

Thermal effects on the structural, electrical, and optical properties of Al-doped ZnO films deposited on glass substrates

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Al-doped ZnO (AZO) thin films were grown on glass substrates using radio-frequency magnetron sputtering. X-ray diffraction patterns of the AZO thin films grown on glass substrates showed that the full width at half-maximum of the (0002) peak corresponding to the AZO thin film decreased with an increase in the annealing temperature, indicative of an improvement of the crystal quality of the AZO films. Atomic force microscopy images showed that the root mean square of the average surface roughnesses of the AZO films decreased with an increase in the annealing temperature. Hall effect measurements showed that the resistivity of the AZO film annealed at 250 °C was as small as $8 \times 10^{-4} \Omega\cdot\text{cm}$. The transmittance spectra showed that the average transmittance in the wavelength range between 400 and 800 nm was above 90%. The optical band gap energies of the AZO films were determined from the transmittance spectra.

Key words: Al-doped ZnO, Thermal annealing, Structural property, Electrical property, Optical property.

Introduction

Transparent conducting oxide (TCO) films have emerged as excellent candidates due to interest in their promising applications in next-generation electrodes [1]. The electrodes fabricated utilizing TCO films in optoelectronic devices have excellent physical properties of high visible transmittance, low resistivity, high infrared reflectance, and large absorbance [2]. Because ZnO materials are large-band-gap semiconductors with peculiar physical properties of high chemical stabilities and large exciton binding energies [3-5], they are of current interest due to their potential applications in optoelectronic devices, such as photodetectors [3], solar cells [6], light-emitting diodes [7], and laser diodes [8]. Low-resistivity ZnO thin films may be realized by using several dopants, such as Al, Ga, and In of the group III [9-11]. Among various types of doped-ZnO thin films, Al-doped ZnO (AZO) thin films with a low resistivity have been considered as suitable electrodes because AZO thin films are more stable in a reducing environment, more abundant, and less expensive in comparison with indium-tin-oxide films [12-14]. Because a thermal treatment is necessary for the fabrication processes of several types of optoelectronic devices, the role of the thermal annealing processes is very important in achieving high-performance devices. Even though some studies on the structural, the electrical, and the optical

properties of AZO thin films formed on various substrates have been reported [15, 16], systematic studies concerning the thermal effect on the structural, the electrical, and the optical properties of AZO thin films are still necessary for enhancement of their physical properties.

This paper reports data for the effects on the structural, the electrical, and the optical properties of AZO films grown on glass substrates by using radio-frequency (RF) magnetron sputtering. X-ray diffraction (XRD) measurements were carried out to investigate the quality of the AZO thin film, and atomic force microscopy (AFM) measurements were performed in order to investigate the surface morphology of the AZO thin films. Van der Pauw Hall effect measurements were carried out in order to determine the resistivity of the AZO thin films. Optical transmittance measurements were performed to investigate the optical properties and to determine optical energy gaps of AZO thin films.

Experimental Details

The AZO thin films used in this study were prepared on glass substrates using a tilted dual target RF magnetron sputtering system. Polycrystalline stoichiometric 2 wt% Al_2O_3 -doped ZnO was used as the source target material and was pre-cleaned by repeated sublimation. After the glass substrates were degreased in an acetone ultrasonic bath, rinsed in de-ionized water, they were dried using N_2 gas with a purity of 99.9999%. After the substrates were chemically cleaned, they were mounted onto a susceptor in a growth chamber. After the chamber was evacuated to 2.666×10^{-4} Pa, the deposition was done at room temperature. Ar gas with a purity of 99.9999% was used

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as the sputtering gas, and the flow rate of the Ar gas for the growth of AZO films was 10 sccm. Prior to AZO film deposition, the surface of the target was polished for 10 minute by Ar^+ pre-sputtering to remove any contaminant and to maintain stable sputtering conditions. The AZO film depositions were done on the glass substrates at a system pressure of 0.266 Pa and a RF power (radio frequency = 13.26 MHz) of 75 W. The distance between the substrate and the target was 7 cm. After the AZO film deposition, the films were in situ annealed without breaking the vacuum in an argon and hydrogen mixture atmosphere of 6.666 Pa. The thermal annealing process was carried out for 1 h at 150, 200, 250, 350, 400, and 450 °C.

