



Thin-film solar cells

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ABSTRACT

The rapid progress that is being made with inorganic thin-film photovoltaic (PV) technologies, both in the laboratory and in industry, is reviewed. While amorphous silicon based PV modules have been around for more than 20 years, recent industrial developments include the first polycrystalline silicon thin-film solar cells on glass and the first tandem solar cells based on stacks of amorphous and microcrystalline silicon films ("micromorph cells"). Significant thin-film PV production levels are also being set up for cadmium telluride and copper indium diselenide.

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1. Introduction

The photovoltaics (PV) industry is booming, with growth rates well in excess of 30% per year over the last decade [1]. This explosive growth has been driven by market development programs to accelerate the deployment of sustainable energy options and rapidly increasing fossil fuel prices. While current PV module production is around 3 GW_p (gigawatt peak) per year, PV production levels of hundreds of gigawatts per year are required to contribute measurably to global electricity generation. The main challenge along this path are ongoing incremental reductions of the €/W_p costs for the PV modules. Today's mainstream PV technology is based on crystalline silicon wafers. This is a robust and proven PV technology, however, due to the high cost of silicon wafers, its cost reduction potential seems limited. In contrast, due to greatly reduced semiconductor material consumption and the ability to (i) fabricate the solar cells on inexpensive large-area foreign substrates and (ii) to monolithically series-connect the fabricated solar cells, thin-film PV has the potential of achieving module costs of well below €1 per W_p. In this paper the rapid progress that is being made with inorganic thin-film PV technologies, both in the laboratory and in industry, is reviewed. While amorphous silicon based PV modules have been around for more than 20 years, recent industrial developments include the first polycrystalline silicon thin-film solar cells on glass and the first tandem solar cells based on stacks of amorphous and microcrystalline silicon films ("micromorph cells"). Significant thin-film PV production levels are also being set up for CdTe (cadmium telluride) and CIS (copper indium diselenide). For a description of the fundamentals of solar cells, the interested reader is referred to the literature [2,3].

2. Major thin-film solar cell technologies

2.1. Amorphous silicon solar cells

Work with low-temperature (<600 °C) supporting materials (mainly glass) in the 1970s and 1980s has established hydrogenated amorphous silicon (a-Si:H) deposited by plasma-enhanced chemical vapour deposition (PECVD) at about 200 °C as the baseline thin-film PV technology [4]. The technology possesses a number of excellent properties for low-cost PV electricity, including a high optical absorption coefficient (enabling very thin absorber thicknesses of 300 nm or less), large-area silicon diode deposition at low temperature (~200 °C) onto rigid or flexible substrates, and monolithic series interconnection of the individual cells. The only reason why a-Si:H has not been able to conquer a significant share of the global PV market is the low stable average efficiency of 6% or less of large-area single-junction PV modules [5]. One factor behind this modest stable efficiency is the "Staebler-Wronski effect" [6], i.e. the light-induced degradation of the initial module efficiency to the stabilized module efficiency. Research is continuing into finding ways to reduce this effect, however, after two decades of intense global research the prospects seem limited. The highest confirmed stable efficiency for a single-junction a-Si:H cell is 9.5% [7,8], obtained in 2003 by University of Neuchatel. Another reason are manufacturing related issues associated with the processing of large (>1 m²) substrates, including spatial non-uniformities in the Si film and the transparent conductive oxide (TCO) layer [5]. There is scope for significant improvement in this area, and hence large single-junction a-Si:H modules with stable efficiency of over 7% should soon be available. For example, the company Kaneka is already relatively close to this goal using a *p-i-n* structure on a glass superstrate [9]. The Kaneka approach is based on excellent light trapping, enabling the use of a thinner (and hence more stable) a-Si:H cell. The light trapping is

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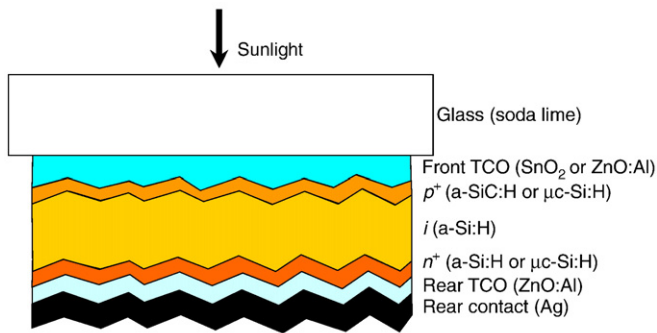


Fig. 1. Schematic of a state-of-art *p-i-n* a-Si:H solar cell on a glass superstrate.

provided by a textured TCO onto which the cell is deposited and a back surface reflector consisting of a double-layer stack of ZnO:Al (i.e., Al-doped ZnO) and silver [9,10].

