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Study of the light-trapping effects of textured ZnO:Al/glass structure TCO for improving photocurrent of a-Si:H solar cells

Y. Sobajima · S. Kato · T. Matsuura · T. Toyama · H. Okamoto

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Abstract Effects of using ZnO:Al (AZO) transparent conducting oxide films on the performance of the hydrogenated amorphous Si (a-Si:H) solar cells are studied. AZO films are prepared by the sol-gel method. Rapid thermal annealing (RTA) in vacuum of these films results in a decrease in resistivity. AZO films exhibit a high transmittance in the visible region and excellent resistance against hydrogen radical exposure. The light-trapping effect is proven by a measured decrease in the transmittance and reflectance spectra of the textured AZO/glass structure with a RMS roughness of 67.5 nm. It is concluded that highly textured AZO/glass structures enhance the photocurrent in a-Si:H-based thin film solar cells.

1 Introduction

Hydrogenated amorphous Si (a-Si:H) thin film solar cells attract interest because they can be mass produced. a-Si:H solar cells are fabricated on transparent textured conducting oxide (TCO) films [1]. A TCO film weakly traps absorbed light and hence improves the long wavelength collection efficiency. To date, textured SnO_2:F TCO (Asahi Type-U) films with an RMS surface roughness (σ_{RMS}) of 20 nm [2] are considered as the standard TCO. However, SnO_2 films can be deoxidized during the deposition of a-Si:H films by hydrogen radical exposure [3], which results in a degradation of the conversion efficiency. In addition, a more highly textured structure TCO is desired for enhanced light-trapping effects [4].

Aluminum doped zinc oxide (AZO) thin film is one of the more promising materials for the TCO film instead of SnO_2 because AZO has low electric resistivity, high transparency in the visible region, and resistance against hydrogen radical attack [5]. The sol-gel method is one of the simplest and lowest-cost methods in preparing various kinds of functional oxide films [6]. Although, AZO films prepared by the sol-gel method have been already reported [6, 7], their application on a-Si:H solar cells has not been studied.

In this article, we present a study of the optical properties of the AZO films prepared by the sol-gel method with a focus on the effects of annealing after the sol-gel preparation. The application of AZO as a possible TCO to solar cells is discussed mainly from the optical aspect.

2 Experiments

AZO films were prepared by the sol-gel method. First, zinc acetate dihydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$) was dissolved into 2-methoxyethanol and methanol solution. The molar ratio of zinc acetate to the 2-methoxyethanol and methanol solution was 0.2 mol/L. Aluminum chloride ($AlCl_3{\cdot}6H_2O$) was used as the dopant source. The doping ratio, $[Al^{+}]/[Zn^{2+}]$, was 1.0 mol%. The solution was spin-coated on glass substrates (Corning #7059) and then heated to 250 °C for 10 min in air. Spin-coating and heating was repeated 10 times. These films were then oxidized in air by an annealing process in a conventional

Y. Sobajima (✉) · S. Kato · T. Matsuura · T. Toyama · H. Okamoto
Department of Systems Innovation, Graduate School of Engineering Science, Osaka University, Toyonaka Osaka 560-8531, Japan
e-mail: sobajima@semi.ee.es.osaka-u.ac.jp

furnace for 1 h at 550 °C. Finally, rapid thermal annealing (RTA) was carried out in a quartz tube in vacuum (ca. 4.0×10^{-6} Torr) for 5 min. The RTA temperature (T_{ann}) varied from 350 to 550 °C. The thickness of AZO films ranged from 120 to 150 nm. These dimensions were estimated from cross-sectional images taken by a scanning electron microscope.

Optical characterization was done using a Shimadzu UV-3100 spectrometer. Crystallographic orientations were measured using a Rigaku RINT-2200 X-ray diffractometer with CuK_{α} line. Surface morphologies were obtained by AFM (SPA400/SPI3800N: Seiko Instruments Inc.) in contact mode. The electrical properties of AZO films were characterized by four-point probe and Hall effect measurements with the Van der Pauw configuration.

