

## Thin-film-silicon solar cells

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*The traditional development of photovoltaics has been based on crystalline-silicon wafer technology. In the early 1970's, however, a new approach arises based on the possibility to grow silicon in the form of a thin film onto a given substrate. Several techniques are used for such a deposition, among which plasma-enhanced chemical vapour deposition (PECVD) is clearly outstanding given its widespread use and success. More recently, very-high-frequency (VHP PECVD) and hot-wire CVD have appeared as very promising and fast developing alternatives with important potential and actual advantages.*

*Thin-film technology introduces completely novel concepts and challenges in silicon photovoltaics. Low-temperature processes particularly adequate for large-area devices open up not only very important cost-reduction potential, but also new possibilities such as making semi-transparent or flexible modules. Additional important features are a highly automated production system, an enormous potential for building integration, a good performance at realistic working temperatures (around 40°C) and an excellent durability in outdoor conditions among others.*

*Photovoltaics are facing important challenges for the near future. Silicon-wafer technology is evolving towards making thinner, cheaper, multicrystalline silicon. Thin-film-silicon researchers are in turn striving to make thicker, better, more crystalline films. Both ways seem to converge to new-generation photovoltaics in which wafer and thin-film technologies may be used in a synergistic rather than competing manner. Silicon heterojunction cells (made up of a crystalline silicon absorber onto which one or more thin-film silicon layers are deposited), such as the well-known HIT cell, are in the forefront of photovoltaics and may represent a breakthrough in the next few years.*

**Keywords:** photovoltaics, silicon solar cell, thin-film technology.

### 1. Introduction

Solar-module production has grown quickly in the last few years, making the solar-module market one of the fastest growing ones in the world. Photovoltaics are dominated by bulk mono- and multi-crystalline silicon (c-Si) solar cells which account for about 85% of the total production. Wafer PV technology is mainly limited by raw-material costs whereas thin-film technologies allow for important reduction in semiconductor thickness because of the capacity of certain materials to absorb most of the incident sunlight within a few microns of thickness, in comparison to the several hundred microns needed in wafer technology. In addition, thin-film technology has an enormous potential in cost reduction, based on the easiness to make robust, large-area monolithic modules with a fully automatic fabrication procedure. Among thin-film solar cells, silicon dominates the solar-module market by taking 9% of the global PV market.

The beginning of amorphous-silicon PV goes back to 1965, when Sterling *et al.* [1] reported deposition of silicon onto a substrate using a silane glow discharge. Shortly afterwards, in 1969, Chittick *et al.* [2] obtained the first intrinsic amorphous silicon of acceptable quality by PECVD.

These milestones and the investigations made by Spear and LeComber in 1975 [3], which demonstrate the possibility to dope (both n- and p-type) amorphous silicon, were soon followed by the work by Carlson and Wronski, who in 1976 announces the first experimental-a-Si:H solar cell made at RCA Laboratory [4]. This single junction p-i-n a-Si:H solar cell deposited on a glass substrate coated with transparent conductive oxide (TCO) and aluminium back contact exhibits 2.4% conversion efficiency. In 1983, Matsuda [5] introduced another milestone in the development of thin-silicon technology by obtaining both p- and n-type microcrystalline silicon ( $\mu$ c-Si). This new material was used in 1987 by Hattori *et al.* [6] to make the first thin-film silicon solar cells having microcrystalline-silicon emitters. More recently, in the 1990's, the need for a better-quality, more stable absorber material, leads to an increasing interest in intrinsic microcrystalline silicon, with important milestones in 1992 by Faraji *et al.* [7] who used very-high-frequency PECVD (VHF-PECVD) and in 1997 by Rath *et al.* [8] who used hot-wire CVD (HW-CVD).

