



Controllable a-Si:H/c-Si interface passivation by residual SiH₄ molecules in H₂ plasma



Wenzhu Liu^{a,b}, Liping Zhang^{a,b}, Shiyuan Cong^c, Renfang Chen^{a,b}, Zhuopeng Wu^{a,b},
Fanying Meng^{a,b}, Qiang Shi^a, Zhengxin Liu^{a,b,*}

^a Research Center for New Energy Technology (RCNET), Shanghai Institute of Microsystem and Information Technology (SIMIT), Chinese Academy of Sciences (CAS), Jiading, 201800 Shanghai, PR China

^b University of Chinese Academy of Sciences (USAS), Shijingshan, 100049 Beijing, PR China

^c School of Physics and Optoelectronic Engineering, Dalian University of Technology, Dalian, 116024 Liaoning, PR China

ARTICLE INFO

Keywords:

Residual SiH₄

PECVD

Silicon heterojunction solar cell

A-Si:H/c-Si interface

C-Si surface passivation

ABSTRACT

Silicon heterojunction (SHJ) solar cell that combines traditional pure H₂ plasma treatments has been frequently reported in the literature. However, this method requires an individual gas blending step between a-Si:H film deposition and post H₂ plasma treatment to stabilize the gas environment in the PECVD chamber. Here, we report the introduction of residual SiH₄ molecules in H₂ plasma to treat SHJ solar cell devices. In contrast to the traditional H₂ plasma treatments, it requires no time interval between the a-Si:H film deposition and H₂ plasma treatment, i.e., we merely closed the SiH₄ inlet after the a-Si:H deposition. In the meantime, all other PECVD parameters were kept unchanged. Taking advantage of the decreasing SiH₄ density during the H₂ plasma process, a dense silicon layer was grown onto the top layer of the as-deposited a-Si:H film, which inhibited free H atoms effusing out of the low-mass-density a-Si:H network. The better a-Si:H/c-Si interface passivation results in improvements to both the short-circuit current density (J_{sc}) and open-circuit voltage (V_{oc}) of the SHJ solar cell in comparison to the counterpart cell treated by the traditional pure H₂ plasma. For instance, when the n⁺ a-Si:H window layer is as thin as ~ 1.8 nm, the power-conversion efficiency skyrockets from 2.35% treated by the traditional pure H₂ plasma to 16.09% treated by the H₂ plasma containing residual SiH₄ molecules. For a thicker n⁺ a-Si:H window layer of ~ 4.3 nm, the efficiency is also enhanced from 20.66% to 22.74%. This finding paves the way for a more efficient H₂ plasma treatment in pursuit of an outstanding SHJ solar cell.

1. Introduction

Today's high-tech industry productions depend on both technologies and economics. Si solar cells are still the main building blocks in the photovoltaic field and occupy the largest market share. Among the four mainstream types of Si photovoltaic devices, i.e., single crystal, multi-crystalline, thin-film crystal, and heterojunction solar cells, the Si heterojunction (SHJ) solar cell has recently achieved a world-record efficiency of 26.6% [1]. This solar cell is known for high open-circuit voltage (V_{oc}) [2], low temperature process [3], and superior temperature coefficient [4–6]. For SHJ solar cells, the c-Si surface passivation is always a critical issue because the short-circuit current density (J_{sc}), V_{oc} , and fill factor (FF) rely on the a-Si:H/c-Si interface defect density (D_{it}) [7]. Achieving low D_{it} is of broad interest for scientific research and mass production. The nanoscale a-Si:H films are usually coated onto c-Si substrate using chemical vapor deposition (CVD) techniques,

for instance, PECVD and Cat-CVD [8–11]. In practice, these CVD methods often encounter difficulties to obtain a high-quality a-Si:H/c-Si interface owing to incompatible structural nature: for a dense a-Si:H film covered on the c-Si surface, a high-defect-density Si epitaxial layer emerges at the a-Si:H/c-Si interface irrespective of gaining low-defect-density bulk a-Si:H layer [12]; in contrast, for the low-mass-density a-Si:H passivation layer, huge amounts of Si–dangling bonds on the c-Si surface are unsaturated regardless of an abrupt a-Si:H/c-Si interface [13]. A viable tradeoff is to separate the passivation process into two individual steps. First, the low-mass-density a-Si:H film is deposited on the clean textured c-Si surface so as to achieve an abrupt a-Si:H/c-Si interface. Next, the H₂ plasma is utilized to furnish H atoms into the high-defect-density a-Si:H/c-Si interface, which decreases the surface recombination velocity [14]. The H₂ plasma treatments reported in the literature usually use pure H₂ as the source gas, where the glow-discharge plasma was necessarily terminated after the film growth so as to

* Corresponding author at: Research Center for New Energy Technology (RCNET), Shanghai Institute of Microsystem and Information Technology (SIMIT), Chinese Academy of Sciences (CAS), Jiading, 201800 Shanghai, PR China.

