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Nanostructured silicon *p*-layer obtained by radio frequency power profiling process for high-efficiency amorphous silicon solar cell



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ABSTRACT

A RF power profiling process has been developed to efficiently grow nanostructured silicon (nc-Si:H) *p*-layers for high-efficiency amorphous silicon solar cells. The *p*-layer deposition starts at a relatively low power in the initial stage, which is then continuously and rapidly increased to a high level until the bulk *p*-layer deposition is finished. Incorporating the *p*-layer into a-Si:H solar cell resulted in high V_{oc} and high *FF* simultaneously, which can be ascribed to the reduced recombination at the *i/p* interface caused by the suitable band-gap of *p*-layer, low ion damage to *i/p* interface, and appropriate band-gap matching between *p*- and *i*-layers during the RF power profiling process. An initial efficiency of 10.8% for an a-Si:H solar cell with both high V_{oc} of 0.99 V and high *FF* of 0.72 was obtained. This power profiling scheme is potentially advantageous since it is easier to integrate into continuous process.

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1. Introduction

In silicon thin-film solar cells the *p*-layer serves several roles including establishing a built-in potential together with the *n*-layer and acting as a window layer for incident sunlight. The essential requirements for the *p*-layer include high conductivity, low activation energy, and wide band-gap. The low active energy helps to increase the built-in potential and the high conductivity reduces the series resistance between the *p*-layer and the transparent conductive oxide (TCO) layer, while a wide band-gap allows more sunlight transmitting through the *p*-layer and being absorbed by the *i*-layer. In addition, an appropriate band-gap matching between *p*- and *i*-layers is necessary to reduce carrier recombination at the *i/p* interface and then improve the total device performance. Thus, the *p*-layer plays a crucial role in achieving high-efficiency a-Si:H based thin-film solar cells.

In the past decades, a variety of *p*-type hydrogenated silicon alloy layers have been intensively investigated for the V_{oc} improvement in a-Si:H solar cells, such as amorphous silicon carbide (a-SiC:H) [1], amorphous silicon oxide (a-SiO_x:H) [2], microcrystalline silicon carbide (μc-SiC:H) [3], protocrystalline silicon (proto-Si:H) [4], nanocrystalline silicon oxide (nc-SiO_x:H) [5,6], microcrystalline silicon (μc-Si:H) [7], nanocrystalline silicon(nc-Si:H) [8–10], and double *p*-layer [1,11]. The

deposition of the SiC:H and SiO_x:H may cause carbon and oxygen diffusion into *i*-layer and deteriorate the *i*-layer quality, while proto-Si:H is sensitive to thickness as its growth is just below the threshold of an amorphous-to-microcrystalline phase transition [4,11]. Recently, *p*-nc-Si:H with a mixed-phase structure, which consists of Si nanocrystals (Si NCs) embedded in a-Si:H matrix, was proved to be a very effective *p*-layer for high-efficiency a-Si:H based thin-film solar cells [8–10]. Usually, a combination of high RF power, high hydrogen-to-silane flow ratio, high pressure, and low temperature is required to achieve the *p*-nc-Si:H layer with wide band-gap, which is commonly explained by the quantum-size confinement effect in Si nanocrystals [8–13]. However, the high power inevitably leads to ion damage to *i/p* interface and results in poor-quality devices. In terms of optical absorption, a wide band-gap *p*-layer is preferable. On the other hand, the band-gap of a-Si:H *i*-layer is 1.8 eV and it is even lower for amorphous silicon germanium (a-SiGe:H) *i*-layer (1.4–1.6 eV) and microcrystalline silicon (μc-Si:H) *i*-layer (~1.2 eV). A much wider band-gap of *p*-layer undoubtedly causes a large band-gap-discontinuity between the *p*-layer and *i*-layer, resulting in high carrier recombination rate at *i/p* interface and deterioration of the solar cell performance [14–17]. Therefore, how to produce a wide band-gap *p*-layer that not only matches the *i*-layer band-gap, but also does little damage to the *i/p* interface is a crucial issue to achieve high-efficiency a-Si:H based solar cells. In this paper we have developed a RF power profiling scheme for *p*-layer deposition. The experimental results indicate that the performance of solar cell using this *p*-layer can be greatly improved.

