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R&D activities of silicon-based thin-film solar cells in China

Yuwen Zhao[*, 1], **Xinhua Geng**[**, 2], **Wenjing Wang**[1], **Xudong Li**[1], and **Ying Xu**[1]

[1] Beijing Solar Energy Institute, No. 3 Huayuan Road, Beijing 100083, China
[2] Institute of Photo-electronic Thin Film Device and Technology, Nankai University, Tianjin, 300071, China

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The status and progress of R&D activities of silicon-based thin-film solar cells in China are described briefly in this paper, including amorphous Si solar cells and microcrystalline Si film solar cells based on PECVD technology and polycrystalline film solar cells based on RTCVD technology. Especially, the microcrystalline thin-film solar cells and the tandem solar cells of amorphous Si with microcrystalline Si have made great progress. The polycrystalline film solar cells have made remarkable achievements as well.

1 Introduction

Since the crystalline silicon solar cell was invented and used in space and ground applications, owing to crystalline material being very expensive, a variety of technology routes have been explored for reducing the cost of solar cells, among them the thin-film solar cell is regarded as the most promising photovoltaic (PV) technology and is the main aspect of R&D activities in the photovoltaic area. Silicon is the second most abundant element on earth, is nontoxic and Si-based thin-film solar cell has a plentiful and advanced technology resource in the semiconductor industry. The achievements and mature technology from crystalline silicon solar cells can be used for reference, which has high conversion efficiency with stable properties. Therefore, the Si-based thin-film solar cell is one of the focus areas of thin-film solar cells. The invention and development of amorphous silicon solar cells was one of the most brilliant achievements of PV specialists in the 20th century. At the same time, new types of microcrystalline silicon thin-film solar cell and polycrystalline silicon film solar cell are being explored unceasingly based on the advantages of both amorphous silicon and crystalline silicon solar cell, and notable achievements have been made. The R&D activities in this aspect of PV specialists in China are described in this paper.

2 Amorphous silicon solar cells

2.1 R&D history of a-Si solar cells in China

David Carlson and Christopher Wronski reported an a-Si solar cell with an efficiency of about 2.4% [1], which showed the birth of the a-Si solar cell. Thereafter, the R&D activities of amorphous silicon thin-film solar cell spread out vigorously all over the world.

The R&D activities on a-Si solar cell started in the late of 1970s in China. Since 1980 up to now, a-Si solar cell technology has made great progress in the aspects of film materials, cell structure, boundary

* Corresponding author: e-mail: zhaobts@public.bta.net.cn, Phone: +86-10-6201 2881, Fax: +86-10-62028651
** e-mail: xhgeng@public.tpt.tj.cn, Phone: +86-23502778, Fax: +86-23502778

features, deposition technology and assembly technology etc., the double-junction and triple-junction solar cells have appeared, and the efficiency and stability have improved greatly.

Since 1990, some fundamental research related to the a-Si film cell has been made by Chinese PV specialists, such as the mechanism of light-induced degradation, the transport mechanism, simulation and diagnosis of growth mechanism etc. Some theoretical issues related to a-Si solar cells were established, such as those by the scientists at the Institute of Semiconductor in Chinese Academic Science (ISCAS) who not only reported the light-induced Si–H bond variation for the first time, but also discovered the photodilation effect of undoped a-Si film, and found proof for light-induced microstructural variations from the electrical point of view [2]. The scientists in Nankai University had acquired a deep insight into the controversial question concerning "high" and "low" mobility of a-Si. They firmly sustained the "low" mobility viewpoint through the small displacement current experiment [3]. They also adopted the three-phase model to complete the calculation of the effective conductivity of microcrystalline silicon, which explained and guided successfully the achievement of high doping efficiency with a minor dopant, obtained p-μc-SiC with conductivity of 0.2 s/cm [4]. The scientists in the Gradated School of Chinese Academic Science (GSCAS) have developed the thermal activation conductivity model for a-Si in the whole temperature range that explained the exceptional phenomenon in the transport characteristic at low temperature [5] and this method for determination of defect density was adopted by the international community.

Before 2000, a series of good results in R&D activities of a-Si solar cell have been obtained, such as, an efficiency of a one-junction a-Si solar cell reached 11.2% for small size in ISCAS, 8.6% for 10×10 cm^2 in Nankai University, 6.5% for 30×30 cm^2 in the Institute for Nonferrous Metal, respectively, an initial efficiency 8.3% and stable efficiency 7.4% of a two-junction a-Si solar cell for 20×20 cm^2 has been reached in Nankai University [6, 7].