The film thicknesses and surface morphologies were measured using a XE-100 AFM. The XRD measurements were performed using a Rigaku D/Max-B diffractometer with $\text{CuK}\alpha$ radiation. The AFM measurements were performed using a XE-100 in contact mode. The resistivities of the AZO films were determined using an HMS-300 four-point probe and a Van der Pauw measurement system. The optical transmittance measurements were performed using a ultraviolet-visible spectrophotometer in the wavelength range between 200 and 900 nm.

Results and Discussion

Fig. 1 shows XRD patterns for the (a) as-grown AZO thin films grown on the glass substrates and for those annealed for 1 h at (b) 150, (c) 200, (d) 250, (e) 300, (f) 350, (g) 400, and (h) 450 °C. The dominant (0002) diffraction peaks corresponding to the as-grown and the annealed AZO thin films are clearly observed. These results indicate that the as-grown and the annealed AZO films grown on the glass substrates are a single crystalline, indicative of a (0002) preferred orientation. When the AZO films deposited on the glass substrates are annealed, the strain

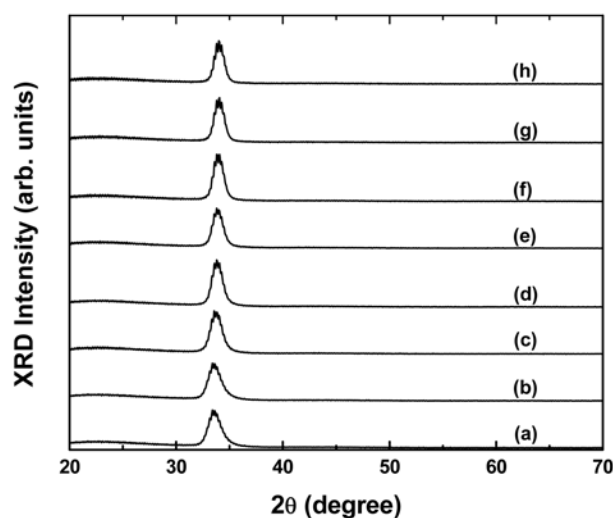


Fig. 1. X-ray diffraction patterns for (a) as-grown Al-doped ZnO films and those annealed for 1 h at (b) 150, (c) 200, (d) 250, (e) 300, (f) 350, (g) 400, and (h) 450 °C.

existing in the AZO thin films is gradually relaxed. The full width at half-maximum (FWHM) of the (0002) peak corresponding to the AZO thin film decreases from 1.5° to 1° with an increase in the annealing temperature from 150 to 450 °C, indicative of an improvement of the crystal quality of the AZO films.

Fig. 2 shows the AFM images of the AZO films annealed for 1 h at 150, 250, 350, and 450 °C. The root mean squares of the average surface roughnesses of the AZO films, as determined from the AFM images, decrease from 3.28 to 1.38 nm with an increase in the annealing temperature from 150 to 450 °C due to a decrease in the grain size of the AZO films and the enhancement of the crystal quality of the films resulting from the higher thermal energy.

