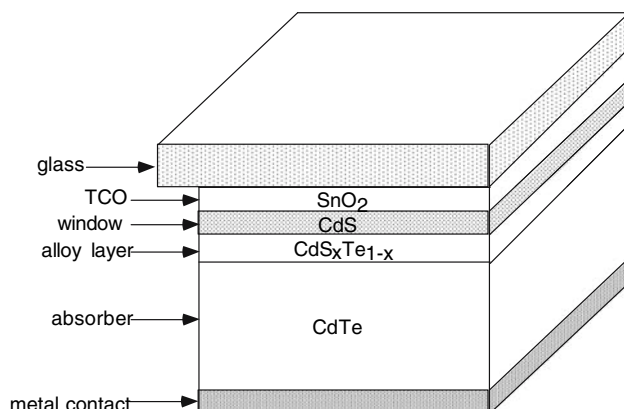
techniques including close-spaced sublimation, vapour transport, chemical spraying, or electroplating.

The main issue with CdTe modules relates to the toxicity of cadmium. Although cadmium-based modules are apparently banned in some countries such as the Netherlands, proponents point out that the required cadmium is a by-product of zinc mining [7]. Concentrating cadmium in the photovoltaic modules is thereby argued to be a positive step for the environment. Others point out this argument can only be true if the cadmium is used in a closed cycle [8]. It has been claimed that only about 4% of NiCd batteries (in Europe) have been collected over the past 20 years, despite a legal obligation to do so [9]. Two of the former key players in the cadmium-telluride area, BP Solar and Matsushita, have both abandoned the technology, citing the effect of these environmental concerns [10, 11].

3.2.3 Copper-indium diselenide (CIS)

CIS technology is a star performer in the laboratory with 19.5% efficiency demonstrated for small cells, but has proved difficult to commercialise. Unlike the other thin-film technologies, which are deposited onto a glass superstrate, CIS technology generally involves deposition onto a glass substrate as shown in Fig. 7 and then interconnection similarly to Fig. 2b. An additional glass top-cover is then laminated to the cell/substrate combination. Present designs require a thin layer of CdS deposited from solution. Considerable effort is being directed to replacing this layer due to the issues associated with the use of cadmium, as previously noted. However, a long-term issue with CIS technology is one of available resources. All known reserves of indium would only produce enough solar cells to provide a capacity equal to all present wind generators [12].

Fig. 6 Device schematic for a cadmium telluride cell
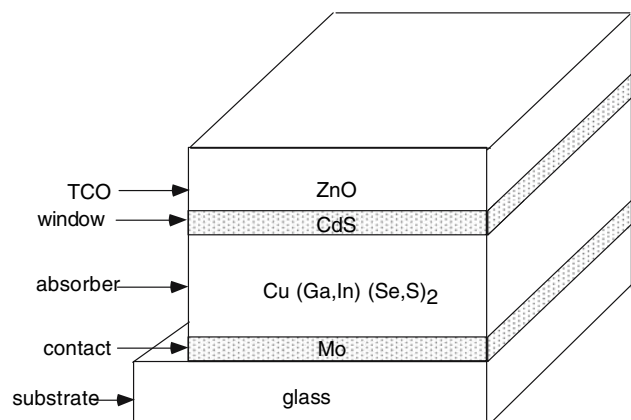
Fig. 7 Basic CIS (copper indium diselenide) cell structure

3.3 Other thin-film technologies

Apart from the activity outlined above with cell technologies based on inorganic material, recent years have seen a burst of activity with organic and mixed organic-inorganic cells. One general strand of activity is based on dye-sensitisation of porous titania films [13] while the other strand builds on the commercial interest in organic light emitting diodes (OLEDs) [14]. Attempts to commercialise the dye-sensitised cell were initially spearheaded by STI of Queanbeyan [15], with small numbers of modules appearing in some attractive building-integrated systems. Work at the laboratory level targets the replacement of the liquid required in present devices by solid-state material. OLEDs are now appearing in consumer products. However, the inverse light conversion process is fundamentally more challenging with organic material, although laboratory progress is being reported. The main challenge is to improve the energy conversion efficiency of the experimental devices while simultaneously improving the stability and durability. While a long way from being able to meet the demands of the outdoor power market, the technology may be able to more readily meet less demanding applications involving integration into consumer products and clothing.

4 Summary

Thin-film solar cell modules are reaching the market in accelerating quantities, giving the opportunity for these potentially lower cost approaches to establish their credentials. Several distinct thin-film technologies are now available, or close to being so, based either on silicon in amorphous, polycrystalline or mixed phases or on chalcogenides (Group 6 elements, specifically S, Se and Te).

Many of these thin-film modules are finding application into MW-scale systems presently being installed in Germany and Spain. Potential future purchasers should soon have a much more extensive experience base with these technologies on which to draw. This may facilitate more widespread acceptance of thin-film technologies and stimulate the on-going investments required to reach production volumes and costs required to make global impact not only for thin-films, but also for photovoltaics in general.

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