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Development of surface-textured hydrogenated ZnO:Al thin-films for μc-Si solar cells

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ABSTRACT

This study addresses the optimization of rf magnetron-sputtered hydrogenated ZnO:Al (HAZO) films as front contacts in microcrystalline silicon solar cells. The front contact of a solar cell has to be highly conductive and highly transparent to visible and infrared radiation. Furthermore, it has to scatter the incident light efficiently in order for the light to be effectively trapped in the underlying silicon layers. In this research, HAZO films were rf-magnetron-sputtered on glass substrates from a ceramic (98 wt% ZnO, 2 wt% Al_2O_3) target. Various compositions of AZO films on glass substrates were prepared by changing the $H_2/(Ar + H_2)$ ratio of the sputtering gas. The resulting smooth films exhibited high transparencies ($T \geqslant 85\%$ for visible light including all reflection losses) and excellent electrical properties ($\rho = 2.7 \times 10^{-4}\ \Omega \cdot \mathrm{cm}$). Depending on their structural properties, these films developed different surface textures upon post-deposition etching using diluted hydrochloric acid. The light-scattering properties of these films could be controlled simply by varying the etching time. Moreover, the electrical properties of the films were not affected by the etching process. Therefore, within certain limits, it is possible to optimize the electro-optical and light-scattering properties separately. The microcrystalline silicon (μc-Si:H)-based p–i–n solar cells prepared using these new texture-etched AZO:H substrates showed high quantum efficiencies in the long wavelength range, thereby demonstrating effective light trapping. Using the optimum AZO:H thin-film textured surface, we achieved a p–i–n μc-Si solar cell efficiency of 7.78%.

1. Introduction

Silicon thin-film solar cells are promising candidates for future photovoltaic power generation [1,2]. The most advanced approach employs hydrogenated amorphous (a-Si:H) and microcrystalline silicon (μc-Si:H) as active layers in single or multi-junction cells [3,4]. Silicon thin-film solar cells in the p–i–n (superstrate) configuration require a transparent conductive oxide (TCO) film as a front contact. Such contacts have to exhibit a low series resistance and a high transparency in the visible light region (400–800 nm). In the case of μc-Si:H based cells, the contact should also be transparent in the near-infrared (NIR) region (up to 1100 nm). Furthermore, an adapted surface topography is required to ensure light-scattering and subsequent light trapping inside the silicon solar cell structure. Optimization of the TCO front contact has proven to be crucial for high cell efficiency [5].

Impurity-doped ZnO films are attractive TCOs due to their low material cost, non-toxicity, relatively low resistivity, and high visible transmission [6]. Recently, there has been particular interest in the properties of hydrogen in ZnO because density functional theory and total energy calculations predict that it should be a shallow donor [7–9]. The generally observed n-type conductivity is thought to be due to the presence of residual hydrogen introduced during the growth process, rather than due to native defects, such as Zn interstitials or O vacancies. Also, it has been reported that hydrogen addition to Al-doped ZnO (AZO) film could give beneficial effect on the electrical properties. Furthermore, it was suggested that hydrogen incorporated between Zn–O bond center might act as an anion donor like fluorine whose electronic perturbation are confined to mainly in the valence band, thereby leading to improvement of the electrical properties while maintaining low absorption loss [10,11].

In this regard, it is of interest to investigate the practical performance of thin-film Si solar cell in which hydrogenated AZO (HAZO) films are applied as front electrodes. In this work, therefore, we examined the electrical properties AZO and HAZO films deposited

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by radio frequency (rf) magnetron sputtering with varying H_2 contents in sputter gas of the sputtering gas mixture, and investigated the evolution of surface morphology with etching time in diluted HCl solution and the corresponding optical characteristics of HAZO film with optimum electrical properties. Finally, we mad a discussion on the cell performance by adopting HAZO films with different etching surface as the front contact of μc-Si solar cell.

2. Experimental details

ZnO:Al films, approximately 1 μm thick, were deposited on glass substrates (Corning Eagle 2000) by radio-frequency (rf) magnetron sputtering. A sintered ceramic ZnO target with 2 wt% Al_2O_3 was used. The glass substrates were sequentially ultrasonically cleaned in acetone, alcohol, and deionized water, and finally dried with nitrogen gas. The distance between the target and the substrate was approximately 60 mm. The rf magnetron working power and deposition time were 50 W and 152 min, respectively. The sputtering system was pumped down to a base pressure of 1×10^{-6} Torr using a turbo molecular pump. The working pressure was approximately 1.2 mTorr with a mixture of H_2 and Ar gases being flowed into the reaction chamber. The $H_2/(Ar + H_2)$ ratio was controlled using mass flow controllers. A series of ZnO:Al films were deposited using $H_2/(Ar + H_2)$ ratios of 0, 2, 4, and 6% (keeping other conditions constant) in order to determine the effects of the H_2 content on the properties of the AZO films. The substrates, which were kept at 150 °C, were rotated at a constant speed of 8 rpm during deposition. The AZO:H films were then etched with dilute hydrochloric acid (0.5% HCl in H_2O). As a result, the films developed textured surfaces that depended on their original structural properties.