3 Results and discussion

3.1 Effects of RTA on AZO films

The four-point probe resistivity (R_{sq}) of AZO films before RTA was as high as 25 Ωcm. This does not satisfy the resistivity requirements for electrodes of thin film solar cells. However, R_{sq} of AZO films decreased with increasing T_{ann}. The lowest R_{sq} of 1.4×10^{-2} Ωcm was obtained at a T_{ann} of 550 °C. Fig. 1 shows R_{sq}, the carrier concentration (n), and the Hall mobility (μ_H) of AZO films as a function of the RTA temperature. An improved R_{sq} by an order of three results from increases in both n and μ_H. Before RTA, the estimated value of n was 1.0×10^{17} cm^{-3} and that of μ_H was1.05 cm^2/Vs in AZO films. After RTA at 550 °C, n and μ_H increased to 2.8×10^{19} cm^{-3} and 16.9 cm^2/Vs, respectively.

Figure 2 shows the X-ray diffraction (XRD) patterns of AZO films before and after RTA at 550 °C. XRD patterns show the preferential (002) peak of hexagonal ZnO. No pronounced shift in the (002) peak angle was observed before and after RTA. However, the full width at half maximum (FWHM) decreased from 0.262° to 0.231° after RTA, indicating an increase in the grain size of AZO in the direction of growth and, perhaps, in the lateral direction as well. The increased grain sizes or decreased grain boundaries are responsible for the increases in n and μ_H.

Figure 3 shows the optical transmittance spectra of AZO films with a thickness of 150 nm before and after RTA as a function of the wavelength. These films show an average transmission of more than 80% throughout the range of wavelengths between 400 and 1200 nm before and after RTA. The optical absorption spectra of AZO films measured before (a) and after (b) RTA are also plotted as a function of the wavelength in the inset of Fig. 3. The optical band gaps were estimated as 3.28 eV

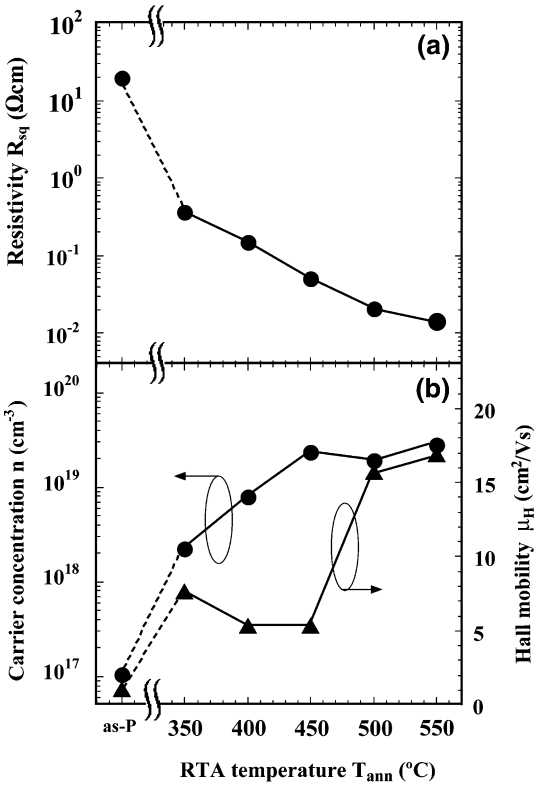

Fig. 1 (**a**) The resistivity, R_{sq} and (**b**) carrier concentrations, n, and Hall mobility, μ_H (of AZO films plotted as a function RTA temperature (T_{ann}). Results in the region denoted by as-P on the horizontal axis are obtained before RTA

and 3.30 eV for the AZO films before and after RTA, respectively. The blue-shift in the optical band gap may be attributed to the band filling (Barstein-Mass) effect corresponding to the increased n after RTA as shown in Fig. 1.