All along this time, what was once a material called amorphous silicon, has evolved into a whole family of semiconductors based on different forms of silicon alloys made by different deposition techniques having in common the deposition in the form of thin films at low temperatures (below 600°C and often around 300°C). It would be there-

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fore appropriate to speak about thin-film silicon or deposited silicon. As will be demonstrated, this technology has opened up new possibilities for the solution of a number of important problems not only in photovoltaics, but in optoelectronics in general. Its most relevant features are:

- considerable potential for cost reduction,
- possibility to use a wide variety of low-cost, even flexible substrates, as derived from the low-temperature processes required,
- adequacy to make large-area devices,
- high degree of automation made possible by the monolithic integration of modules, which in addition provides an excellent durability derived from module robustness and chemical stability,
- low temperature coefficients being responsible for a relatively good performance of modules at realistic working temperatures (about 40°C) as compared to wafer technology,
- outstanding appearance and capacity for building integration, including semitransparent devices, making it possible to make photovoltaic windows, tiles and other elements with a high versatility and excellent aesthetic results.

Different preparation techniques have been tested to make thin-film silicon. Sputtering and evaporation were among the first ones in chronological order. The resulting material had, nevertheless, a very high density of defects. The preparation of amorphous silicon by PECVD of silane ( $\text{SiH}_4$ ) and silane-containing mixtures allowed to obtain a much higher quality, derived from the incorporation of hydrogen coming from the decomposition of the gas molecules. These features have made PECVD the most widely used preparation technique for thin-film silicon. An outline of a typical PECVD system is given in Fig. 1.

More recently, new deposition techniques have appeared, such as very-high-frequency PECVD (VHF PECVD) and hot-wire CVD (HWCVD), offering the possibility to make higher-quality material (amorphous, nanocrystalline or microcrystalline) at the significantly higher growth rates (of the order of a few nanometers per second as compared to the traditional PECVD 1–2 Å/s). Table 1 summarises some key optoelectronic properties and related parameters for prototypical PECVD thin-film silicon.

Table 1. Typical values of some parameters for standard PECVD thin-film silicon.

Parameter	p-type a-Si:C:B	Intrinsic a-Si	n-type a-Si:P
Optical (Tauc) gap (eV)	2.0	1.75	1.75
Dark conductivity (S/cm)	$10^{-6}$	$10^{-10}$	$10^{-3}$
Photoconductivity at 100 mW/cm <sup>2</sup> AM 1.5 (S/cm)		$10^{-5}$	
ES-conductivity activation energy (eV)	0.45	0.85	0.20
Mobility-lifetime product (cm <sup>2</sup> /V)		$10^{-7}$	
Hydrogen content (%)		9–11	

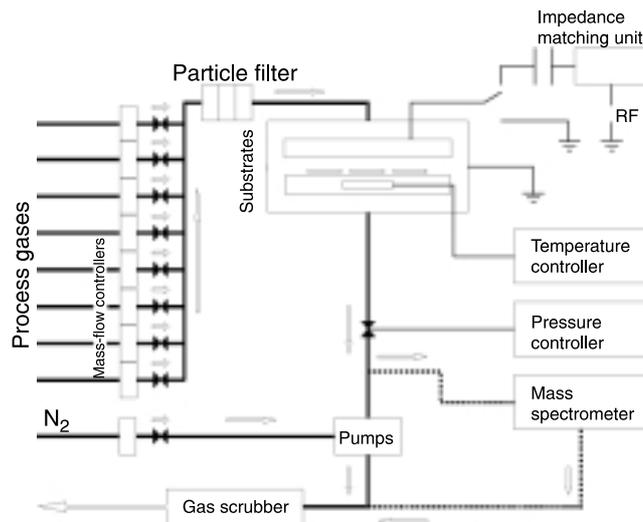


Fig. 1. Basic scheme of a capacitively-coupled PECVD reactor.

## 2. Amorphous-silicon p-i-n cells and modules

Although thin-film silicon cells may have different structures, both in substrate and superstrate configuration, one simplified version of the most widely used superstrate structure can be shown as a good example for p-i-n thin-film silicon solar cells.