Fig. 3 shows the electrical resistivity as a function of the annealing temperature for the AZO films grown on

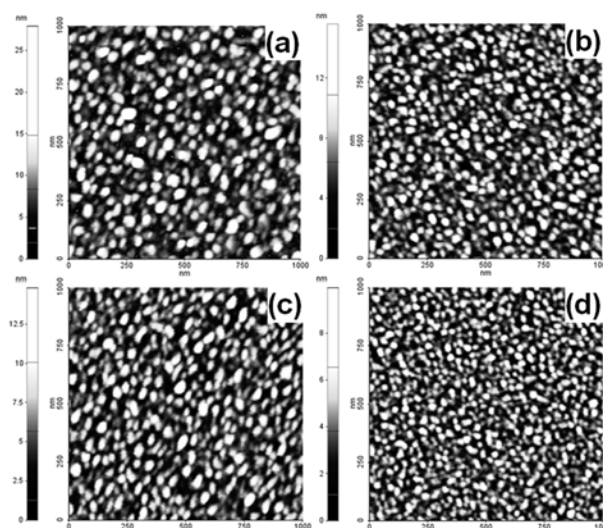


Fig. 2. Atomic force microscopy images for the annealed Al-doped ZnO films annealed for 1 h at (a) 150, (b) 250, (c) 350, and (d) 450 °C.

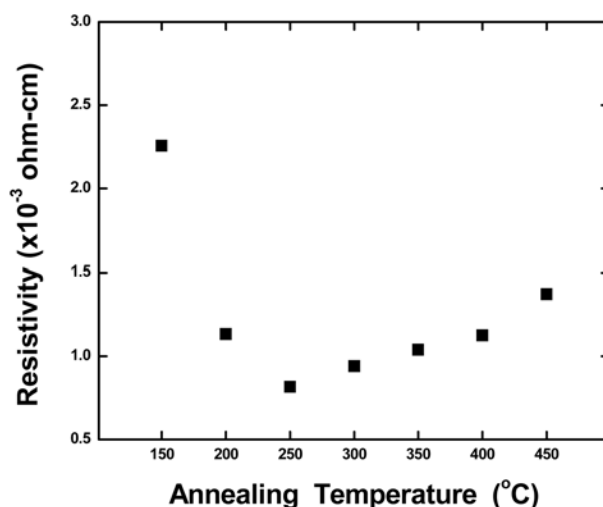


Fig. 3. Resistivity as a function of the annealing temperature for Al-doped ZnO thin films.

glass substrates. While the resistivity of the AZO films decreases with an increase in the annealing temperature from 150 to 250 °C, the resistivity increases with an increase in the annealing temperature from 300 to 450 °C. The lowest resistivity of $8 \times 10^{-4} \Omega\cdot\text{cm}$ for the AZO films is obtained at an annealing temperature of 250 °C. The electrical resistivity of the AZO films is significantly affected by the carrier concentration. The variation of the carrier concentration for the annealed AZO films might affect the shift of the energy band gap [17].

Fig. 4 shows the transmittance spectra in the wavelength range between 200 and 900 nm for the as-grown AZO films grown on the glass substrates and for those annealed for 1 h at 150, 200, 250, 300, 350, 400, and 450 °C. The inset represents enlarged optical transmission spectra in a wavelength range between 340 and 370 nm for the as-grown and annealed AZO films. The average transmittance in the wavelength range between 400 and 800 nm is above 90%. The transmittance spectra for the as-grown and annealed AZO films show excellent optical transparency in the visible spectral region, which plays an important role for potential applications in transparent optoelectronic devices. While the transmittance of the AZO films increases with an increase in the annealing temperature from 150 to 250 °C, that of the AZO films decreases with an increase in the annealing temperature from 300 to 450 °C.

The $(\alpha h\nu)^2$ as a function of the photon energy ($h\nu$) is plotted to determine the energy band gap of the AZO films. The sharp absorption edges are accurately determined for the AZO films using linear fitting. The optical band gap energies of the AZO films, as determined from the obtained transmittance spectra, are shown in Fig. 5. The energy band gap for the as-grown AZO thin film is about 3.67 eV, which is much larger than that of bulk ZnO (3.3 eV). The