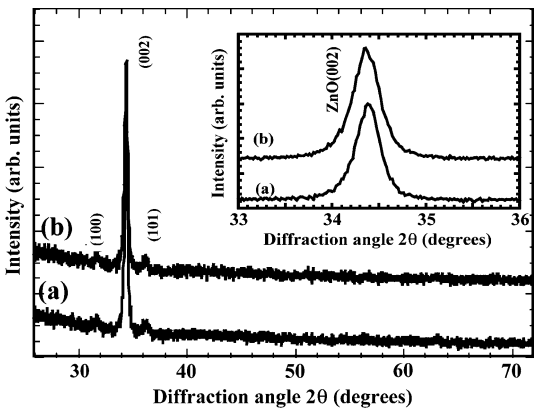

Fig. 2 X-ray diffraction patterns of AZO films (**a**) before and (**b**) after RTA at 550 °C in vacuum. Inset shows enlarged patterns at around (002) peak

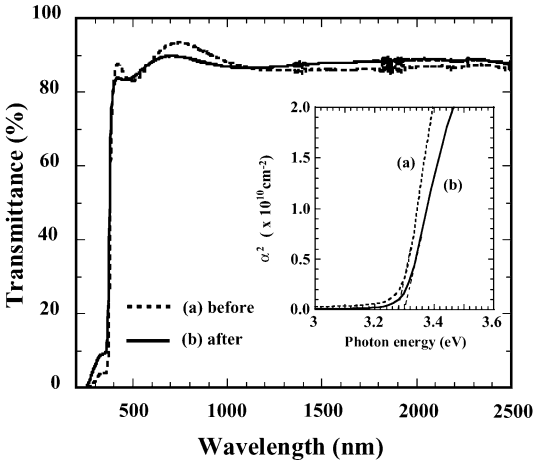

Fig. 3 Optical transmittance spectra for AZO films (**a**) before and (**b**) after RTA in vacuum at 550 °C. Inset shows spectra of the square of the absorption coefficient α for AZO films (**a**) before and (**b**) after RTA

3.2 Application to a-Si:H solar cells

To evaluate the chemical stability against hydrogen radical exposure, an AZO film was exposed to hydrogen plasma that was generated by RF excitation with an input power of 0.2 W/cm^2. The exposure time, hydrogen dilution, hydrogen pressure, and substrate temperature was 5 min, 90 sccm, 1.4 Torr, and 200 °C, respectively. These parameters were determined after typical deposition conditions for a p-type μc-Si layer in p-i-n a-Si:H thin film solar cells (except for SiH_4 gas flow).

The optical transmission spectra of AZO films before and after exposure to hydrogen radicals are compared in Fig. 4, and no marked change in the transmittance can be detected. In contrast, Ikeda et al. [5] reported that the optical transmittance in the visible region of an AZO film prepared by the conventional DC magnetron sputtering on the SnO_2:F film decreased after exposure to the hydrogen radicals. Although in their case, the thickness of the AZO film was very thin (10 nm) and the exposure conditions were different than ours, this result encourages us to propose that the sol-gel method can be used as an alternative method for the preparation of AZO films.

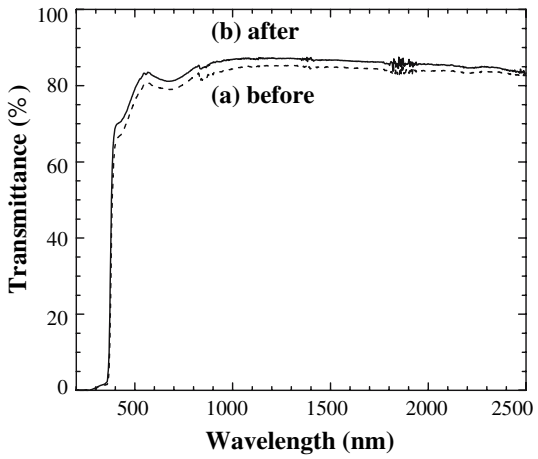

Fig. 4 Optical transmittance spectra of AZO films before (dashed line) and after (solid line) hydrogen radical exposure

Figure 5 shows the AFM topological surface images of AZO films that were deposited on two different kinds of substrates; (a) flat and (b) textured. The scanning area in AFM measurement is 10 × 10 μm^2. The thickness of both AZO films was 200 nm. The surface RMS roughness of the AZO film coated on the flat and the textured substrates were estimated to be 8.0 and 67.5 nm, respectively. The sheet resistivity in both was kept constant at 8.0 × 10^{2}Ω/sq.