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2. Experimental details

Hydrogenated silicon (Si:H) thin films and solar cells were deposited using radio frequency (RF, 13.56 MHz) plasma enhanced chemical vapor deposition (PECVD) in an ultrahigh-vacuum, multi-chamber, cluster-tool system. Mixtures of B_2H_6 , SiH_4 and H_2 were used for the deposition of *p*-type Si:H layers, while the p - μc - SiO_x :H layers were obtained by mixing SiH_4 , H_2 , CO_2 and trimethylboron (TMB). Si:H films on Eagle2000 glass substrates were used for structural and opto-electrical characterization, while stainless steel (SS) and Ag/ZnO back reflector (BR) were used as substrates for *a*-Si:H solar cells with configuration of BR/*n*-*a*-Si:H/*i*-*a*-Si:H/*p*-*nc*-Si:H or p - μc - SiO_x :H/ITO/Al grid. The parallel conductivity was measured with coplanar electrode structure, while activation energy (E_a) was calculated from the temperature dependent conductivity. The absorbance and reflectance spectra were measured with a Varian Cary 5000 UV–vis–NIR spectrophotometer to calculate the band-gap (E_g). High-resolution transmission electron microscopy (HR TEM) was adopted for structural characterization using Philips Tecnai G²F20. Current–voltage curves were measured using a dual-lamp Wacom solar simulator (WXS-156S-L2, AM1.5GMM) under AM1.5, 100 mW/cm² and 25 °C. Quantum efficiency (QE) measurements were made in the range of 350–800 nm using QEX10 (PV Measurement) system.

In general the Tauc's equation is not strictly valid for the exact estimation of the band-gap of the mixed-phase materials [18–20]. However, the Si NCs are generally considered to behave direct or quasi-direct band-gap because of quantum confinement effect [21]. The dominate part of the mixed-phase sample is amorphous phase, which behaves direct band-gap. Hence, the mixed-phase sample can be regarded as direct band-gap material. The Tauc's equation can be used to estimate an approximate band-gap of such mixed-phase materials in this paper [19]. In order to avoid the influence of thickness on the reliability of absorption measurement, a multiple bilayer structure is developed. A *p*-*nc*-Si:H layer was first deposited with thickness of 20 nm, followed by an ultra-thin *a*-Si:H layer with thickness of 1–2 nm. Then the *p*-*nc*-Si:H layer and ultra-thin *a*-Si:H layer were alternatively deposited with ten pairs of *p*-*nc*-Si:H/*a*-Si:H with a total thickness of about 210 nm. The ultra-thin *a*-Si:H layer can block the epitaxy growth of *p*-*nc*-Si:H to avoid the micro-structure evolution. Simultaneously, the ultra-thin thickness of 1–2 nm guarantees a very low absorption. The transmission and reflection measurement of ten pairs of *p*-*nc*-Si:H/*a*-Si:H with a total thickness of 210 nm is much more reliable than that of single *p*-*nc*-Si:H layer with a thickness of 20 nm.

3. Results

3.1. RF power profiling process for Si:H *p*-layers

Fig. 1 shows schematic diagram of different *p*-layer deposition processes in the *n*-*i*-*p* *a*-Si:H based solar cells. For the standard *nc*-Si:H *p*-layer shown in Fig. 1(a) (dash line), all the deposition parameters were kept constant with high hydrogen-to-silane flow ratio ($R=[H_2]/[SiH_4]$) of 200, high RF power P_2 of 150 W, high pressure of 2 Torr and low temperature T_s from 100 °C to 150 °C. For the RF power profiled *p*-layer shown in Fig. 1(b) (solid line), the deposition started at a relatively low power P_1 that had a value in the range from one third to one half of P_2 during the time from 0 to T_1 , resulting in a typical thickness 2–3 nm. Then the power continuously and rapidly increased from P_1 to P_2 during the time from T_1 to T_2 , leading to a typical thickness 2–3 nm. Then the *p*-layer is completed at P_2 during the time from T_2 to T_3 with typical thickness 15 nm. Thus the total *p*-layer thickness was around 20 nm. By changing the deposition time (T_1 , T_2 and T_3) and RF power (P_1 , P_2), the *p*-layer structures and properties can be conveniently adjusted.