Industrial production of a-Si solar cells started early in the 1980s. The market share of a-Si solar cells in the PV industry in the world had reached more than 40% in the middle of the 1980s. In the late 1980s, Harbin and Shenzhen in China imported two a-Si solar cell production lines with 1 MWp capacity for each from Chrona in US.

An a-Si solar cell industry also development in the late 1990s in China, there are five a-Si solar cell module manufactures, in which Tianjin Jinneng produce the double-junction a-Si solar cell modules with glass substrate, the main products exported to Europe in 2004. The single-junction a-Si solar cell modules in China take an important share in the consumer goods (such as computer cells) market of the world.

2.2 Recent progress for a-Si thin-film solar cells in China

Energy and environment considerations have become more and more critical since entering the 21st century. The Chinese government enhances the support for R&D of the renewable energy technology, especially for the PV technology, in which Si-based thin-film solar cells are one of the most important aspects.

There are two tasks for the R&D of Si-based thin-film solar cells: the first is improvement of stable efficiency of large-area (20×20 cm^2) a-Si solar cell to 7–8% with a degradation rate less than 15% and a life of 20 years, and the study of advanced manufacturing technology with large area and low cost in order to move toward industrialization; the second is R&D of low-temperature deposition techniques of a-Si and μc-Si thin film with large area and high rate and a-Si/μc-Si tandem cell with improving efficiency further to 8–10% and a life of 20 years. By many years of effort, numerous achievements of Si-based thin-film solar cells have been obtained.

2.2.1 High deposition rate of device-grade a-Si thin films

The first VHF generator in China was developed in Nankai University. In this generator, the deposition rate of a-Si film has reached 5.3 nm/s with $\sigma_{ph}/\sigma_d \sim 10^6$, and superior stability than that deposited by RF-PECVD at 0.18 nm/s. By improving the electric field and gas-flow distribution, good homogeneity over

Table 1 Comparison of some thin-film properties and deposition techniques.

deposition technique	deposition rate	σ_{ph}/σ_d	homogeneity	stability	institution
VHF-PECVD	~5.3 nm/s	10^6	<10% on 400 cm^2 of area	better than RF-PECVD	Nankai University
VHF-PECVD	~0.5 nm/s	10^5–10^6	<10% on 100 cm^2 of area	light-degradation rate <10%	ISCAS
MW-PECVD	>2 nm/s	$>10^5$	–	–	BTU

a region of 20 × 20 cm^2 has been obtained with thickness variations within ±10%. ISCAS has obtained a-Si material by VHF-PECVD at 0.5 nm/s with σ_{ph}/σ_d from 10^5 to 10^6 and a light-induced degradation rate less than 10%. The thickness homogeneity over a region of 10 × 10 cm^2 is within ±10%. When the growth rate increase from 0.25 nm/s to 0.91 nm/s, the V_{oc} of a-Si solar cells decrease from 0.97 V to 0.91 V, while the FF is nearly constant at 0.7 and the performance of solar cells remains constant. On increasing hydrogen dilution and decreasing CH_4 of the p-layer, the V_{oc} is increased to 0.97–0.99 V. a-Si material with σ_{ph}/σ_d more than 10^5 at 2 nm/s was also obtained by MW-PECVD in Beijing Technology University of (BTU). Table 1 shows the comparison of some thin-film properties and deposition techniques.

2.2.2 a-Si solar cells

The properties of a-Si solar cells have seen large improvements, the conversion efficiency of an integrated single-junction a-Si solar cell module has reached 9.1% (V_{oc} = 18.23 V and FF = 70%) for 20 × 20 cm^2. The degradations were less than 10% after 500 h indoor light-soaking and 15% after one year outdoor light-soaking. The degradation test under high temperature and high humidity is regarded as the most rigorous degradation condition by standardization organizations. According to the international standard (IEC1646) for thin-film solar cell evaluation, a-Si solar cells with a size of 20 × 20 cm^2 showed almost no degradation, actually some sample's showed improved performance.

The conversion efficiency of a double-junction a-Si solar cell module has reached 9.2% for 20 × 20 cm^2, and conversion efficiencies of all cells of 40 successive batches are over 8%. And a 600 Wp PV power system has been installed for demonstration.

