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Characteristics of aluminum-doped zinc oxide films with oxygen plasma treatment for solar cell applications

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ABSTRACT

The influence of oxygen plasma treatment on the electro-optical and structural properties of aluminum-doped zinc oixde (AZO) films fabricated by radio frequency (RF) magnetron sputtering method were investigated. The films were exposed to various oxygen (O_2) plasma treatment conditions. The plasma was created in a plasma enhanced chemical vapor deposition method. The resistivity, optical tranmittance, and work function of AZO films fabricated by RF magnetron sputtering was 5.6×10^{-4} Ω · cm, 80%, and 4.6, repectively. The resistivity, optical trasmittance, and work function of the AZO films that were post-treated by O_2 plasma treatment showed 9.2×10^{-4} Ω · cm, 82%, and 5.6, respectively. The resistivity, carrier concentration, and hall mobility properties of AZO films deteriorated with increasing O_2 plasma treatment power and time, whereas the work function and optical transmittance properties improved.

1. Introduction

Transparent conductive oxide (TCO) films including indium-tin-oxide (ITO) have been widely applied in optoelectronic devices such as organic light emitting diode (OLED), solar cell, and liquid crystal displays (LCD) due to their low resistivity and high transmittance of visible light [1–3]. Among the various TCO materials, aluminum doped zinc oxide (AZO) is a potential alternative to ITO because it is a low cost and non-toxic as well as it exhibits good stability in plasma. For silicon based thin-film solar cell, AZO layers are important building blocks as a TCO layer due to good conductivity, high optical transmittance, and chemical stability under hydrogen and/or oxygen plasma environments [4–7]. However, AZO still has some drawbacks in the amorphous silicon (a-Si:H) thin film solar cell. The conductivity of the AZO films can be controlled by changing the oxygen and/or zinc vacancy contents with the crystallinity. In particular, hydrogen can make the shallow donor in zinc oxide (ZnO) films for the improvement of the electrical characteristics. For the hydrogen contents in AZO films, many researchers have studied various post-treatment techniques, such as hydrogen ion implantation, hydrogen annealing, and hydrogen plasma exposure [8–12]. Also, oxygen plasma treatment can control the oxygen vacancies in AZO films, attributing to the change of the electrical properties. Therefore, in this work, we fabricated AZO films on the glass substrates by radio frequency (RF) magnetron sputtering method and we investigated the effects of oxygen plasma treatment on the electrical, optical, and structural properties of the fabricated AZO films with various O_2 plasma treatment powers and times by plasma enhanced chemical vapor deposition (PECVD) method.

2. Experimental details

AZO films were prepared on Corning 1737 glass substrate by RF magnetron sputtering method with Al doped ZnO ceramic disk (Al_2O_3 2.5 wt%, 4 inch, 99.99%). The distance between the target and the substrate was 6 cm. For the deposition of AZO films, the base pressure of the chamber was maintained at 9×10^{-5} Pa using a a turbomolecular pump and the working pressure in the chamber was maintained at 0.4 Pa. AZO films were deposited under room temperature and RF power of 150 W, and the sputtering rate of AZO films was about 73 nm/min. The film thickness was controlled to be about 500 nm. The O_2 plasma treatment was performed by PECVD method with oxygen gas about 30 SCCM. The AZO films were exposed to O_2 plasma for 20 min at RF power from 100 W to 300 W and were post-treated under various O_2 plasma treatment times at 300 W RF power. The pressure in PECVD system was 25 Pa for O_2 plasma and the substrate temperature was fixed at 50 °C.

Film thickness and surface morphology were measured using a surface profiler [Alpha-Step 500, TENCOR, USA] and a FE-SEM [XL-40FEG Field Emission Scanning Electron Microscope]. Hall mobility and carrier concentration of the films prepared with/without O_2 plasma treatment were examined by Hall measurement using the Van der Pauw geometry at a constant magnetic field of 0.5 T. The crystalline structure of the AZO films was characterized by X-ray diffractometer [XRD: Bruker, AXS D8 Discover] using Kα radiation in the 20 ~ 80° 2θ range. The spectral transmittance of the films was observed using a

