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Advanced materials processing for high-efficiency thin-film silicon solar cells



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ABSTRACT

Available online 2 July 2013 Keywords: Hydrogenated amorphous silicon Hydrogenated microcrystalline silicon Plasma-enhanced chemical vapor deposition Light-soaking stability Tandem cell Microstructure We report on recent developments of hydrogenated amorphous silicon (a-Si:H) and microcrystalline silicon (μ c-Si:H) for high-efficiency thin-film silicon solar cells. For a-Si:H, the light absorber layers were grown by a remote plasma technique using a triode electrode configuration in plasma-enhanced chemical vapor deposition (PECVD). Despite the relatively low deposition rate (0.01–0.03 nm/s) compared to the conventional diode-type PECVD process (~0.2 nm/s), the light-induced degradation in conversion efficiency ($\Delta \eta/\eta_{ini}$) of single-junction solar cell is substantially reduced (e.g., $\Delta \eta/\eta_{ini} \sim 10\%$ at an absorber thickness of 250 nm). As a result, we have obtained confirmed stabilized efficiencies of 9.6% and 11.9% for a-Si:H single-junction and a-Si:H/ μ c-Si:H tandem solar cells, respectively. Meanwhile, for μ c-Si:H solar cells, we have investigated the structural properties of the μ c-Si:H absorber layers grown at high deposition rates (> 2 nm/s). Several design criteria for the device grade μ c-Si:H are proposed in terms of crystallographic orientation, grain size and grain boundary passivation.

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1. Introduction

Thin-film silicon solar cells offer several advantages over conventional wafer-based silicon solar cells such as low silicon consumption, large area deposition, short energy pay-back-time, and better outdoor performance under high temperature. In the last two decades, solar cell efficiency has been improved by employing a hydrogenated amorphous silicon (a-Si:H) and microcrystalline silicon (μ c-Si:H) double-junction tandem structure, known as micromorph [1] and hybrid [2] solar cells, fabricated by plasma-enhanced chemical vapor deposition (PECVD). Despite their excellent combination in terms of the band gaps of the absorber materials, however, the conversion efficiency of the a-Si:H/ μ c-Si:H tandem cell remains nearly half of that of high-efficiency wafer-based silicon solar cells, while the production cost of the tandem module is not yet sufficiently low.

A bottleneck that primarily hinders the efficiency progress in thin-film silicon solar cells is the light-induced degradation in a-Si:H, known as the Staebler–Wronski effect [3]. Although a variety of deposition techniques have been proposed to improve the light-soaking stability of a-Si:H, the substantial reduction of the light-induced degradation has not been satisfactorily demonstrated, particularly for the device exhibiting high initial efficiency. Concerning the μ c-Si:H bottom cell, on the other hand, a technological issue remains in the production throughput. Due to the requirement of the

thicker absorber layer (~2 μ m) than a-Si:H top cell (~0.2 μ m) in tandem device, the μ c-Si:H bottom cell layer has to be formed at higher deposition rate, which is essential in reducing the production cost. However, it has been recognized that increasing the deposition rate while keeping device-grade quality is generally difficult because the film quality is damaged by high-energy bombardment of ionic species during the high-rate plasma deposition process [4].

In AIST, we have implemented fundamental research to demonstrate highly stable a-Si:H and high-deposition-rate µc-Si:H in the laboratory small area devices. For a-Si:H solar cells, we have applied a triode PECVD technique [5–8] to grow intrinsic a-Si:H layer in the fabrication of p-i-n junction solar cells. It is demonstrated that high-efficiency solar cells with low light-induced degradation can be attained in both a-Si:H single-junction and a-Si:H/µc-Si:H tandem solar cells [8]. For µc-Si:H bottom cells, we have developed a high-rate deposition process based on a combination of veryhigh-frequency (VHF) [9,10] and high-pressure depletion (HPD) [4,11] glow-discharge techniques. This deposition process enables high-rate μ c-Si:H deposition (> 2 nm/s) while preserving excellent film qualities in terms of dense microstructure and stable passivation of grain boundaries [12]. As a result, an efficiency of 9.1% has been obtained at a deposition rate of 2.3 nm/s [13]. The up-scaling of the high-rate deposition technique has been realized in the square meter-sized module production [14].