Figure 6 shows the transmittance and reflectance spectra of the a-Si:H (100 nm) films prepared on the above flat and textured AZO films. As it can be clearly seen in Fig. 6, in the range of wavelengths between 500 and 660 nm, the transmittance spectrum of the textured structure is slightly less than that of the flat structure. Furthermore, the reflectance spectrum of the textured structure in the visible region is also less than that of the flat structure. These are expected to be caused by the light-trapping effects, that is,

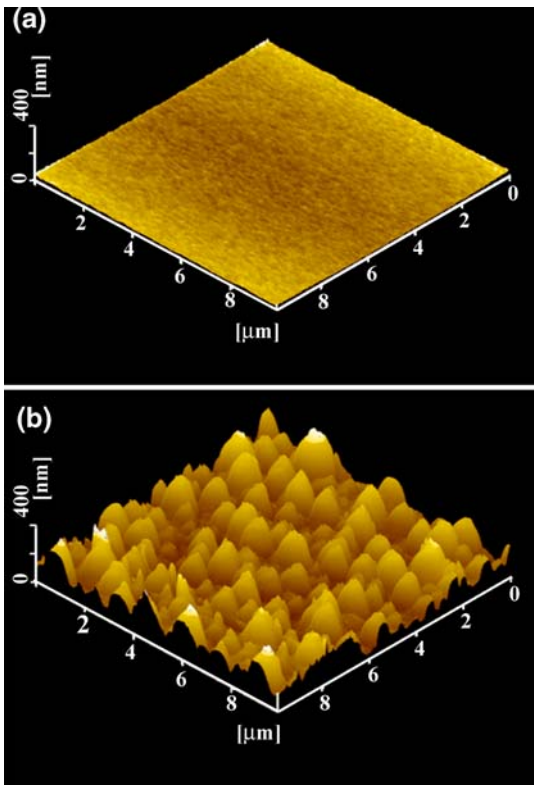

Fig. 5 AFM topographs of AZO surfaces with different glass substrates. The RMS roughnesses of AZO surfaces were as follows; (**a**) 8 nm and (**b**) 67.5 nm. The scan sizes were 10 × 10 μm

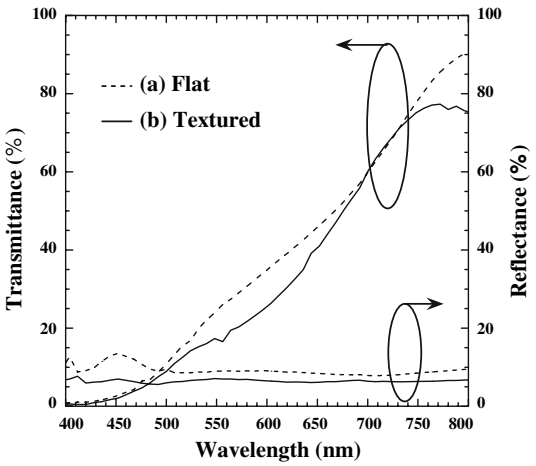

Fig. 6 Transmittance and reflectance spectra of (**a**) flat and (**b**) textured a-Si (100 nm)/AZO(200 nm)/glass structures

the scattering of the incoming light into the a-Si:H layer [4]. It is to be noted that, in the range of wavelengths 300–750 nm, such enhancement in the light-trapping effect is very important for the enhancement of the photocurrent in a-Si:H solar cells [4]. Thus, a highly textured AZO/glass substrate structure may be expected to produce enhanced photocurrent in a-Si:H solar cells.

4 Conclusions

The film properties and application of AZO films prepared by the sol-gel method have been studied. AZO film clearly exhibits a hexagonal (002) orientation. After sol-gel preparation, the RTA process is effective in improving its electrical properties. AZO film after RTA showed excellent resistance against hydrogen radical attack. Finally, the light-trapping effect of a-Si:H deposited on AZO/glass texture with a surface RMS roughness of 67.5 nm was determined to be three times greater than that of a-Si:H deposited on a conventional SnO_2:F surface. The transmittance and reflectance spectra indicate enhanced light-trapping effect in the wavelength region 500–660 nm.

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