The structure of a state-of-art *p-i-n* a-Si:H solar cell on a soda-lime glass superstrate is shown in Fig. 1. The front TCO must have a low sheet resistance of about $10 \Omega/\text{sq}$ and a high optical transmission for visible wavelengths. To obtain the low sheet resistance, a TCO thickness of $\sim 1 \mu\text{m}$ is required [11]. The way how adjacent a-Si:H solar cells are interconnected is shown in Fig. 2. The method is based on two fundamental requirements: (i) the supporting material is electrically non-conductive; (ii) each of the individual layers (p^+ , i , n^+) of the solar cells has very high sheet resistance ($>10^5 \Omega/\text{sq}$), ensuring that the cells are negligibly shunted when a TCO layer is deposited over the exposed sidewall region of each cell. The solar cell process starts with the deposition of the front TCO layer, followed by the first set of parallel scribes (“scribe 1” in Fig. 2) that defines the individual solar cells. Then the three semiconductor layers forming the solar cells are deposited. The next step is the second set of parallel scribes which cuts through the deposited semiconductor layers and thereby locally exposes the buried TCO layer. Then follows the blanket deposition of the rear electrode (rear TCO plus metal). Finally, the third set of parallel scribes cuts through the rear electrode (metal and TCO) and the semiconductor layers, removing the shunting path for the current flow and leading to the series connection of all solar cells on the glass pane. Lasers and/or mechanical tools are used for the three sets of scribes involved.

The a-Si:H PV technology benefits from the development of large-scale, high-throughput PECVD silicon deposition systems for liquid crystal displays (LCDs). Several manufacturers of LCD equipment are now also offering turn-key production lines for a-Si:H PV modules. Various PECVD machine configurations (batch-type, cluster tool, inline) are available. For 1.4 m^2 glass size, modern PECVD machines now have a throughput of well over $10 \text{ MW}_p/\text{year}$ of single-junction a-Si:H PV modules.

2.2. Microcrystalline silicon solar cells

A particularly attractive feature of the a-Si:H PV technology is that the low-T silicon deposition process *immediately* produces device-grade silicon material, i.e. it is not necessary to perform any post-deposition treatments (such as hydrogenation) on the as-deposited diodes. This saves time and money in the factory. Over the past 20 years, research has been conducted along the lines of preserving this attractive feature, but obtaining solar cells with higher stable efficiency. Using the very-high-frequency (VHF) PECVD method (i.e., plasma excitation frequencies well above the standard industrial frequency of 13.56 MHz), researchers at the University of Neuchatel in the early 1990s succeeded to fabricate the first hydrogenated microcrystalline silicon ($\mu\text{c-Si:H}$) cells at 200°C with reasonable efficiencies [12]. Importantly, the efficiencies of up to 4.6% of these cells were stable under light soaking conditions, giving hope to significantly higher stable module efficiency than for a-Si:H modules.

Microcrystalline Si is grown using strong hydrogen dilution of silane. The material has an optical absorption coefficient that is quite similar to that of polycrystalline silicon and its optical bandgap energy is around 1.0 eV. It contains both amorphous and crystalline regions [13]. The crystalline growth starts at nucleation centres near the film/substrate interface. The columnar grains can be several 100 nm wide and several μm long. The space between these crystalline grains is filled with amorphous silicon and/or voids. The crystalline volume content of the films depends on the deposition conditions, in particular the silane concentration in the gas mix. The regime around 6% silane concentration is called the “transition region” and gives the best $\mu\text{c-Si:H}$ solar cells [13].