The conversion efficiency of a triple-junction a-Si solar cell with a-Si/a-SiGe/a-SiGe structure has reached 13 by ISCAS cooperation with international collaboration with Toledo University.

3 μc-Si thin film and solar cells

3.1 μc-Si thin films

Intrinsic μc-Si thin films with good uniformity over 20 × 20 cm^2 have been prepared by RF-PECVD with a showerhead electrode at 4 Torr and the rate of 4 Å/s in Nankai University. Also, the μc-Si films with device quality deposited at 0.6–0.8 nm/s with average grain size 45 nm and mobility 8.4 cm^2/V s are acquired by hot-wire CVD at GSCAS, the thickness homogeneity of the film over a region of 12 × 12 cm^2 is within ±10%. With this film, a solar cell with a high efficiency of 10.2% has been obtained with an n-μc-Si:H/c-Si structure.

3.2 μc-Si thin-film solar cells

Based on a μc-Si thin film with device grade quality, a 9.2% conversion efficiency of a single junction μc-Si solar cell with a pin structure and 0.253 cm^2 area has been obtained. Conversion efficiencies of

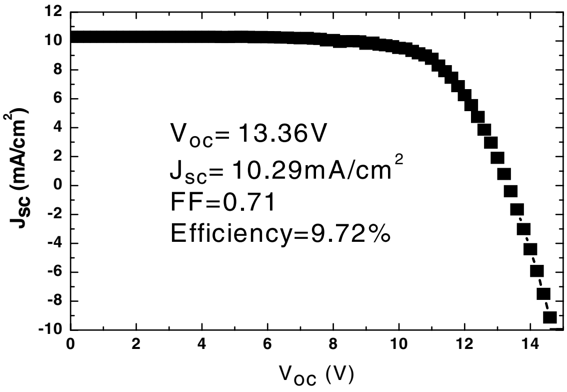

Fig. 1 *I–V* performance of an integrated 100 cm^2 a-Si/μc-Si tandem cell.

11.8% and 9.7% of a-Si/μc-Si tandem solar cell with 0.253 cm^2 and 100 cm^2 area, respectively, have been obtained [6, 8] as well, as shown in Fig. 1.

4 Polycrystalline silicon film and solar cells

4.1 Poly-Si films

The deposition of poly-Si films and solar cells made by RTCVD and ZMR technology have been achieved at the Beijing Solar Energy Institute. These poly-Si films have good crystallization properties with average grain size up to 1 mm and mobility as large as 50 cm^2/V s. Also, these poly-Si films with grain size of some micrometres have been obtained at a substrate temperature of 300 °C using $SiCl_4/H_2$ mixture gases in a conventional radio-frequency PECVD system at Shantou University.

4.2 Poly-Si film solar cells

Poly-Si solar cells are very attractive for their advantages of abundance, nontoxicity and deep technology background from the semiconductor industry. Many deposition techniques have been employed to fabricate silicon film, such as liquid phase epitaxy, sputtering, CVD, etc. Among them, rapid thermal chemical vapor deposition (RTCVD) offers some advantages such as high growth rate, direct growth of high-quality silicon film with large grain and fewer defects, solar cells have high efficiency and stable properties. But low cost substrates with resistance to high temperature are not easy to obtain. To explore the feasibility of this route, nonactive silicon, modeling ceramic and ribbon made of Si powder are used for substrates in R&D of polycrystalline film and solar cells, and some success has been obtained.

4.3 Nonactive substrate

The substrates for the thin-film process used are heavily doped ($\rho \sim 10^{-3}$ Ω cm) p-type monocrystalline silicon wafers with electrically nonactive impurities with no contribution to the light-induced current. In order to develop an optimized deposition technique and growth conditions, silicon thin films are deposited on this kind of p^{++} silicon substrates. The polycrystalline silicon films and solar cells were deposited on such silicon substrates by a RTCVD technique in 1100–1200 °C. By optimizing the process, the best result was obtained at the thickness of 37 μm with a 2 μm depth p^{++} buffer layer as a back surface field (BSF) layer deposited simultaneously. The p–n junction is formed by phosphorous diffusion with the square resistance of 80 ~ 200/sq. Then the wafer was thermal oxidized to form a SiO_2 film of thickness 1500 Å. Ti/Pd/Ag front electrodes and MgF_2/ZnS antireflective coating were used. The best conversion efficiency of 15.1% (cell area = 1.051 × 1.05 cm^2, V_{OC} = 637.1 mV, I_{SC} = 31.97 mA, FF = 0.78 AM1.5, 24.5 °C [9] has been achieved without cell surface texture. The cell structure and *I–V* performance and PC1D modeling result are shown in Figs. 2a and b, respectively.