In this paper, we review our recent advances in materials processing and device fabrication for high-efficiency thin-film silicon solar cells. In the first section, we will present the status of our development of the a-Si:H and a-Si:H/ μ c-Si:H solar cells

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towards the high light-soaking stability and high stabilized efficiency. The second section describes the material and device properties of the μ c-Si:H prepared at various high-rate deposition regimes. Some key issues that determine the device-grade quality of the μ c-Si:H are discussed based on our structural investigation.

2. Experimental

All solar cell devices, including a-Si:H and µc-Si:H singlejunction cells, and a-Si:H/µc-Si:H tandem cells, were fabricated in a superstrate p-i-n configuration on textured transparentconductive-oxide (TCO) layer coated glass substrates. The silicon p-, i-, and n-layers were deposited by PECVD in the multichamber systems. The light absorber layers (i-layers) were deposited by a VHF plasma technique at frequency of either 60 or 100 MHz. The detail of the deposition processes for a-Si:H and µc-Si:H layers will be described in the following sections and references therein. The device area (0.25 or 1.04 cm²) was defined by a patterned back contact consisting of ZnO/Ag/ZnO stacked layers deposited by sputtering. The first ZnO/Ag layers act as a back reflector, while the last ZnO layer serves for protection of Ag in the post-deposition processes. For some solar cells, an edgeisolation process was carried out by reactive plasma etching to reduce the contribution of the peripheral dark current component. Before cell characterization, solar cells were annealed at 160-200 °C in vacuum for 2 h. The current density-voltage (I-V)characteristics of the solar cells were measured under standard air mass 1.5 (AM1.5) global illumination condition (irradiance: 100 mW/cm², cell temperature: $T_{\rm C}$ =25 °C). To avoid overestimation of the photocurrent of the solar cells, a black mask was used to define an illumination area (0.23 or 1.00 cm²) that was slightly smaller than the device area. For a-Si:H and a-Si:H/µc-Si:H solar cells, device performance was characterized in the initial and light-soaked states. The light-soaking experiment was carried out under AM1.5 illumination with 100 mW/cm² ($T_{\rm C}$ =50 °C, 1000 h, open circuit) [15] or 125 mW/cm² ($T_{\rm C}$ =48 °C, 310 h, open circuit) [16] intensities. In our experiment, we confirm that stabilized efficiencies after light-soaking tests under these two conditions are almost identical. For some selected samples, *I-V* characteristics after these light soaking were measured by the Calibration, Standards and Measurement Team of AIST. In addition, some of the solar cells were exposed to 300 mW/cm² illumination at $T_c = 60 \,^{\circ}\text{C}$ for 6 h as a quick degradation test. It should be mentioned that this light-soaking condition gives slightly less degradation than the other conditions described above. However, we confirmed that the absolute efficiency after light-soaking differs by only 0.1-0.2%.

3. Results and discussion

3.1. Amorphous silicon

The light-induced degradation in a-Si:H has been a subject of research over the past three decades. Although a considerable amount of effort has been made in aiming to eliminate this adverse effect, the complete suppression of the light-induced degradation has not been demonstrated so far in the practical p–i–n junction solar cell devices. Nevertheless, it is widely known that the light-soaking stability of a-Si:H films [17] and solar cells [18] is improved as the density of dihydoride (Si–H₂) bond (or density of Si–H_n (n=1–3) bond in the internal void surface) decreases in a-Si:H. Furthermore, it is argued that the Si–H₂ bond density can be reduced by preventing the

incorporation of reactive species (such as SiH₂ and higher silane radicals (Si_nH_m, n > 2) generated in plasma) into the film during the a-Si:H deposition [19]. For this purpose, an application of a triode electrode configuration in the PECVD process is proposed as a radical separation technique [5,6], which provides stable a-Si:H films with less Si–H₂ bond density as compared to the films deposited by the conventional PECVD with a diode electrode configuration.

