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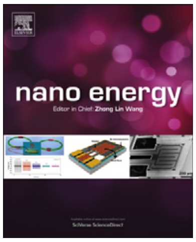

RAPID COMMUNICATION

Conductive white back reflector and scatter based on ZnO nanostructure arrays for harvesting solar energy

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Abstract
We report on the design, fabrication, and measurement of a-Si:H solar cells on a Ag/ZnO back reflector (BR) on a ZnO nanostructured template. The back reflector has a very high haze, which effectively scatters the light back into the absorber layer. Compared to the reference cells on a flat back reflector, a 36.97% increase in the short-circuit current density, with little reduction in the fill factor and open circuit voltage. As a result, the conversion efficiency of the a-Si: H solar cell is increased from 4.12% to 5.47%. Most importantly, the nanostructured BR were fabricated using an inexpensive and scalable nanopatterning method. All the processes were conducted at low temperatures, which is especially suitable for the solar cells on plastic substrate.

Introduction

An effective light trapping is a critical technology for enhancing the performance of thin film solar cells [1–5], which allow for using a thin absorber layer [6,7]. For a-Si:H solar cells, there are two types of structures, one is p-i-n structure on transparent conductive oxide (TCO) coated glass substrates and the other is n-i-p on non-transparent substrates such as metal coated glass, polymer, and stainless steel substrates. The light trapping for p-i-n structured solar cells is mainly from the texture of the TCO. A significant amount of studies has been carried out on the optimization of TCO surface structure for effective light trapping [8–11]. For n-i-p structured solar cells as studied in this paper, the light trapping is mainly from the back reflector because the a-Si:H normally grows conformably and the top indium-tin-oxide (ITO) is not thick enough to provide additional texture. A good back reflector should have three functions of (1) providing high reflection for the long-wavelength light that is not efficiently absorbed during the first path through the absorber layer, (2) scattering the light efficiently back into the absorber layer with large angles and providing additional prolongation of optical lengths

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[12–14], and (3) being conductive enough to exact carriers without significant resistive losses.

In order to scatter light efficiently, several methods have been used to modify the structure of back reflectors. A common approach is employing a surface texture such as the natively textured SnO_2:F (FTO), which is commercially available, and textured Ag back reflector as a substrate for n–i–p solar cells [12]. On the other hand, it has been tried to deposit Ag layers with textured surface directly by optimizing the deposition condition [13]. However, when plastic substrates are used the contact layers are difficult to be textured with above conventional methods. The low thermal sustainability of the substrate does not allow the high temperature depositions, which is usually made at above 400 °C for SnO_2 or at above 200 °C for Ag layers [15,16].

Recently, the application of three-dimensional (3D) nanostructures such as nanocone and nanosphere in thin film solar cells has gained a considerable attention [14,17–19]. Compared to conventional randomly textured substrate, the 3D structure has a much larger surface than the flat surface, such that, in principle, the absorber layer can be both optically thick to capture a sufficient fraction of incident photons and electrically thin to enable the minority carrier collection length being larger than the thickness of the absorber layer. If it were successfully realized, it would allow for ultimate light trapping and excellent charge separation at the same time.

In this paper, we fabricated ZnO nanorods by a solution method, during which no mask or lithography was used. In order to control the space between the ZnO nanorods, a wet chemical etching process is applied. To simultaneously increase the reflection and scattering, the ZnO nanorods were used as a template to form a 3D back reflector with an evaporated flat Ag layer and a sputtered thin Al doped ZnO (AZO) layer. Here, the AZO layer serves as a diffusion barrier between the Ag and a-Si:H during the growth of a-Si:H layers at an elevated temperature to reduce an unwanted contamination of the semiconductor by Ag, which is known to cause carrier recombination centers in a-Si:H. This 3D back reflector exhibits excellent electrical and optical properties, and also with a white color. So, we named it as conductive white back reflector (CWBR). It is important that the whole fabrication process of CWBR is at the temperatures lower than 100 °C, which implies that this back reflector has a large potential application in solar cells not only on glass substrate but also on plastic substrate. The application of this back reflector for thin film silicon solar cells demonstrates an improved light trapping effect.

Experimental

The chemicals used in this study are zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$, 99.0%), $C_6H_{12}N_4$ (99.0%), and NaOH (96.0%), which were purchased from Guangfu Co., Ltd. The deionized (DI) water used in all experiments was prepared in a three-stage Millipore Milli-Q Plus purification system and had a resistivity higher than 18.2 MΩ cm.

First, we cleaned the glass substrate thoroughly using a sequence of acetone, isopropanol, ethanol, and DI water. Second, we deposited a ~200-nm thick seed layer on the substrate using a direct current (DC) magnetron sputtering of an Al doped (0.5 wt%) ZnO ceramic target. Third, we chemically etched the substrate by immersing it in 1 M NaOH solution at room temperature for 10 min. Finally, we synthesized the ZnO nanorods by floating the substrate on the nutrient solution surface, which was composed of a 15 mM solution of 1:1 ratio zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$) and hexamethylenetramine ($(CH_2)_6N_4$) at 90 °C for 40 min. The specimens were mounted upside-down on beakers (200 ml) to prevent any precipitate that formed in the nutrient solution from falling onto the substrates, which would have inhibited the growth of the nanorods [20]. The samples were then rinsed with DI water and ethanol alternately for several times to remove any residual organics, and then dried by nitrogen gas. Up to this step, the fabrication of ZnO nanorod arrays was finished, which was used as the template for back reflector preparation. Subsequently, we deposited a ~200-nm thick Ag layer on the template by a thermal evaporation method. Finally, we sputtered a 180-nm thick AZO layer at room temperature. For a comparison, a reference back reflector with a ~200-nm thick flat Ag layer and 180-nm thick AZO was directly deposited on the glass substrate. The reference back reflector is named as FAR.

After the back reflectors were fabricated, we deposited hydrogenated amorphous silicon (a-Si:H) solar cells in a multichamber system. Plasma-enhanced chemical vapor deposition was employed for the deposition of the n, i, and p layers. Except for the SiH_4 and H_2, $B(CH_3)_3$ and PH_3 were used for p- and n-doping, respectively. Evaporated ITO dots were used to form front contact and define the area of the cells. The active cell area was 0.19 cm^2. The thickness of i layer was 400 nm. The thickness was measured on the solar cells deposited on the FAR substrate. The same deposition condition was employed to deposit the solar cells on the CWBR substrate.

A field emission scanning electron microscope (SEM) was used to investigate the morphology of the samples. The surface morphology and roughness of the films were also characterized by atomic force microscopy (AFM, NanoNavi-SPA400). Optical reflectance measurements on the back reflectors were carried out using a photo spectrometer equipped with an integrating sphere on a larger area of 15 mm^2 to improve the signal-to-noise ratio. The open circuit voltage (V_{oc}) and fill factor (FF) of the solar cells were calculated from the J-V characteristics measured in standard test conditions (25 °C, global air mass 1.5 (AM1.5G) spectra, 100 mW/cm^2). External quantum efficiency (EQE) spectra were measured under zero electrical bias. The short circuit current density (J_{sc}) was calculated by convolution integral of the EQE and the photon flux of the AM1.5G spectrum.

Results and discussion

In the case of using a wet chemical method, ZnO nanorods are usually prepared by two steps. A ZnO seed layer template is required, which strongly affects the geometry and orientation of the nanorods [21]. The seed layers have been prepared by sol-gel [22], pulsed laser deposition [20], or sputtering [23]. It can reduce the energy of nucleation. The ZnO nanorod arrays can only grow the areas with the