



# Review of thin-film silicon deposition techniques for high-efficiency solar cells developed at Panasonic/Sanyo

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## ABSTRACT

Criteria and techniques of device-grade thin film silicon deposition for high efficiency solar cells developed in Panasonic/Sanyo were reviewed. By applying these techniques, record efficiencies were achieved for a-Si single junction, a-Si/a-SiGe tandem junction. We have also fabricated very high-efficiency a-Si/ $\mu$ c-Si tandem solar cells and modules with a very high  $\mu$ c-Si deposition-rate ( $>2.0$  nm/s) of device-grade  $\mu$ c-Si layers using Localized Plasma Confinement CVD.

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## 1. Introduction

Thin-film silicon, such as hydrogenated amorphous silicon (a-Si), microcrystalline silicon ( $\mu$ c-Si) and related alloys, are promising materials for very low-cost solar cells. Sanyo has conducted R&D on thin-film silicon solar cells for more than 30 years, and released the first a-Si solar cell products, the AMORTON<sup>TM</sup>, in 1980, and the highest-performing photovoltaic modules, called the HIT<sup>TM</sup>, in 1997. As a result of acquisition, the R&D history of Sanyo [1–24] was inherited by Panasonic.

The R&D history of a-Si and  $\mu$ c-Si dates back to the 1960 s. Amorphous silicon films were initially deposited from crystalline silicon (c-Si) using thermal deposition and sputtering [25,26]. The first  $\mu$ c-Si was deposited using a chemical transport method in which c-Si was chemically decomposed with atomic hydrogen and deposited on a substrate [27]. In 1969, Chittik et al. reported a method of depositing hydrogenated a-Si by decomposing  $\text{SiH}_4$  gas by glow discharge [28]. When Spear and LeComber succeeded in controlling valence electrons in 1975 by building on existing technology [29], a-Si received sudden attention as a new semiconductor material. Industrial production of a-Si solar cells began in 1980 using plasma chemical vapor deposition (CVD) [30]. The potential for depositing a-Si using  $\mu$ c-Si plasma CVD equipment was also confirmed around this time [31,32]. This paper reviews progress in thin film silicon deposition technologies for high-efficiency solar cells at Panasonic/Sanyo.

## 2. Record efficiencies of Panasonic/Sanyo

We have continuously proposed innovative technologies and achieved record efficiency values for various types of Si-based

solar cells (Table 1) [1–24]. In 1993, the world's highest initial conversion efficiency of 12.0% was achieved for an a-Si single junction solar cell ( $100 \times 100$  mm) [1]. In 2001, the world's highest stabilized conversion efficiency of 10% was also achieved for an a-Si/a-SiGe tandem module ( $900 \times 900$  mm<sup>2</sup>) with a deposition-rate of over 0.2 nm/s [6,7] for the bottom a-SiGe layer. Replacing the bottom a-SiGe layer with  $\mu$ c-Si effectively improves long-wavelength sensitivity and conversion efficiency. However, there are some trade-offs. Which is more suitable for the bottom of a tandem solar cell for this purpose, a-SiGe or  $\mu$ c-Si? This question has been continuously asked now for more than 15 years. A comparison of a-SiGe (in 2001) versus  $\mu$ c-Si (in 2011) for the bottom of tandem solar cells is enumerated in Table 2 [17]. A relatively thick  $\mu$ c-Si layer (around 2.0  $\mu$ m) could be a bottleneck in the manufacturing process. Much effort has been devoted to increasing both the stabilized efficiency and the process throughput of  $\mu$ c-Si deposition. The very high-rate deposition technique could compensate for the disadvantage of the thicker  $\mu$ c-Si. Although the module efficiency is almost the same level, there is more room for further improvement in  $\mu$ c-Si.

## 3. Criteria for device-grade a-Si:H deposition

Higher RF power and/or higher  $\text{SiH}_4$  partial pressure allow the higher deposition-rate due to increased concentrations of silyl radicals ( $\text{SiH}_x$ ). However, the higher density of defects, particularly dangling bonds, degrades the electrical characteristics of the material at higher deposition-rate [33]. This phenomenon can be understood intuitively in that the increased rate of accumulation of Si-based radicals shortens the time available to relieve stress in the film surface structure; as a result, the Si network solidifies with more defects left in an energetically unstable, non-equilibrated condition. Under high power conditions, adverse effects such as increased ion damage to the deposited film surface and powder generation caused

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**Table 1**  
Efficiency of Panasonic's thin-film silicon solar cells.