As it can be seen in Fig. 2, different layers are consecutively deposited onto a common-glass superstrate. When the process has finished, the device is illuminated by turning it upside down. Of particular importance is the need to keep the device at all fabrication steps at temperatures not higher than the highest temperature attained in the previous steps. This means that this superstrate configuration allows the cheap deposition of  $\text{SnO}_2\text{:F}$  by spray pyrolysis (involving temperatures of 600°C to 800°C) at the beginning, so that the 200 to 300°C PECVD process is performed afterwards.

As mentioned above, one of the main advantages of thin-film technology is the possibility to make monolithic modules in a highly automated process. This is illustrated in Fig. 3. The laser-scribing processes applied successively to the TCO, the thin-film silicon layers as a whole and the

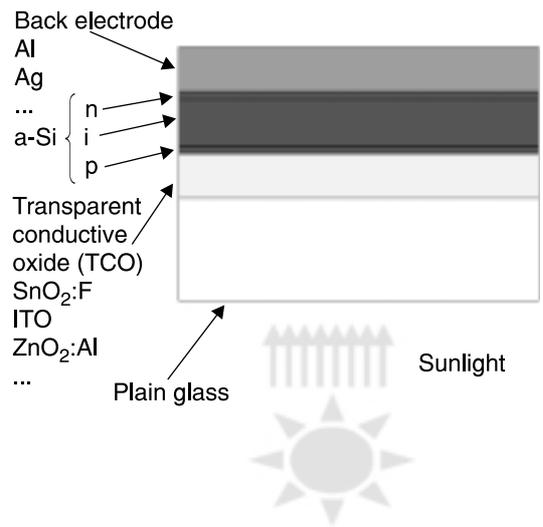


Fig. 2. Basic structure of a typical p-i-n thin-film silicon solar cell in superstrate configuration.

back contact, allow to separate the material deposited into a number of single cells which at the end turn out to be series-connected. This process does not need any manual intervention, such as contact welding, wafer arrangement, bonding, and other operations which make the fabrication of wafer modules and panels far less automatic. In addition, once the module has been encapsulated, the structure is highly robust both mechanically and chemically, resulting in a durable product particularly resistant against changing temperatures and climatic conditions. The structure of the module as it comes out from the process line can be appreciated in Fig. 4.

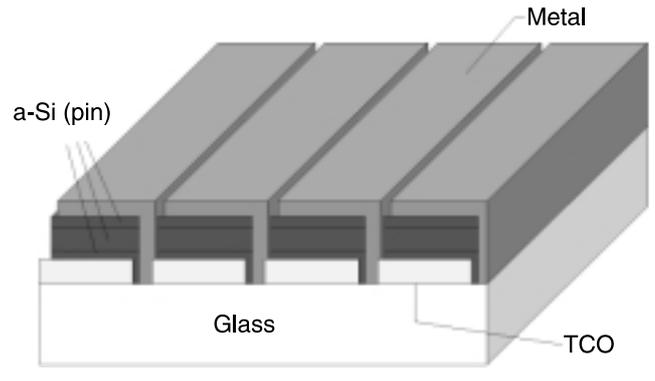


Fig. 4. Basic scheme of a monolithic integrated thin-film silicon module.

The band diagram of such a p-i-n device is represented in Fig. 5. A particularly important conclusion to be drawn thereof is that the absorber layer, the intrinsic one, is indeed the space-charge zone. This means that:

- carrier transport is performed by drift, not by diffusion. The mobility-lifetime product is now the key parameter determining an effective carrier recombination. The average distance covered by a carrier before recombining is given by  $\mu\tau E$ , where  $E$  is the electric field present,
- usual hypothesis (in wafer-based PV) of a negligible recombination in the space-charge zone is not valid,
- also usual superposition principle, according to which the J-V curve under illumination may be obtained just by shifting the dark characteristics is not also valid.