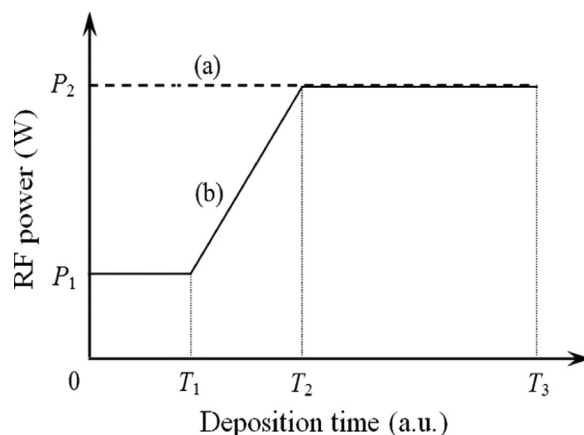


Fig. 1. Schematic diagram of different *p*-layer deposition processes for *n*-*i*-*p* *a*-Si:H solar cells. (a) Standard process (dash line), (b) RF power profiling process (solid line).

3.2. Opto-electrical properties and micro-structural characterization of Si:H *p*-layers

Here five different *p*-layers with similar thickness of 20 nm were prepared under identical pressure of 2 Torr. Sample *a* and *b* were standard *p*-layers deposited at 50 W and 150 W, respectively. Sample *c* was deposited with profiled power from 50 W to 150 W, while the profiled power from 75 W to 150 W was used to deposit sample *d*. Sample *e* was μc - SiO_x :H *p*-layer deposited at 13 W. Opto-electrical and structural properties of different *p*-layers on glass substrates were listed in Table 1. Sample *b*, *c* and *d* show similar conductivities, E_a and E_g , while sample *a* shows higher conductivity, slightly lower E_a and a relatively low E_g of 1.82 eV. Sample *e* demonstrates parallel conductivity $\sim 10^{-7}$ S/cm, E_a of 0.3 eV and E_g of 2.2 eV.

HR TEM characterization was carried out to get detailed micro-structure of the above *p*-layers. In order to simulate the actual *i/p* interface in the *n*-*i*-*p* *a*-Si:H solar cells, a double-layer structure was adopted for the preparation of the samples (a), (b), (c) and (d) for the TEM imaging (see Fig. 2). In these samples, an identical 5 nm *a*-Si:H *i*-layer was first deposited, following by the *p*-layer deposition. All the deposition processes and parameters were the same as those corresponding to the samples *a*, *b*, *c* and *d* in Table 1. Fig. 2 shows that these four samples have similar mixed-phase structure with Si NCs embedded in the *a*-Si:H matrix. However, the Si NC sizes obviously differ with each other. It is well-known that the electrical and optical properties of Si:H films are remarkably affected by the size, density, and size distribution of the Si NCs [12,13,22,23]. In Fig. 2(a), Si NCs with diameter from 6 nm to 8 nm or even larger could be seen. Samples illustrated in Fig. 2(b)–(d) have much smaller Si NCs with diameters from 2 nm to 5 nm, which is comparable to the Bohr radius of bulk crystalline Si or even smaller. The Si NC density is low and most of Si NCs exist in isolated states. The small size and dispersed distribution of Si NCs are believed to induce strong quantum confinement effect, which is regarded as the general exploitation for wide band-gaps [12,13,18,19]. In addition, the dominated part of the mixed-phase silicon-films is amorphous tissues, which will lead to better surface passivation of Si NCs and then help to improve the properties. Furthermore, these mixed-phase samples were deposited with very high hydrogen dilution ($R=[H_2]/[SiH_4]=200$). The hydrogen-induced band-gap broadening by the hydrogen rich shell surrounding the Si NC is another possible reason [23,24].

3.3. Influence of *p*-layers on *a*-Si:H solar cell performance

The influence of *p*-layers on a solar cell performance can be most convincingly judged from factual devices. We prepared five

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