Year	Size (cm <sup>2</sup> )	Structure	Init. eff.	Stab. eff.	Ref.
1993	1	a-Si	12.7%	–	[1,2]
1993	100	a-Si	12.0%	–	[1,2]
1994	1	a-Si	–	8.9%	[3]
1994	1	a-Si/a-SiGe	11.6%	10.6%	[4]
1997	1200	a-Si/a-SiGe	11.1%	9.5%	[5]
2001	8252	a-Si/a-SiGe	11.2%	10.0%	[6,7]
2007	1	a-Si/ $\mu$ c-Si	13.5%	–	[10]
2010	15,400	a-Si/ $\mu$ c-Si	11.1%	10.0%	[13–15]
2011	14,300	a-Si/ $\mu$ c-Si	12.0%	10.7%	[16–22]
2011	1	a-Si/ $\mu$ c-Si	13.5%	12.2%	[16–22]

**Table 2**  
Comparison of a-SiGe vs.  $\mu$ c-Si bottom cells.

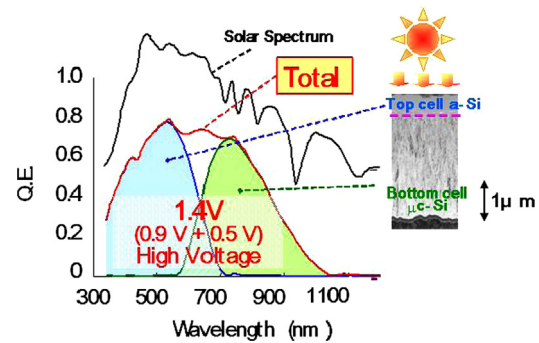
	a-SiGe	$\mu$ c-Si
Stabilized efficiency of tandem module	10%	>10%
Module size	900 × 900	1100 × 1400
Photo-stability	Comparative	
Thickness of bottom cell	0.2 $\mu$ m	~2.0 $\mu$ m
Material cost factor	GeH <sub>4</sub> gas	Thickness
Deposition rate	~0.2 nm/s	>2.5 nm/s
Throughput	~1000 s	~800 s

by in-vapor polymerization reaction are unavoidable. Increased substrate temperature promotes structural relief of the deposited surface with increased thermal energy, but at temperatures exceeding 250 °C, solar cell characteristics deteriorate due to thermal damage to the underlying layer [34]. If using non-diluted SiH<sub>4</sub>, the film deposition-rate needs to be kept to around 0.1 nm/s to form sufficiently high-quality a-Si film at practical substrate temperature of around 200 °C [1,33]. This criteria was also effective for a-SiGe:H deposition [4,5,35,36]. There exists the optimum hydrogen content, which corresponds to the minimum defect density and maximum conversion efficiency, which were found for a-Si:H and a-SiGe:H. When too much hydrogen is incorporated, increased dihydride-Si (SiH<sub>2</sub>) deteriorates film properties [33,35–38].

One effective technique for superseding the limitations of the process using 100% SiH<sub>4</sub> is the hydrogen dilution method [33,34,39,40]. If the SiH<sub>4</sub> supplied to the process is diluted with hydrogen, high concentrations of atomic hydrogen are generated in the plasma. These protons promote structural relief of the film surface by providing chemical energy, and at the same time, they collide with highly reactive over-decomposed radicals that tend to damage the film quality and generate powder, thereby inactivating the radicals. Optimized film deposition conditions using the hydrogen dilution method can produce high quality a-Si:H and a-SiGe:H film even at relatively high deposition-rate of over 0.5 nm/s.