This last assertion can be illustrated by means of the equations applicable. Certainly, as the first approximation, one can use typical diode equation to which a photocurrent

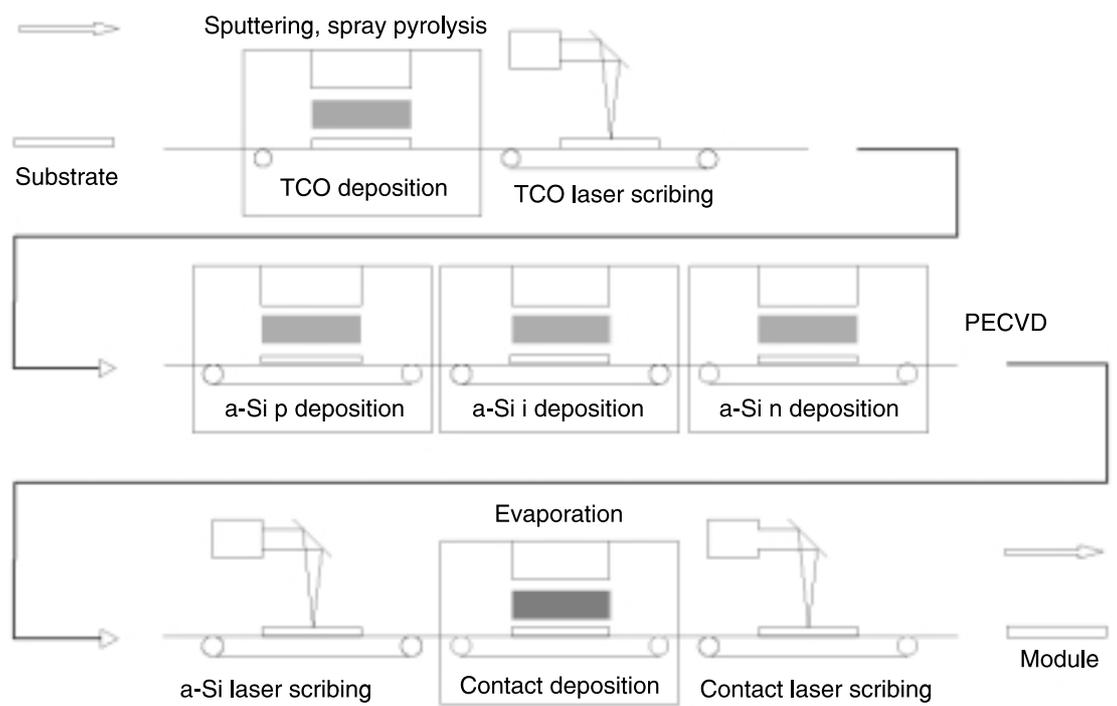


Fig. 3. Scheme of the basic steps for fabrication of a thin-film silicon photovoltaic module.

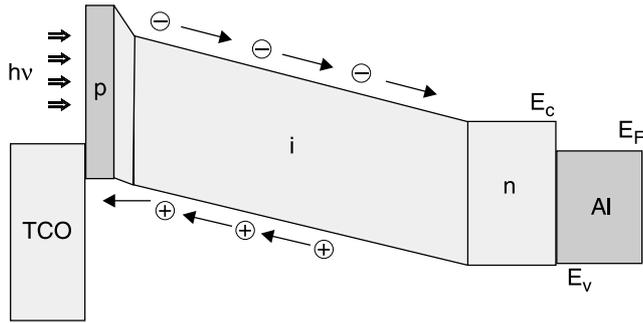


Fig. 5. Band diagram of a p-i-n thin-film silicon solar cell.

term has been added on the basis of the superposition principle

$$J = -J_L + J_S(e^{qV/nkT} - 1), \quad (1)$$

with

$$J_S = J_{s*} \exp\left(-\frac{E_a}{kT}\right), \quad (2)$$

and  $n = 1.8$ .