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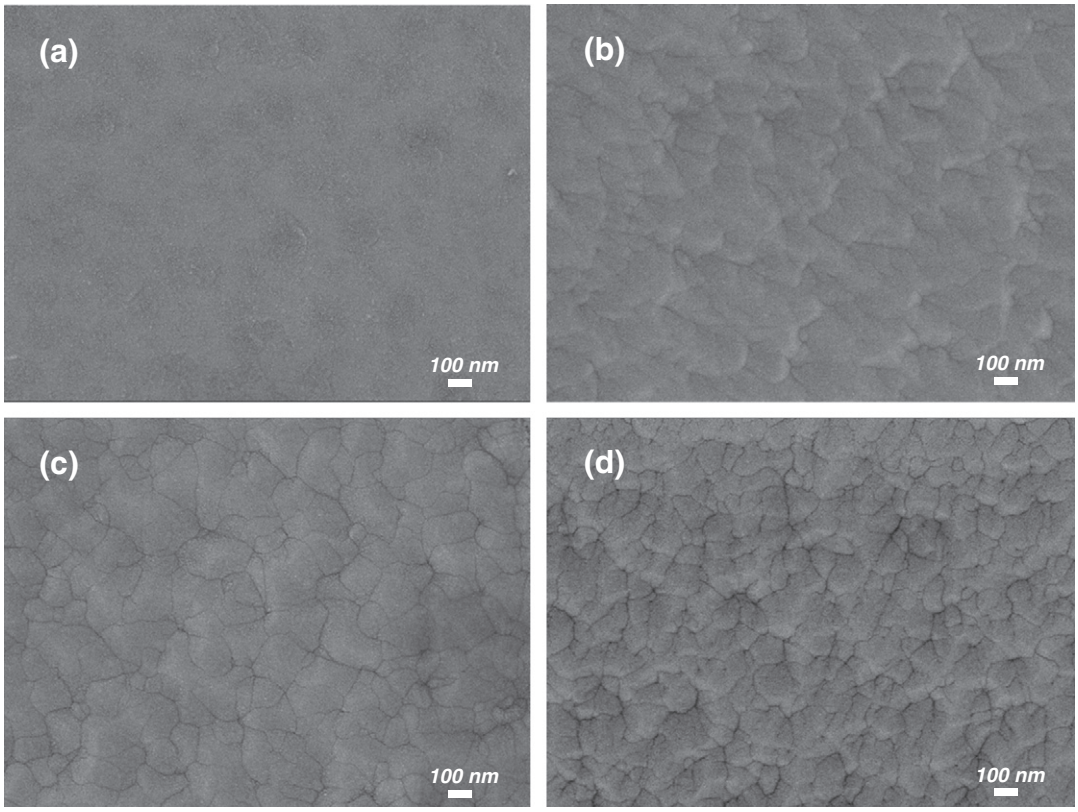

Fig. 1. FESEM surface images of AZO films prepared at various plasma treatment conditions ; (a) as-deposited, (b) 100 W 20 min, (c) 300 W 20 min, and (d) 300 W 60 min.

UV-visible spectrophotometer [Sinco, S-3100] in the visible wavelength range of 300 ~ 1000 nm and the work function of the films was measured by surface analyzer [AC-2, RIKEN].

3. Results and discussion

Fig. 1 shows the FESEM surface morphology images of AZO films prepared at various O_2 plasma treatment conditions. It can be seen that the surface of plasma-treated AZO films had more rough than that of as-deposited AZO film. In other words, AZO films that were plasma-treated at O_2 plasma treatment conditions show rough surfaces and the surfaces contain a lot of grains. The surface grains of AZO films increased with increasing O_2 plasma treatment power, and also the grains on the surface consist of smaller grains at the treatment power and long treatment time over 60 min. These results are associated with the etching effect in grain boundary regions by energetic oxygen ions.

Fig. 2 shows the XRD patterns, full width at half-maximum (FWHM), and crystallite size of the AZO films deposited as a function of O_2 plasma treatment power and time. All AZO films prepared with/without O_2 plasma treatment had a strong (002) plan and a weak (004) plan at $2\theta = 34.4°$ and 72.5°, respectively, indicating a preferred orientation with the c-axis perpendicular to the substrate (a hexagonal wurtzite structure). The peak intensity of AZO films decreased and the FWHM and crystallite size of the (002) peak slightly increased with increasing O_2 plasma treatment power and time. In particular, the peak intensity and crystallite size of AZO films sharply decreased from the conditions of the plasma power of 150 W and the treatment time of 60 min. At low plasma powers (0 ~ 100 W) and short times (0 ~ 40 min), the crystallite size is similar maintained owing to the decrease of oxygen vacancies on film surface, however it sharply decreased at the treatment conditions of high powers and long time. This may be due to the etching effect by energetic oxygen ions, contributing to the surface modification such as the passivation of oxygen vacancies and the decrease of metal contents by the metal emission [13,14].

Fig. 3 shows the resistivity (ρ), Hall mobility (μ), and carrier concentration (N) of AZO films post-treated as a function of O_2 plasma treatment power and treatment time. The resistivity of as-deposited AZO films showed about $5.6 \times 10^{-4}\ \Omega \cdot$ cm and the film resistivity slightly increased from $5.6 \times 10^{-4}\ \Omega \cdot$ cm to $9.2 \times 10^{-4}\ \Omega \cdot$ cm and from $5.6 \times 10^{-4}\ \Omega \cdot$ cm to $7.5 \times 10^{-4}\ \Omega \cdot$ cm with increasing plasma treatment power and time, respectively. There is little change in the carrier concentration with increasing O_2 plasma treatment power and time. The hall mobility decreased with increasing O_2 plasma treatment power and slightly reduced with increasing plasma treatment time. These results are associated with the surface modification by the etching effect. In other words, in low plasma treatment powers and short treatment time, the decrease of the resistivity may be due to the compensation of the oxygen deficiency by O_2 plasma treatment on the AZO surface, however, in the high powers and long treatment time, the increase of resistivity may be due to the defects by the generation of the amorphous phase or/and the emission of metal contents by the O_2 plasma etching of energetic oxygen ions [15,16].

Fig. 4 shows the optical transmittance of AZO films post-treated at various O_2 plasma treatment powers and times. The average transmittance of these films in the visible wavelength range (not shown here), from 400 nm to 800 nm, exceeded 80%. In addition, the transmittance of the AZO film slightly decreased with increasing plasma treatment power and increased with increasing plasma treatment time. The optical absorption coefficient (α) near absorption edge is given by

$$\alpha \propto \left(h\upsilon - E_{opt}\right)^{1/2} \tag{1}$$

where, $h\upsilon$ is the photon energy. The optical band gap (E_{opt}) was determined by measuring the optical transmission using Eq (1). The results