#### 4. LPC-CVD method for very high-rate deposition of $\mu$ c-Si

By additionally increasing the hydrogen dilution ratio, structural relief of the Si networks is further promoted, and  $\mu$ c-Si containing crystalline Si can be formed [1]. Due to the inclusion of crystalline Si,  $\mu$ c-Si has a smaller light absorption coefficient and higher activation rate of impurities than a-Si. These provide advantages as a doping layer of solar cells; however, the power generation layer needs to absorb incident light efficiently. Although the film thickness of the power generation layer of a-Si solar cells is generally around 300 nm, a  $\mu$ c-Si solar cell requires a film thickness that exceeds 2  $\mu$ m (Fig. 1). In conventional industrial processes, the film deposition-rate of a-Si is 0.3–0.5 nm/s, so the



**Fig. 1.** Schematic image of the spectra sensitivity and cross-section of a-Si/ $\mu$ c-Si tandem-junction solar cell.

film deposition-rate of  $\mu$ c-Si should preferably be over 2.0 nm/s to bring down the production cost to a level comparable to that of a-Si.

If the hydrogen dilution ratio is increased while keeping the total pressure constant during film deposition, the film deposition-rate decreases due to the reduced partial pressure of SiH<sub>4</sub>. For this reason, the film deposition-rate of  $\mu$ c-Si was thought to be unavoidably lower than that of a-Si. However, when a high pressure depletion method was proposed in the 1990s, using high pressures of over 200 Pa and high power capable of fully decomposing SiH<sub>4</sub>, high-rate film deposition of  $\mu$ c-Si became practical [41,42]. As another strategy for high rate film deposition, the use of VHF (30–300 MHz), much higher frequencies than normally used (13.56 MHz), as a power source also proved effective [43–45]. Because VHF plasma provides high electron density and low ion energy, it delivers such advantages as (a) increased film deposition-rate with efficient decomposition of SiH<sub>4</sub>, (b) fewer particles generated during high-rate film deposition, and (c) high quality film deposition even at high rates. By applying both the high pressure depletion method and VHF plasma, ultra high rate film deposition of over 5 nm/s has been reported using compact R&D equipment [46,47].

Although the high pressure depletion method is a useful technology, its application to processing large areas remains a challenge. To maintain stable SiH<sub>4</sub> plasma discharge under high-pressure conditions, the distance between the facing electrodes in the CVD equipment needs to be kept to within several millimeters. However, due to the thermal expansion, maintaining an accurate electrode distance is problematic in equipment for processing large areas of over 1 m<sup>2</sup>, because even a slight loss of parallelism between the facing electrodes causes uneven plasma distribution and thus an uneven thickness of the deposited film. The flow rate of SiH<sub>4</sub> and high-frequency power needs to be increased during high-rate film deposition, but Si particles generated by radical polymerization reactions in the vapor phase are absorbed in the formed film [33], thus substantially impacting the film quality of  $\mu$ c-Si.

To achieve large-area and high-rate deposition of  $\mu$ c-Si film by generating stable and uniform SiH<sub>4</sub> plasma in the high-pressure range of over 1000 Pa, we have been developing a unique process that we term “localized plasma confinement (LPC) CVD” [8–24]. Fig. 2 shows the schematic illustration of LPC-CVD equipment. One of the features of the LPC-CVD method is a pyramid-shaped protrusion installed on the cathode electrode surface. Because high-frequency fields are concentrated at the tip of each of the protrusions and become a starting point for plasma generation, stable plasma discharge is possible under high-pressure conditions, even at relatively large electrode distances. After the plasma transitions to normal condition, a large-area and high-pressure SiH<sub>4</sub> plasma can be maintained uniformly and stably, as if anchored to each protrusion tip. Another feature of LPC-CVD is the supply of gas from the tip of each pyramid-shaped protrusion on the cathode surface and removal via the canyon part between

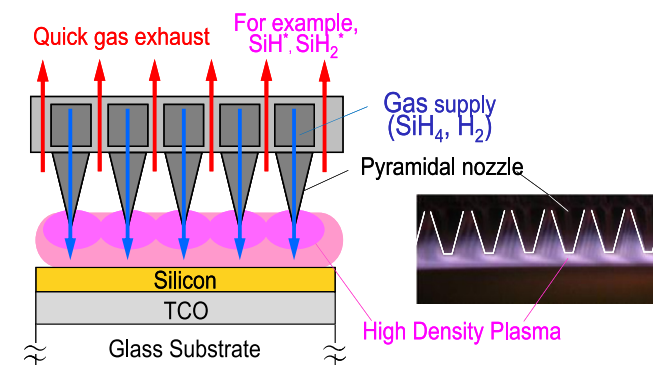


Fig. 2. Schematic image of the Localized Plasma Confinement CVD (LPC-CVD) method.