In Fig. 1, a schematic diagram (a) and a typical photo (b) of the SiH₄–H₂ glow discharge in the triode PECVD reactor are shown. The plasma was generated with a 60 MHz excitation at a power density of 60 mW/cm², and SiH₄/H₂ flow rates of 20/20 sccm. A mesh electrode was placed 20 mm above the powered electrode. A dc voltage of -25 V was applied to the mesh to confine the glowdischarge plasma between the powered and mesh electrodes. This negative bias application is a necessary step to avoid the penetration of the accelerated electrons through the mesh. As a result, no visible plasma exists between the mesh and grounded electrodes, as shown in Fig. 1(b). Note that the bluish portions appearing at the mesh and grounded electrodes are due to the reflection of light coming from the plasma zone underneath. In our deposition setup, the deposition rate can be controlled in the range from ~0.01 to ~0.05 nm/s by varying the distance between the mesh and substrate (L_{M-S}) without changing plasma-generation condition. As a reference material, a-Si:H films were also deposited by our standard diode PECVD system (13.56 MHz) at a deposition rate of 0.25 nm/s.

In the triode PECVD process, the growth of a-Si:H is dominated by the diffusion of long-lifetime radicals such as SiH₃ [5]. Thus, the incorporation of short-lifetime radicals such as SiH₂ and higher silane radicals (Si_nH_m, n > 2) can be reduced effectively by moving the surface of the growing film away from the plasma zone. In Table 1, some properties of the a-Si:H lavers deposited by triode PECVD and our standard diode PECVD are compared. Although the deposition rate is reduced by an order of magnitude for triode PECVD, the material parameters such as the optical band gap and hydrogen content are nearly identical to those of the reference a-Si:H films. In the Fourier-transform infrared (FTIR) spectra, however, the a-Si:H films grown by triode PECVD exhibit low intensity of the silicon-hydride stretching mode at ~2100 cm^{-1} , which is a signature of the material having a compact microstructure [17]. The Si-H₂ bond density, deduced from the high stretching mode in the FTIR spectrum, is reduced from 2.1 to 0.7 at%, while the Si-H bond density, deduced from the low stretching mode (~2000 cm⁻¹), remains almost constant at 10-11 at%. The slightly lower hydrogen content in the a-Si:H film grown by triode PECVD reflects the relatively narrower optical band gap.

For the fabrication of a-Si:H single-junction and a-Si:H/ μ c-Si:H tandem solar cells, a commercially available SnO₂-coated glass (Asahi-VU) was used as the substrate. In our experiment, the SnO₂ surface was covered with TiO₂ (30 nm)–ZnO:Al (10 nm) to improve the light in-coupling at the TCO/Si interface [20]. As shown in Fig. 2, this bilayer coating reduces the reflection loss and increases the external quantum efficiencies (EQEs) by 3% in the wavelengths between 400 and 700 nm. Consequently, the short-circuit current density (J_{sc}) increases by 0.6 mA/cm². The reflection is reduced to almost 0% due to the multiple antireflection layers design, whereas the maximum EQE peak is still as low as ~92%. It can be considered that the rest of the incident light (~8%) is absorbed by the layers other than the i-layer and/or scattered towards the lateral direction through the glass and TCO.

For the doped layers, we deposited p- and n-layers consisting of μ c-Si:H (p)/a-SiC:H (p)/a-SiC:H (undoped) triple layers and a μ c-Si: H (n) single layer, respectively, in separate reactors. The a-SiC:H p-layer and a-SiC:H p-i layer were designed as thin as possible so

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