E-mail address: z.x.liu@mail.sim.ac.cn (Z. Liu).

<http://dx.doi.org/10.1016/j.solmat.2017.09.009>

Received 4 May 2017; Received in revised form 17 August 2017; Accepted 7 September 2017

0927-0248/© 2017 Published by Elsevier B.V.

exhaust the SiH_4 molecules and stabilize the H_2 gas environment in the CVD chamber. After the H_2 plasma is quenched, the free H mobility from the cell device to the vacuum is a negative factor in fabricating excellent SHJ solar cells, which is significant for the low-mass-density a-Si:H thin film.

In contrast to the majority of the H_2 plasma treatment, this work deliberately retained residual SiH_4 molecules in the H_2 plasma to treat the a-Si:H/c-Si hetero-structures. Compared to the traditional pure H_2 plasma, there was no time interval between the a-Si:H film growth and the post H_2 plasma. The characteristics of the SHJ solar cells treated by the H_2 plasma with residual SiH_4 molecules showed a substantially higher J_{sc} and V_{oc} in comparison to those treated by the traditional pure H_2 plasma. This finding shows a clear technical guide to optimize the SHJ solar cells.

2. Experimental

2.1. SHJ solar cell fabrication

180 μm , 1–6 Ωcm , 12.5 \times 12.5 cm^2 (100) CZ Si wafers were textured with alkali solution, cleaned with the standard RCA process, and etched by 2% HF water solution. They were utilized as the absorption layers of the SHJ solar cells. After the cleaning process, the a-Si:H layers and the tungsten-doped indium oxide (IWO) anti-reflection layers were respectively deposited by PECVD and reactive plasma deposition (RPD) on both surfaces. Finally, Ag electrodes with the traditional finger and busbar patterns were screen printed onto both sides of the cells. There are three main grids and 64 fine grids on the front side, and there are three main grids and 111 fine grids on the rear side. The cell structure is designed with a rear emitter (as schematically shown in Fig. 1a) with the potential to achieve a high efficiency [15]. In this investigation, deposition time of the n^+ a-Si:H layer was varied, i.e., 15 s, 25 s, and 35 s. For each case, the front-side a-Si:H was treated differently (see Fig. 1b–d). In Fig. 1b, the as-deposited n^+ a-Si:H window layer was not treated by the post H_2 plasma, and these solar cells are named as AS-DEPOSITED. In Fig. 1c, the H_2 and PH_3 blending gas was stabilized for 60 s after the n^+ a-Si:H growth, during which the residual SiH_4 molecules were exhausted. After that, 20 s H_2 plasma was applied to the a-Si:H layers; thus, the corresponding solar cells are denoted as hydrogen plasma treatment (HPT). In Fig. 1d, the SiH_4 inlet was closed as soon as the n^+ a-Si:H window layer was finished. However, other parameters such as the H_2 and PH_3 flow rates, power density, gas pressure, and chamber temperature were kept unchanged. This H_2 plasma process differs from the traditional one in Fig. 1c because the residual SiH_4 molecules remained in the PECVD chamber, and the partial pressure ratio of $[\text{H}_2]/[\text{SiH}_4]$ increased monotonously as the H_2 plasma time

advanced. It was a non-equilibrium plasma process due to the gradual exhaustion of the SiH_4 molecules. To distinguish from the solar cells in Fig. 1c, those in Fig. 1d are denoted as HPT– SiH_4 . The H_2 , SiH_4 , and PH_3 flow rates were 400 sccm, 150 sccm, and 7 sccm, respectively, during the deposition of the n^+ a-Si:H layers, and the H_2 , PH_3 flow rates were 400 sccm and 7 sccm, respectively, during the H_2 plasma treatments in Fig. 1c and d. Although the PH_3 molecules were sustained during the post H_2 plasma processes, we still call them H_2 plasma treatments because the PH_3 molecules were diluted in H_2 with a volume fraction of 2%; therefore, the partial pressure ratio of $[\text{PH}_3]/[\text{H}_2]$ was as low as ca. 0.03%, and thus, the H densities were dominated by H_2 .