The electrical resistivity, Hall mobility, and carrier concentration were determined from Hall-effect measurement equipment using a Van der Pauw method. Optical characterization of the ZnO:Al coated glass was performed using a dual beam UV–visible spectrophotometer equipped with an integrating sphere (Perkin Elmer, Lamda35) at wavelengths ranging from 250 to 1100 nm. We measured the reflectance and total and diffuse transmittance, and then calculated the haze factor as the quotient of the diffuse and total transmission. Also, scanning electron microscopy (SEM) and atomic force microscopy (AFM) were used to examine the surface morphologies and structures of the films. The AFM data was used to determine the rms roughness of each film. The light trapping abilities of the TCO films were evaluated by their application in thin-film silicon solar cells. The solar cell illuminated current–voltage characteristics were measured using a solar simulator (Wacom WXS-140S-Super) at standard test conditions (AM 1.5, 100 mW/cm^2, 25 °C). The external quantum efficiency (QE) of each solar cell was calculated from the spectral response measured at zero bias.

To compare the light-scattering abilities of the four different textured surfaces, the films shown in Fig. 2 were applied as front contacts in identical μc-Si:H p–i–n solar cells, each with an i-layer thickness of 1 μm. The results are shown in Fig. 8. Each solar cell structure was as follows: glass/textured HAZO(1 μm)/p-μc-Si:H(~20 nm)/i-μc-Si:H(~1 μm)/n-a-Si:H(~30 nm)/ZnO:Al(2.5 wt%, 100 nm)/Ag. The p and n layers were prepared by a PECVD method and the i (insulator) layer by a VHFCVD method. The illuminated current–voltage characteristics of the p–i–n structured solar cells fabricated on different textured-etched AZO:H substrates were measured under an illumination intensity of 100 mW/cm^2 and an AM1.5 G spectrum.

3. Results and discussion

Fig. 1 summarizes the electrical resistivity, free carrier concentration, and Hall mobilities of the AZO and HAZO films with respect to H_2 in sputter gas. The electrical resistivity and carrier concentration of the as-grown AZO film were $8.51 \times 103\,\Omega \cdot cm$ and $5.54 \times 1020\,cm^3$, respectively. The resistivity first decreased significantly with increasing the H_2 flow ratio from 0 to 2% and then increased slightly with increasing the H_2 flow ratio further. A minimum resistivity of $2.7 \times 104\,\Omega \cdot cm$ was detected for the HAZO film deposited using an H_2 flow ratio of 2%. This was caused by the significant increases in the carrier concentration and the Hall mobility. The Hall mobility was highest for the films deposited with an H_2 flow ratio of 2%. It then decreased gradually for further increasing the H_2 flow ratio. On the other hand, the carrier concentration kept on increasing slightly. The large increase in Hall mobility combined with small increase in carrier concentration by addition of small amount hydrogen is attributed to the passivation effect of grain boundaries and increased hydrogen donor sites [11]. Further addition of hydrogen will lead to increase of donor sites without affecting the once-passivated grain boundaries. This will cause increase of ionized impurity scattering, resulting in slight decrease in Hall mobility. As was shown in Fig. 1, the electrical

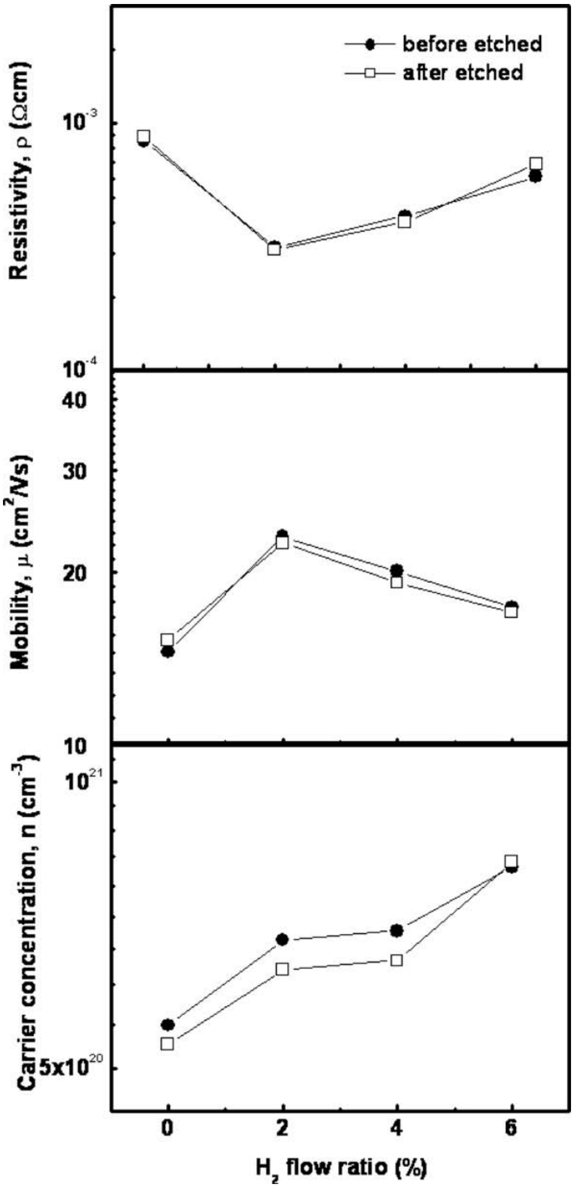

Fig. 1. Resistivity, carrier concentration and mobility as a function of the H_2 flow ratio as determined by Hall measurement at room temperature.