By the end of the 1990s, low-T fabricated $\mu\text{c-Si:H}$ solar cells on glass had reached stable efficiencies of up to 8.5%. However, due to the low deposition rate ($<40 \text{ nm}/\text{min}$) of the $\mu\text{c-Si:H}$ film and technical difficulties with the development of industrial-scale VHF PECVD systems, $\mu\text{c-Si:H}$ single-junction solar cells do not seem to be commercially viable at present. The same conclusion appears to apply to the $2 \mu\text{m}$ thick, 10% efficient $\mu\text{c-Si:H}$ STAR solar cell developed at Kaneka using intermediate-T ($\sim 550^\circ\text{C}$) and standard 13.56-MHz PECVD [14]. Nevertheless, these results showed that a c-Si thickness of merely $2 \mu\text{m}$ is all that is needed for obtaining a short-circuit current density J_{sc} of $>24 \text{ mA}/\text{cm}^2$.

2.3. Micromorph tandem silicon solar cells

The industrial relevance of $\mu\text{c-Si:H}$ solar cells improves enormously if they are combined with thin a-Si:H top cells, forming a 2-cell tandem stack in which the a-Si:H cell faces the sun. This device structure has been pioneered by University of Neuchatel in the 1990s [15]. Given the large difference in the bandgap values of these two semiconductors (about 1.0 eV and 1.7 eV), a much better utilization of the solar spectrum and hence a higher PV efficiency is achieved. Importantly, because of the low J_{sc} of stable a-Si:H cells ($\sim 13 \text{ mA}/\text{cm}^2$), the thickness of the $\mu\text{c-Si:H}$ cell in the stack does not have to be increased significantly compared to a stand-alone $\mu\text{c-Si:H}$ cell. It thus seems that, using PECVD, a high PV module efficiency can be achieved using an economic process. In 1994, University of Neuchatel reported excellent initial (i.e., non-stabilized) efficiencies of up to 13.1% [15]. The same team later coined the term “micromorph” for this tandem cell.

The micromorph concept has been taken up by various organisations, including Kaneka [16]. In 2001 this company started a pilot production of their so-called “hybrid” thin-film PV technology [9,16]. The silicon is deposited at low temperature by 13.56-MHz PECVD onto a large ($\sim 0.85 \text{ m}^2$) TCO-coated soda lime glass superstrate and metallisation is performed such that two separate PV modules are formed [16]. The $\mu\text{c-Si:H}$ cell is about $2 \mu\text{m}$ thick, whereas the a-Si:H top cell is about 5 times thinner. Light trapping is realised as in the company’s *p-i-n* amorphous silicon solar cells (see above), however,

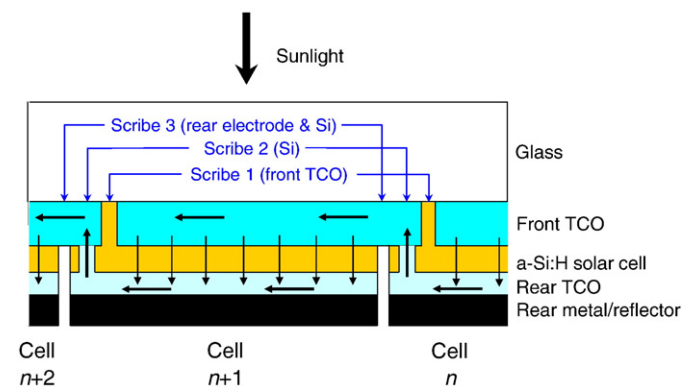


Fig. 2. Series connection of a-Si:H solar cells on a TCO-coated glass superstrate.

to further boost the efficiency a thin TCO interlayer is inserted between the a-Si:H and the $\mu\text{-Si:H}$ cell [10]. The purpose of this interlayer is to increase the current of the a-Si:H top cell, enabling a thinner a-Si:H cell and hence a more stable tandem device. Excellent initial efficiencies (aperture area) of over 12% were reported for these large (0.41 m²) all-silicon modules. The best cell (area 1 cm²) made so far has an initial efficiency of 14.5% [9]. Due to the thinness of the a-Si:H cell in the stack, micromorph (or hybrid) PV devices are expected to degrade very weakly in the field. The best stable efficiency confirmed as yet is 11.7% [8], realised by Kaneka in 2004 [17]. The strengths of the technology are the expected high stable average efficiency of about 10% for large-area mass-produced modules and the fact that established large-area low-T processing equipment from the LCD industry can be used. Weaknesses are the requirement of a textured TCO layer and the high capital cost of the deposition tool for the $\sim 2\ \mu\text{m}$ thick $\mu\text{-Si:H}$ cell.