2.2. Characterization and numerical analysis

The fabricated SHJ solar cells were first annealed at 200 $^\circ\text{C}$ for 30 min, and then were measured by a solar simulator at 25 $^\circ\text{C}$, AM 1.5 G. Minority carrier lifetime (τ_{eff}) of n^+ a-Si:H/i a-Si:H/c-Si/i a-Si:H/p a-Si:H symmetrically passivated architectures were probed using a Sinton tester (Sinton WCT-120). The external quantum efficiencies (EQE) of the cell devices were detected shortly after the efficiency measurements so as to interpret the J_{sc} deviations. The EQE and band offset analysis of the SHJ solar cells were conducted by means of the AFORS-HET simulations [16], during which the front-side a-Si:H/c-Si interface D_{it} was adapted from $1 \times 10^{10} \text{cm}^{-2}$ to $5 \times 10^{13} \text{cm}^{-2}$. The dependence of the EQE curve shape on the emitter junction was also separately considered.

A piece of a single polished (100) float-zone Si wafer (FZ; thickness, $525 \pm 25 \mu\text{m}$; resistivity, $> 3000 \Omega\text{cm}$) was dipped in 2% HF water solution for 2 min to remove its surface native oxides, followed by a scan using the Fourier transform infrared spectroscopy (FTIR; PerkinElmer, Spectrum 100) in the background mode. Another three FZ Si wafers were also etched by the HF solution. Subsequently, 10 nm i a-Si:H, 5 nm i a-Si:H/3 nm n^+ a-Si:H (treated by traditional H_2 plasma, identical to the front side of cell HPT), and 5 nm i a-Si:H/3 nm n^+ a-Si:H (treated by H_2 plasma with residual SiH_4 molecules, identical to the front side of the cell HPT– SiH_4) were coated onto their mirror surfaces. These samples were then characterized with the FTIR in the sample mode. The deposition conditions of i a-Si:H and n^+ a-Si:H were the same as those of the passivation layer and window layer of the SHJ solar cells. Si 2p spectra of these two i/ n^+ a-Si:H layers were acquired by the X-ray photoelectron spectroscopy (XPS; ESCALAB 250Xi, Thermo Fisher, USA; Al K_{α} source) to probe the surface Si–Si and Si–H bond environments.

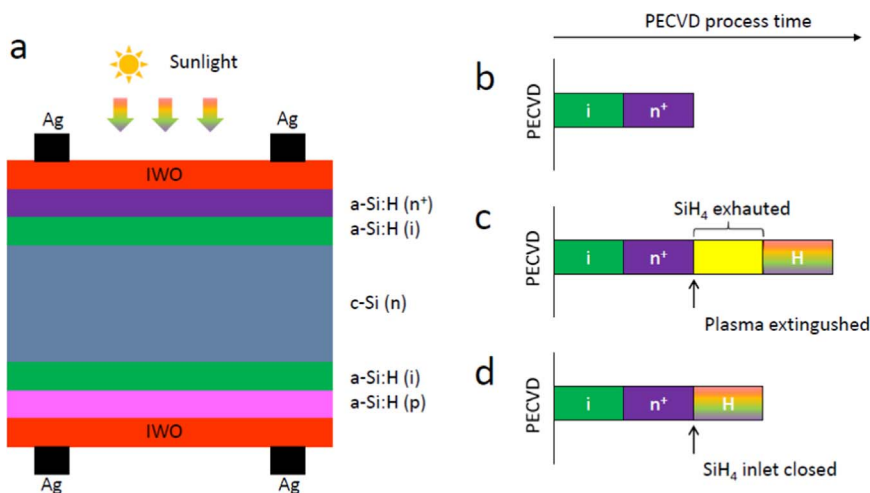


Fig. 1. a) is the architecture of the SHJ solar cell. b), c), and d) are deposition processes of the front-side a-Si:H layers of the SHJ solar cells AS-DEPOSITED, HPT, and HPT– SiH_4 , respectively.

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