Nonetheless, these equations are not accurate enough to describe the behaviour of the cell in most (if not in all) cases, so the addition of a term accounting for the recombination in the intrinsic layer becomes necessary, as expressed in the following equation [9]

$$J = J_S \left( e^{\frac{V-AJR_s}{nkT}} - 1 \right) + \frac{V - AJR_s}{R_{sh}} - J_L + \frac{J_L d_i^2}{(\mu\tau)_{ef} [V_{bi} - (V - AJR_s)]} \quad (3)$$

The state-of-the-art stable efficiencies are given in Table 2. The present research and development on this field is focused on addressing a number of issues which represent the main challenges of thin-film silicon PV technology today:

- to increase fabrication throughput by raising growth rate (from 1–2 to several tens Å/s),
- to minimise photodegradation (Staebler-Wronski effect) by making a better absorbing material ( $\mu$ c-Si,

$nc$ -Si) – better  $\mu\tau$  product and making the intrinsic layer thinner (tandem cells),

- to develop and apply new high-quality p- and n-type emitters,
- to raise current density by improving light trapping (TCO haze and similar techniques).

### 3. Commercial amorphous-silicon photovoltaic products

Wafer (mono- and multicrystalline) silicon dominates the photovoltaic market. Only about 15% corresponds to thin-films, new-generation ribbon silicon, and silicon heterojunction cells. The situation is summarised in Fig. 6. With 9% of the total PV market, thin-film silicon commercial products hold a particularly advantageous position in the consumer-electronics sector.

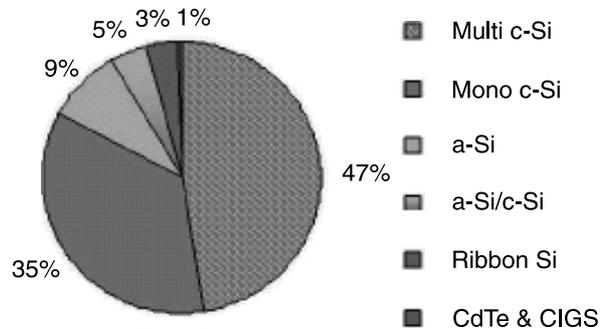


Fig. 6. PV market share in 2001. Source PV News 21/4, April 2002.

The most important thin-film PV manufacturers in the world are indicated in Table 3.

The products manufactured and commercialised by these and some auxiliary companies cover a wide range:

- modules (rigid or flexible) – area between 30×30 cm<sup>2</sup> and 150×100 cm<sup>2</sup> approximately, power between 5 and 50 W approximately, efficiency from 6 to 9% approximately,
- portable lamps,
- power supply units for stand-alone systems,
- traffic signals,
- on-road SOS points,
- public lighting,
- weather-analysis systems,
- consumer electronics; calculators, watches, battery chargers, ventilation systems, car sun roofs,

Table 2. Stable conversion efficiencies of the state-of-the-art thin-film silicon photovoltaic devices.

	Single-junction	Double-junction	Triple-junction
Record cell	9.3%	12.4%	13.2%
Record module		10.4%	
Commercial module	5% to 7%	9%	

Table 3. Main thin-film silicon PV manufacturers in the world.

Europe	USA	Japan
RWE Schott Solar (Germany)	Unisolar	Fuji
Akzo Nobel (Netherlands)	BP Solarex	Kaneka
Free-Energy Europe (Netherlands)		Sanyo
Intersolar (United Kingdom)		Canon
Dunasolar (Hungary)		Sharp

- pumping systems,
- facades and roofs; solar tiles, semitransparent PV windows.

The latter application is of particular relevance, given the outstanding features of thin-silicon PV technology, which allow building integration in optimum conditions of modularity, aesthetics and versatility. The key features behind this are: the possibility to make modules on large areas, with irregular shapes, on flexible or bent surfaces and even semitransparent.

#### 4. Thin-film silicon and new-generation photovoltaics

For a long while, wafer and thin-film technologies have evolved as competing options, i.e. as if the solutions to the technical problems could have come out from only one of these two research lines. In the last few years, however, new possibilities have arisen on the basis of a number of technological approaches for the fabrication of inexpensive multicrystalline silicon, for the growth of polycrystalline silicon thin films on cheap substrates or for the deposition of high-quality microcrystalline-silicon thin films at competitive growth rates. Among these techniques and materials are: edge-defined film-fed growth (EFG), string ribbon silicon, Silicon Film™, dendritic web growth, RGS silicon foil preparation [10] molecular-beam graphoepitaxial growth (MBGE), solid-phase crystallisation (SPC), zone-melting recrystallisation (ZMR), plasma-spray silicon growth (PSSG), liquid-phase epitaxy (LPE) molecular-beam epitaxy (MBE), hot-wire CVD, VHF-PECVD and more [11,12].