Kaneka has announced to soon offer hybrid thin-film modules with a glass size of 1.22 m² and a rated power of 125 W_p [18]. This corresponds to a total-area efficiency (stabilised) of 10.2%, suggesting that these will be the first commercial Si-based thin-film PV modules with an efficiency of >10%. Several other companies have also announced to manufacture micromorph PV modules.

2.4. Polycrystalline silicon solar cells

Work at Sanyo Electric during the early 1990s showed that solid phase crystallisation (SPC) at $\sim 600\ ^\circ\text{C}$ of a relatively thick ($\sim 5\ \mu\text{m}$) PECVD-deposited a-Si film gives 9.2% efficiency on a metal substrate [19]. The cells featured a p^+ -doped a-Si heterojunction emitter on a n^+n polycrystalline silicon (pc-Si) structure crystallised by SPC. The open-circuit voltage (V_{oc}) of 553 mV is the highest ever reported for a thin-film solar cell having a pc-Si absorber layer made at low or intermediate temperature. Despite these excellent results, this thin-film work seems to have been abandoned at Sanyo around 1996.

In the late 1990s, Pacific Solar Pty Ltd, a spin-off company of the University of New South Wales (UNSW) in Australia, successfully transferred the PECVD-based SPC approach to borosilicate glass sheets (Borofloat33 from Schott AG, Germany). Major breakthroughs have been achieved at Pacific Solar in the following years in the areas of light trapping (novel glass texture [20]) and cell metallisation and interconnection (point contacts [21,22]). The best efficiency obtained so far with this so-called CSG (Crystalline Silicon on Glass) technology is 10.4%, realised in 2007 with a 94-cm², 20-cell mini-module with a fill factor (FF) of 72.1%, a J_{sc} of 29.5 mA/cm², and an average cell V_{oc} of 492 mV [23]. The J_{sc} is remarkably high for a silicon film thickness of merely 2.2 μm , confirming that CSG devices feature excellent light trapping properties. To achieve light trapping, both surfaces of the glass superstrate are textured with a dip coating process that leaves a monolayer of silica beads embedded in a sol-gel matrix (baseline CSG sequence; the 10.4% high-efficiency CSG devices mentioned above use a different glass texturing method [23]). A silicon nitride antireflection coating is deposited onto one surface, followed by deposition using PECVD at 45 nm/min of a-Si having an n^+pp^+ structure. The Si-coated glass sheets are heated to 600 $^\circ\text{C}$ in a batch oven for several hours to achieve solid-phase crystallisation. Crystallographic defects are annealed by heating the c-Si briefly ($\sim 1\ \text{min}$) to over 900 $^\circ\text{C}$, using a rapid thermal anneal (RTA) process. Most of the remaining defects are passivated by exposure to atomic hydrogen [24]. Device fabrication starts by using a pulsed laser to slice the Si layer into a series of adjacent, $\sim 6\ \text{mm}$ wide strip cells. The module is then coated with a thin layer of novolac resin loaded with white pigments to make it more reflective and thus improve light trapping in the cell. Next the openings for the n -type contacts (“craters”) are formed. This involves etching of openings into the resin layer (using an ink-jet printhead), followed by chemical etching of the Si. Then the openings for the p -type contacts are formed using the same ink-jet process. A blanket deposition

of sputtered aluminium provides electrical contact to the n^+ and p^+ Si layers. The aluminium film is then sliced into a large number of individual pads using laser pulses. Each metal pad series connects one line of p -type contacts in one cell with a line of n -type contacts in the next cell [24]. The strengths of the CSG technology include a simple solar cell structure (single-junction back-surface-field cell (“BSF cell”)), the elimination of TCO layers from the fabrication process, and an expected excellent long-term stability of the modules. Further details on the technology can be found in Ref. [25].

In 2004 a group of investors acquired a license for the CSG technology and formed a new company in Germany, CSG Solar AG. The company established a CSG factory in Germany with a rated capacity of 10 MW_p/year. Silicon deposition is conducted in a KAI-1200 PECVD tool from Oerlikon Solar, using 1.4 m² glass sheets. The sale of large-area CSG modules started in late 2006. In mid-2007 the module efficiencies were in the 6–7% range and were improving steadily [23]. A second KAI-1200 machine has been installed in 2007, doubling the rated factory capacity to 20 MW_p/year. For a factory producing 20 MW_p/year of 8% efficient CSG modules, the expected module fabrication costs are about 120 €/m² or, equivalently, about 1.50 €/W_p [24].