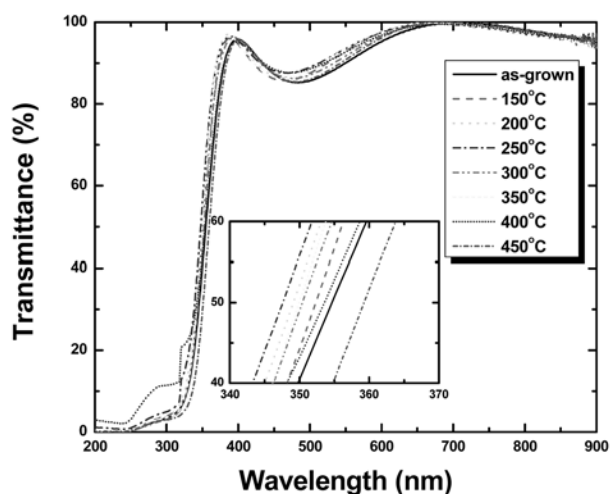


Fig. 4. Optical transmittance spectra for as-grown Al-doped ZnO films and those annealed for 1 h at 150, 200, 250, 300, 350, 400, and 450 °C. The inset represents enlarged optical transmission spectra in a wavelength range between 340 and 370 nm for the as-grown and annealed Al-doped ZnO films.

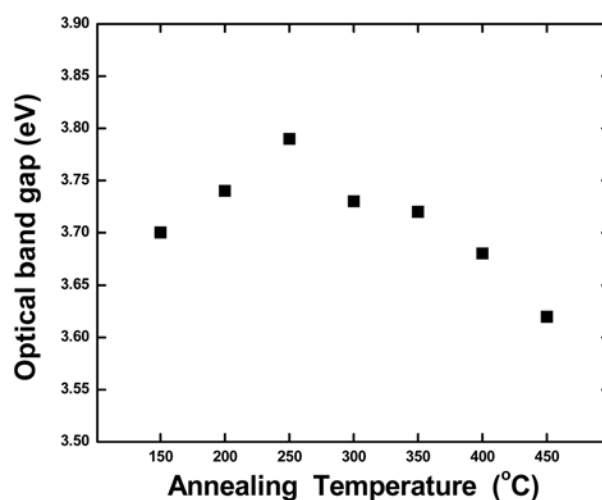


Fig. 5. Optical band gap energy as a function of the annealing temperature for Al-doped ZnO thin films.

larger energy band gap of the AZO films in comparison with that of bulk ZnO is attributed to the Burstein-Moss effect due to Al doping [18, 19]. Because ZnO materials are typically n-type, the Fermi level of the heavily-doped ZnO material is located near the conduction band edge. Because the interstitial states below the conduction band edge of the AZO films are occupied by the dopants, the absorption edge shifts to a higher energy. Fig. 5 shows the optical band gap as a function of the annealing temperature for AZO films grown on glass substrates. While the optical band gap of the AZO films increases with an increase in the annealing temperature from 150 to 250 °C, that of the AZO films decreases with annealing from 300 to 450 °C, which might be attributed to ZnO decomposition due to the higher thermal energy.

Summary and Conclusions

The effects of annealing on the structural, the electrical, and the optical properties of AZO thin films prepared by a tilted dual RF magnetron sputtering system were investigated. XRD patterns for the AZO thin films grown on glass substrates showed that the FWHM of the (0002) peak corresponding to the AZO thin film decreased from 1.5° to 1° with an increase in the annealing temperature from 150 to 450 °C. AFM images showed that the root mean square of the average surface roughnesses of the AZO films decreased from 3.28 to 1.38 nm with an increase in the annealing temperature from 150 to 450 °C. Hall effect measurements showed that the resistivity of an AZO film annealed at 250 °C was as small as $8 \times 10^{-4} \Omega\cdot\text{cm}$. The transmittance spectra showed that the average transmittance in the wavelength range between 400 and 800 nm was above 90%. While the optical band gap of the AZO films increased with an increase in the annealing temperature from 150 to 250 °C, that of the AZO films decreased with annealing from 300 to 450 °C, which might be attributed

to ZnO decomposition due to the higher thermal energy. These results can help improve an understanding of the thermal effects on the structural, the electrical, and the optical properties of AZO films deposited on glass substrates.

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