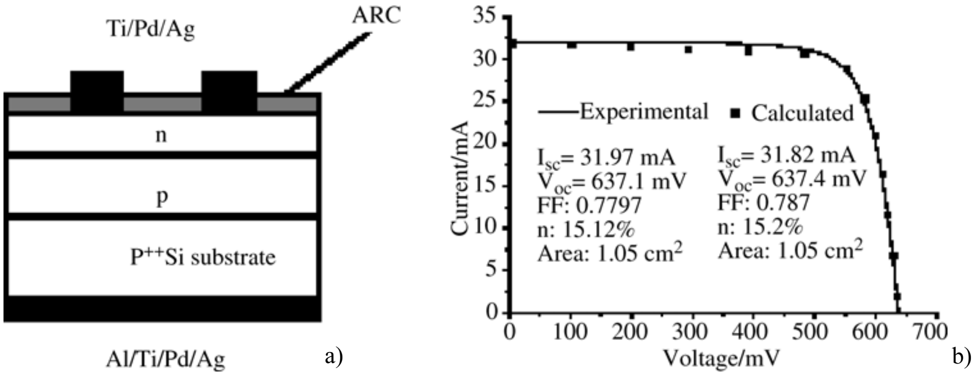

Fig. 2 Poly-Si film solar cell on nonactive silicon substrate, (a) cell structure, (b) $I-V$ performance of the cell.

4.4 Modeling ceramic substrate (nonactive-Si substrate covered by SiO_2 layer)

Poly-Si films and solar cells are fabricated by RTCVD and ZMR (zone melting recrystallization) on modeling ceramic substrate. A thermal oxidized SiO_2 layer is grown on nonactive p^{++} c-Si substrates surface. Then 20 × 20 μm apertures with space of 20 μm are formed by photolithography on this SiO_2 layer. The heavily doped seed layer is deposited by RTCVD, and SiO_2/Si_3N_4 capping layer is followed by electron-beam evaporation and LPCVD. The capping layer is used to prevent balling-up of the seed layer during the ZMR process. After the ZMR process, the capping layer is removed and the active layer is deposited by RTCVD. The resistance of the active layer is about 0.1 Ω cm, which is suitable for the thin-film solar cell. The p–n junction is formed by phosphorus diffusion under the optimized conditions. A SiO_2 layer of 1040 Å is formed by thermal oxidization as an antireflection coating, and evaporating Ti/Pt/Ag contacts are formed by a photolithography process.

The best efficiency of the thin-film solar cells is 10.2% (AM1.5, 24.5 °C) with a cell area of 1.07 cm^2. The structure and $I-V$ performance of the solar cell [10] are shown in Figs. 3a and b.

4.4 SSP silicon sheet from powder ribbon substrate

Silicon ribbon made of cheaper silicon powder is a possible candidate for a low-cost substrates for poly-Si film solar cells. R&D activities of Si ribbon materials and solar cells on such substrates are underway

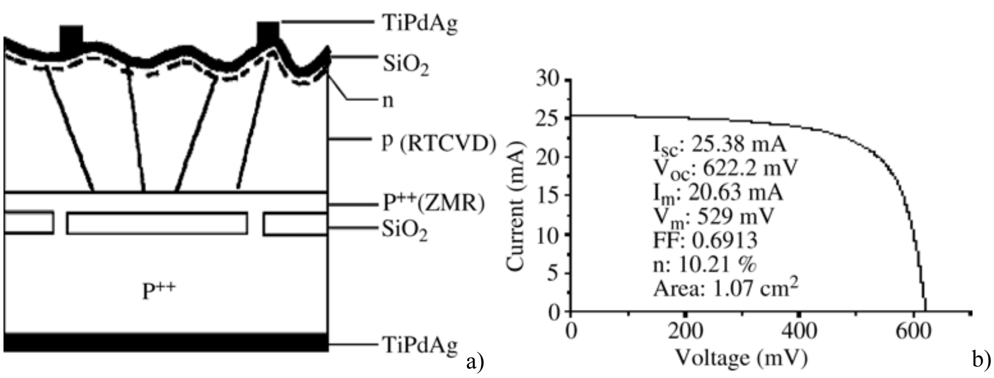

Fig. 3 Poly-Si film solar cell on modeling ceramic substrate (nonactive Si substrate covered by SiO_2 layer), (a) solar cell structure, (b) $I-V$ curve of the cell.