Some of these approaches have evolved from a wafer technology as the possible ways to lower costs by producing solar-grade silicon *ad hoc* rather than consuming material initially devised for the microelectronics industry. As compared to CZ mono-c-Si, the subordination to lowering costs leads to the following key features:

- multicrystalline instead of monocrystalline silicon,
- thinner active layers ( $\sim 10^1$  instead of  $\sim 10^2$   $\mu\text{m}$ ),
- more efficient use of raw materials.

The rest of the above mentioned techniques arise from the need of the thin-film-silicon technology (basically PECVD) to overcome certain limitations (defect density,

photostability and fabrication throughput). This leading force results in the following targets (taking standard amorphous silicon as the reference starting point):

- increased crystallinity,
- thicker active layer ( $\sim 10^0$ – $10^1$  instead of  $\sim 10^{-1}$   $\mu\text{m}$ ),
- higher growth rates.

A rough view at the guidelines of both tendencies leads to conclude that the following characteristics define the key silicon material in next-generation photovoltaics:

- medium crystallinity (multi- or polycrystalline silicon),
- medium active-layer thickness, in the range from a few microns to a few tens of microns,
- high fabrication throughput, either by epitaxy, fast solidification of melted silicon, fast film growth from gaseous silicon sources or similar processes.

Whereas it is unclear whether this kind of material will be obtained from the evolution of wafer technology, from that of thin-film technology or even from hybrid approaches, the mutual convergence of these two research lines is more and more obvious. Furthermore, the characteristics of new materials impose new limitations to device technology, thus requiring innovative solutions.

For instance, the use of cheaper, non-highest-quality, absorbers involves the risk of degradation of minority-carrier lifetimes associated with high-temperature processes such as those used in conventional wafer technology for the formation of cell emitters. Additionally, the decrease in active-layer thickness demands a more accurate definition of the junction, and correspondingly, of emitter thickness.

These requirements, added to other factors such as the search for automatic module-assembly approaches, the need to lower costs by simplifying technology and spending less energy, or the tendency to produce large-area devices, have led to the development of a new PV sub-field: that of silicon-heterojunction solar cells (Si HJ). The low-temperature processes ( $< 250^\circ\text{C}$ ) of this technology are not only cost-effective by themselves, but also allow for the use of low-cost substrates that cannot be annealed at high temperatures, such as silicon ribbon and thin c-Si grown on glass [13].

Silicon-heterojunction cells (see Fig. 7), basically made of a crystalline-silicon (mono- or multi-crystalline) wafer or ribbon absorber and one or two thin-film-silicon emitter(s), are excellent examples of technological convergence and represent a promising option in seeking breakthroughs in photovoltaics.

Key features of silicon-heterojunction technology are [14]:

- very simple fabrication process,
- important cost-reduction capability,
- relatively high efficiencies, with a high potential for significant improvements.

Particularly remarkable is the work done by Sanyo who has reported 21% efficiency on solar cells of this kind (so-called HIT) [15]. These solar cells have consequently attracted much attention of the international scientific community.

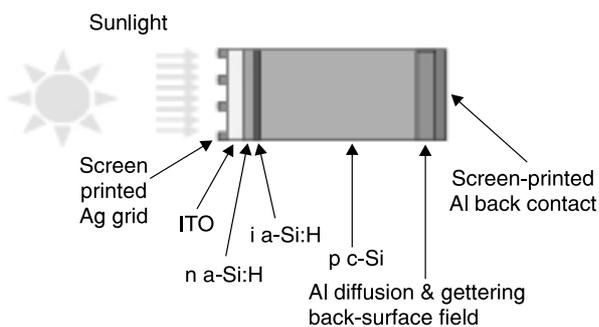


Fig. 7. Basic structure of n-on-p silicon heterojunction solar cell.

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