Independent research on PECVD-deposited n^+pp^+ SPC pc-Si solar cells on glass (“PLASMA” cells) in the author’s previous group at UNSW has so far led to cell efficiencies of up to 9%. The best cells have a V_{oc} of around 500 mV, a FF of around 70%, and a J_{sc} of around 26 mA/cm². Cell area is 4 cm² and the silicon film thickness is in the 2–3 μm range. The main differences to the CSG devices described above are alternative methods for creating the textured glass surface, the p^+ BSF layer, and the cell electrodes [26]. While the BSF layer in CSG devices is grown in-situ, in PLASMA cells it is realised using dopant diffusion from a sacrificial doped dielectric layer [27]. Dopant diffusion occurs during the high-temperature defect anneal (RTA) and hence no extra processing step is required for the BSF layer formation. Metallisation of PLASMA cells is based on interdigitated comb-like grids for both cell electrodes. Both grids consist of about 500 nm of aluminium thermally evaporated in a vacuum chamber. The metallisation does not involve the use of a TCO layer. The glass texturing method (Aluminium-Induced Texturisation, AIT) is based on a thermally activated chemical reaction between the glass and a thin, sacrificial aluminium layer [28]. The high temperature ($\sim 600\ ^\circ\text{C}$) during the AIT anneal induces a spatially non-uniform redox reaction between the aluminium and the glass (SiO₂). Following this anneal, the reaction products (Al₂O₃, Si) are removed by wet-chemical etching. The aluminium layer can be deposited by evaporation or sputtering and hence the AIT method is suitable for large-area applications such as thin-film PV. Fig. 3 shows the surface morphology of a representative PLASMA solar cell grown on AIT-textured glass.

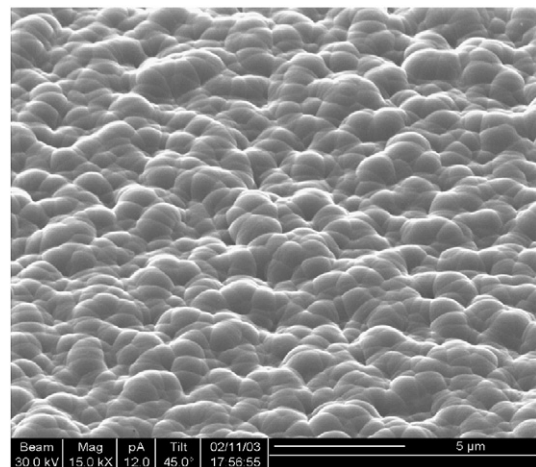


Fig. 3. Focused ion beam microscope image of the rear surface of a PLASMA pc-Si solar cell made on AIT-textured glass.

2.5. Cadmium telluride solar cells

CdTe PV modules are fabricated in the superstrate configuration and charge carrier separation occurs via a heterojunction. The process starts with the deposition of a TCO layer onto the planar soda lime glass sheet and a first set of scribes, as previously described for a-Si solar cells. Then follows the deposition of the cadmium sulphide (CdS) window layer (thickness ~100 nm) and the CdTe absorber layer (thickness ~5 μm , bandgap ~1.5 eV [2]). These two polycrystalline semiconductor materials are chemically very stable and are relatively easy to deposit stoichiometrically at 400–600 °C. Typically the close-spaced sublimation method is used to deposit these semiconductor films, but other techniques such as electroplating are also possible [29]. A slight natural non-stoichiometry automatically produces the desired p-type doping of the CdTe layer and the n-type doping of the CdS layer. Thus, in contrast to silicon thin-film PV technologies, no dopant atoms need to be added during the film deposition process. Then follows an “activation step” that improves the PV properties of the heterojunction diode. This process consists of a thermal anneal at 400–500 °C in a chlorine-containing atmosphere, usually CdCl₂ [29]. A second set of scribes then patterns the CdS/CdTe layers, followed by the formation of the back contact and the third set of scribes. Scribe 1 is usually done with a laser, while scribes 2 and 3 are usually done mechanically. Efficiencies of up to 16.5% have been achieved with small-area cells, while the best commercial modules are presently 10–11% efficient [29]. There has been good progress with commercialisation of this PV technology in recent years, particularly at First Solar whose production capacity now exceeds 300 MW_p/year [30].