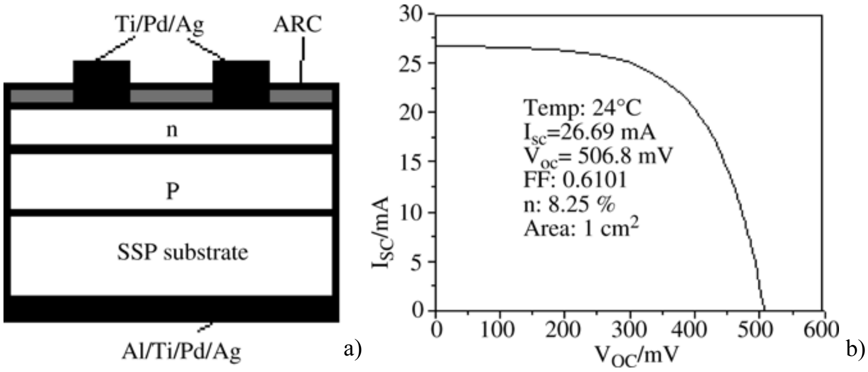

Fig. 4 Poly-Si film solar cell on SSP ribbon substrate, (a) cell structure, (b) *I–V* curve of the solar cell.

in Guangzhou Institute of Energy Conversion (GIEC), CAS. Using SSP ribbon made by GIEC as substrates, the poly-Si solar cells are made as following: After SSP ribbon substrate being cleaned, a p-type poly-Si film active layer is deposited by RTCVD, and then a p–n junction is formed by phosphorus diffusion, then an antireflection coating and contacts are formed in the same way as above. The conversion efficiency of the best solar cell is 8.3% V_{oc} = 506.8 mV, J_{sc} = 26.69 mA/cm^2 AM1.5, 24 °C, area = 1 cm^2 [11]. The structure and *I–V* performance of the solar cell are shown in Figs. 4a and b, respectively.

It can be seen from the R&D results above that poly-Si films and solar ells prepared by RTCVD have advantages with high deposition rate and high film quality. Experimental results show that solar cells with high efficiency and stable property can be made by this technique. The R&D activities are now focused on techniques for film deposition and cell manufacture. However, to get substrates with resistance to high temperature is the key issue of this technology route.

5 Summary

The status of R&D of Si-based film solar cells in China is introduced in this paper, including a-Si and µc-Si thin-film solar cells based on a low-temperature PECVD route and poly-Si film solar cells based on a RTCVD route. From the point view of the present technology, the low-temperature route based on PECVD technology is a more hopeful prospect with a lower energy budget, easy to get cheaper substrates and more mature technology and industry background. Some outstanding achievements in this aspect have obtained, such as the properties of a-Si and µc-Si thin film and solar cells have improved greatly with advanced technology, the conversion efficiency of integrated single-junction a-Si solar cell module has reached 9.1% with an area of 20 × 20 cm^2 the conversion efficiency of double-junction a-Si solar cell module has reached 9.2% with an area of 20 × 20 cm^2, and conversion efficiencies of all cells of 40 successive batches are over 8%. The conversion efficiency of triple-junction a-Si solar cells with a-Si/a-SiGe/a-SiGe structure has reached 13%. The conversion efficiency of single-junction µc-Si solar cells has reached 9.2%. Conversion efficiencies of 11.8% with 0.253 cm^2 area and 9.7% with 100 cm^2 area for a-Si/µc-Si tandem solar cell have been obtained, respectively, as well.

For poly-Si film solar cells based on the RTCVD route many achievements have also been obtained, such as a conversion efficiency of 15.1% on nonactive Si substrate, 10.2% on modeling ceramic substrate (nonactive Si substrate covered by SiO_2) and 8.3% on SSP ribbon substrate have been obtained, respectively, the true substrates with good resistance to high temperature and low cost are the key problem in this technology route.

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