the protrusions. This configuration enables efficient decomposition of the gas supplied from the hole at the tip of each protrusion in a high electric field and achieves high film-deposition-rate and high efficiency of gas utilization [8,23]. Because the gas, after staying in the plasma for a fixed time period, is rapidly exhausted from the exhaust port near the supply port, over-decomposition of the material gas and polymerization can be minimized. The dwell time of  $\text{SiH}_4$  gas in the plasma and the rate of depletion can be maintained relatively uniformly within the electrode plane, leading to better uniformity of the deposited film. Although concerns existed in the early stages of development about possible transfer of pyramid-shaped protrusion pattern onto the substrate, avoidance of this potential problem has been confirmed by controlling the balance of film deposition parameters such as supplied power, pressure and electrode distance. The key point of this technology is to use the non-uniform plasma localized at each tip of the protrusion on the cathode electrode in the micro-view to obtain a uniform Si thin film over a large area by generating a uniform plasma from the macro view.

The hollow cathode method, in which the cathode is given a peak-and-valley shape, is a common technique for generating plasma. However, this method generates high-density plasma using electrons enclosed in the hollow part of the electrode [46]. Our LPC-CVD uses an entirely different mechanism for generating high-density plasma, since it utilizes the field concentration effect at the tip of the protruding cathodes. There is as yet no definitive answer as to which method is best suited for generating high density plasma for high-rate deposition of  $\mu\text{c-Si}$  for solar cells, but based on the need to transport the Si-based radicals generated in plasma efficiently to the substrate surface at high rate for film generation and ensure high efficiency of gas use, LPC-CVD, which radiates a high electric field from the protruding part of the electrodes to the substrate appears to be more suited to the LPC-CVD method than the hollow cathode method in which high density plasma is, by design, confined to the hollow part of the electrode.

Table 3 shows examples of film deposition parameters using LPC-CVD. As a high frequency power source, VHF (27.12 MHz) with double the conventional frequency (13.56 MHz) was adopted. This provides a uniform and stable plasma discharge, even in the high-pressure range of around 2000 Pa. The  $\mu\text{c-Si}$  produced by this method has been confirmed to show a good crystalline structure and crystal orientation suited for use in solar cells. For a substrate size of 550 mm  $\times$  650 mm (equivalent to the FPD industry's 3.5th generation), a film deposition-rate of 2.7 nm/s and film thickness distribution of  $\pm 2.4\%$  has been obtained, indicating good uniformity in the plane [10,23]. Development of a-Si/ $\mu\text{c-Si}$  tandem solar cells with  $\mu\text{c-Si}$  produced by LPC-CVD and adopted for the bottom cell are in progress in parallel. These cells, produced at a

Table 3

Examples of process parameters for LPC-CVD and conventional plasma-CVD.

Deposition parameters	LPC-CVD	Conventional plasma-CVD
Frequency of power source	27–40 MHz	13.56 MHz
Power density	1.0–3.0 W/cm <sup>2</sup>	< 1.0 W/cm <sup>2</sup>
Gas pressure	600–4000 Pa	100–500 Pa
Process temperature	180–230 C	180–230 C
Deposition rate	>3.0 nm/s	< 0.3 nm/s

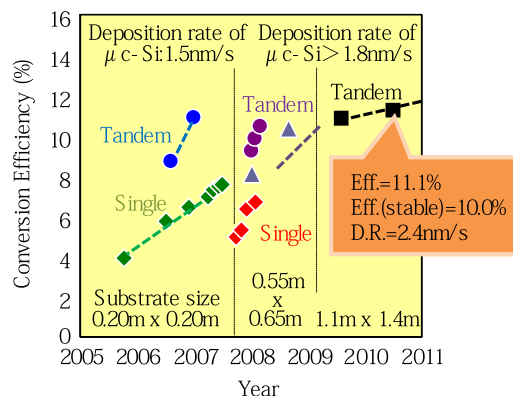


Fig. 3. Trends in the conversion efficiency of solar cells, the substrate size and deposition rate of the intrinsic layer of  $\mu\text{c-Si}$ .