The main technical issue of the CdTe technology is related to the back contact. Specifically, the relatively light p-type doping of the CdTe layer complicates the realisation of a low-resistance, long-term-stable back contact. One possible solution is the formation of a thin heavily doped p⁺ layer at the back surface of the CdTe layer. Another approach is the deposition of a thin p⁺ doped buffer layer having a smaller bandgap than CdTe (i.e., forming a heterostructure). The standard method for realising the back contact structure of CdTe solar cells presently consists of chemical etching of the CdTe surface, followed by the deposition of a p⁺-type buffer layer and then the metal film [29]. Another technical issue is the activation step, which involves a toxic atmosphere and thus should be modified or eliminated. The main issue of the CdTe PV technology, however, is related to the toxicity of Cd. Even if proper recycling of the modules is offered by the module manufacturers, it is questionable whether the production and deployment of Cd-based modules is sufficiently benign environmentally to justify their use instead of less problematic PV technologies. Furthermore, Te is a scarce element and hence, even if most of the annual global Te production is used for PV, CdTe PV module production seems limited to levels of a few GW_p per year.

2.6. Copper indium diselenide solar cells

CIS modules are fabricated in the *substrate* configuration, i.e. from back to front. In this case there is no need for a transparent supporting material, giving flexibility with respect to the choice of the substrate. While flexible substrates are being investigated, the standard substrate is soda-lime glass due to its availability, cost effectiveness, and the enhancement of the doping concentration in the CIS absorber layer by sodium atoms that diffuse from the substrate into the CIS layer during the module fabrication process. The process starts with a glass substrate clean, followed by the deposition of a thin molybdenum (Mo) film and scribing of the Mo film. Then comes the deposition of the polycrystalline CIS absorber film, which is actually a complex system involving the five elements Cu, In, Ga, Se and S. The bandgap is 1.0 eV for copper indium diselenide and increases when gallium is added to replace indium [2]. Again, as in the case of CdTe, the absorber layer is automatically p-type doped. The CIS film can either be

deposited directly, for example by thermal coevaporation of the elements, or indirectly by first depositing more simple precursor layers which then react in a subsequent processing step to form the compound semiconductor. The CIS materials system is more complex than CdTe and has higher demands on the process control systems. As with CdTe solar cells, the separation of the photo-generated carriers occurs via a heterojunction formed by n-type CdS. The CdS is very thin (~50 nm) and is deposited in a chemical bath process to ensure uniform coating of the CIS absorber. Then follows scribing of the semiconductor layers. A thin intrinsic ZnO layer is then sputtered onto the CdS, followed by sputter deposition of a thick (~1 μm) front TCO (Al-doped ZnO) and scribing of the front TCO. Scribing is done as in the case of CdTe. The CIS technology is a star performer in the laboratory, with confirmed efficiencies of up to 19.9% for small cells [8]. However, the technology has proved difficult to commercialise. The best commercial modules are presently 11–13% efficient [29].

The main technical issue of the CIS technology is associated with the complexity of the CIS absorber layer (a 5-element system), which imposes significant challenges for the realisation of uniform film properties across large-area substrates using high-throughput equipment. This affects the yield and the cost ($\text{€}/\text{W}_p$) of the modules. Other issues are the use of cadmium (as previously noted) and the use of the scarce element indium. Estimates indicate that all known reserves of indium would only be sufficient for the production of a few GW_p of CIS PV modules.

3. Conclusion

Today's mainstream PV technology is based on crystalline Si wafers. This is a robust and proven PV technology, however, its cost reduction potential seems limited. Due to greatly reduced semiconductor material consumption and the ability to (i) fabricate the solar cells on inexpensive large-area foreign substrates and (ii) to monolithically series-connect the fabricated cells, thin-film PV has the potential of achieving module fabrication costs of well below €1 per W_p. As shown in this paper, thin-film PV technologies based on inorganic materials are developing rapidly, both in the laboratory and in industry. While amorphous silicon based PV modules have been around for more than 20 years, recent industrial developments include the first polycrystalline silicon thin-film solar cells on glass and the first tandem solar cells based on stacks of amorphous and microcrystalline Si films (“micromorph cells”). Globally, more than a dozen thin-film silicon PV lines are presently being commissioned or planned for amorphous and/or micromorph solar cells. Significant thin-film PV production levels are presently also being set up for CIS and CdTe. The latter technology is expanding particularly rapidly.

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