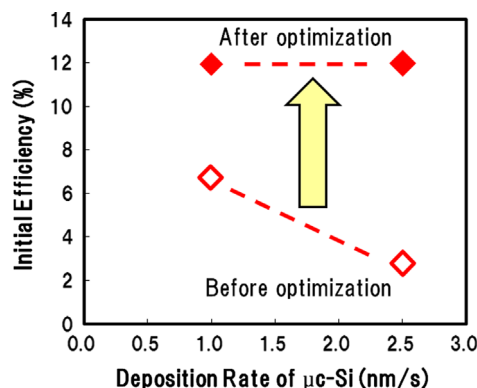


Fig. 4. Performance of tandem solar cells deposited by the G5.5 size plasma-CVD. ( $\diamond$ : before optimization,  $\blacklozenge$ : after optimization).

high rate of 2.0 nm/s, have shown conversion efficiencies that exceeds 10% (Figs. 3 and 4) [15–17].

## 5. Performance of tandem cells and modules

We were able to improve the performance of large-size tandem modules. Fig. 5 shows the  $I$ - $V$  characteristics of an a-Si/ $\mu\text{c-Si}$  tandem solar module (G5 size). An initial module efficiency of 12.0% and a stabilized module efficiency of 10.7% were achieved [16–24]. We are also studying very high-efficiency small-area cells. Fig. 6 shows the  $I$ - $V$  characteristics of an a-Si/ $\mu\text{c-Si}$  tandem solar cell (1 cm<sup>2</sup>). The initial conversion efficiency of 13.5% ( $V_{oc}$ : 1.41 V,  $J_{sc}$ : 12.7 mA/cm<sup>2</sup>, and FF: 0.754) and a stabilized conversion efficiency of 12.2% have been achieved for a small cell (area: 1 cm<sup>2</sup>) [16–24]. The stabilized efficiency was among the highest values achieved for a-Si/ $\mu\text{c-Si}$  tandem solar cells.

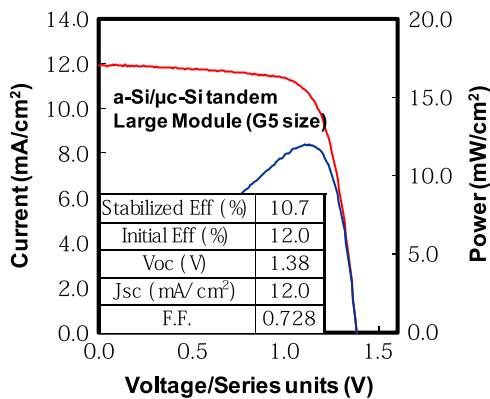


Fig. 5. *I*–*V* characteristics of a large-area (G5 size) a-Si/μc-Si solar module measured under AM 1.5, 100 mW/cm<sup>2</sup> light.

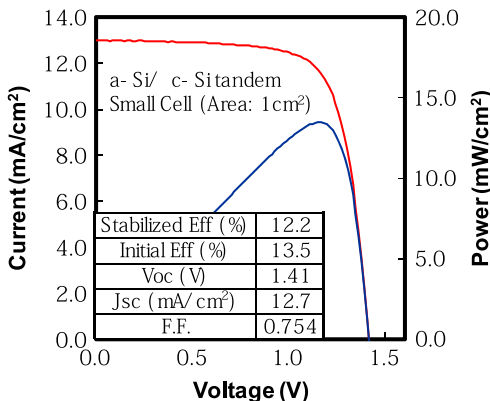


Fig. 6. *I*–*V* characteristics of a small-area (1 cm<sup>2</sup>) a-Si/μc-Si tandem solar cell measured under AM 1.5, 100 mW/cm<sup>2</sup> light.

## 6. Conclusions

Plasma-CVD process and equipment technologies for cost-effective and high performance solar cells and modules developed in Panasonic/Sanyo were reviewed. Low-cost production of solar cells essentially requires the development of high efficiency film deposition technology that is able to produce a high-quality a-Si layer and μc-Si layer using a plasma CVD process. A very high film deposition-rate of over 2.0 nm/s is required to produce the μc-Si layer. Effective technology for high rate production has been confirmed at the R&D level by using the LPC-CVD method. The author anticipates further progress in high-rate film deposition technology for thin-film silicon and a more rapid uptake of solar cells that should result from synergy between plasma CVD equipment technology for producing and maintaining high density uniform plasma over large areas and film deposition process technology for producing high-quality thin-film silicon.

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