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Effect of oxygen partial pressure contents on the properties of Al-doped ZnO thin films prepared by radio frequency sputtering

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Al-doped Zinc Oxide (AZO) films were deposited on glass substrates by radio frequency (R.F.) magnetron sputtering technique. The properties of the films were controlled by adjusting the oxygen flow contents as a mixture of Ar and O_2 gases. The structural, electrical and optical properties of the films were characterized by X-ray diffraction (XRD), atomic force microscopy (AFM), a UV-visible spectrometer, as well as Hall effect measurements. Results revealed that a film deposited with an oxygen partial pressure content of 0% had a hexagonal structure, a strongly preferred orientation with the c-axis perpendicular to the substrate and the lowest resistivity of about 6.9×10^{-4} Ω cm. The optical transmittance spectra showed more than 80% transmittance in the visible region, and the band gap was found to be direct. Strong violet emission located at 2.96 eV was observed in the AZO films deposited with an oxygen partial pressure content of 0%.

Key words: Al-doped ZnO film, Magnetron sputtering, Oxygen partial pressure.

Introduction

Intrinsically, Zinc Oxide (ZnO) is a II-VI n-type semiconductor compound with a wide band gap (3.3 eV at 300 K). ZnO has received extensive research recently for its potential application in optoelectronics, solar cells, gas sensors, ultrasonic oscillators and transducers [1] because it offers advantageous optical and electrical properties over conventional wide band gap materials. ZnO brings the hope to replace the indium tin oxide (ITO) as a transparent electrode in gallium nirtide (GaN) devices because of its wide band gap, non-toxicity and low cost. So far, the highest conductivity of a ZnO film was reported by doping a ZnO film with Aluminum, a group metal when substitution of Zn by Al in the metal sites of the lattice and the release of free electrons occurred. Compared with undoped ZnO, the Al-doped ZnO (AZO) films have a lower resistivity and better stability [2].

Several techniques have been used to fabricate epitaxial and textured ZnO films, including chemical vapor deposition (CVD), molecular beam epitaxy (MBE), pulsed laser deposition (PLD) and radio frequency (R.F.) magnetron sputtering [3-6]. Among these, R.F. magnetron sputtering is widely used in fabricating metal oxide thin films and related materials. From the viewpoint of practical use, the films should be deposited on an amorphous substrate such as glass. Since Krikorian and Sneed [7] have established that the three most important parameters that determine the film properties in sputtering for a given material and substrate are substrate temperature, deposition rate, and background pressure. Many reports already showed that the properties of thin films were mainly influenced by process parameters during sputtering, such as substrate temperature, discharge power, target-substrate distance and oxygen flow content [8-10].

In this study, we explored various oxygen flow contents in R.F magnetron sputtering to achieve high quality AZO films on glass substrates for transparent conducting electrodes in a solar cell application. The structural, electrical and optical properties of the AZO films grown by R.F. magnetron sputtering on glass substrates were fully characterized.

Experimental Details

AZO films were grown on Corning 7059 glass substrates by R.F. magnetron sputtering as function of different oxygen flow contents ($O_2/Ar + O_2$). The substrates were cleaned with acetone, methanol, and isopropyl alcohol for 10 minute each, and rinsed with deionized water and then dried. After cleaning, all samples were loaded into a chamber immediately. A 50 mm diameter Al-doped ZnO (AZO) target contains 2 wt% Al_2O_3 was used for the sputtering. The distance between the target and substrate was about 40 mm. In order to clean up the surface of the target, 10 minute pre-sputtering was performed with a R.F. power of 100 W under a pure Ar atmosphere while the substrate was covered with a shield. The substrate temperature was fixed at 400 °C and then the oxygen flow contents were varied from 0% to 50%.

Changes in the crystal orientation and surface morphology were inspected by X-ray diffraction (XRD) and atomic

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force microscopy (AFM) measurements, respectively. The sheet resistance, Hall mobility, and carrier concentration were measured at room temperature using the van der Pauw method. The optical transmittance was measured using a UV/VIS spectrophotometer operating in a spectral range of 300-1100 nm.

Results and Discussion

Structural properties

X-ray diffraction was carried out to confirm the crystal structures of the films. The XRD patterns of the AZO films deposited at various oxygen flow contents are shown in Fig. 1. The angular positions of Bragg reflections corresponded well to the standard XRD patterns of hexagonal ZnO with a Wurzite-type crystalline lattice. Results indicate that all films were polycrystalline and show a preferential orientation in the (002) direction exhibiting the c-axis perpendicular to the substrate.

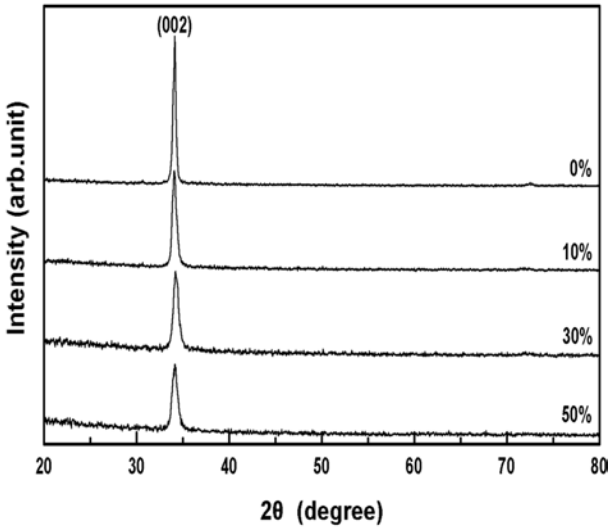

Fig. 1. XRD spectra of AZO films grown at various oxygen flow contents of 0%, 10%, 30% and 50%.

When the oxygen partial pressure content was 0%, the intensity of the (002) plane was observed to be higher than the others. However, as the oxygen partial pressure content was increased to 50%, the crystallinity of the films became poorer. With the content of oxygen in the sputtering ambience further increased, the peak intensity was significantly decreased to a minimum. This could due to adsorbed oxygen atoms in the grain boundaries and the substitution function of Al for Zn atoms, consequently leading to the poorer crystallinity.

The AFM images of the AZO films grown at four different oxygen flow contents are shown in Fig. 2. It is noted that the surface morphology of the films depends strongly on the nature of the substrate because the crystallinity and the substrate surface roughness determine the grain growth in thin films [1]. The surface roughness was characterized by the root mean square (RMS) value. The surface topographies were acquired by scanning over an area 10 × 10 um. A RMS value of 9.8 nm was measured on the surface of the sample grown at an oxygen partial pressure content of 0%, and reduced down to 1.9 nm in the sample deposited on a substrate at the oxygen partial pressure content of 10%, and then slightly increased to 2.7 nm with a further increase of the oxygen partial pressure content up to 30%. The grain size was observed to decrease with an increase of the oxygen partial pressure content, and finally the grains were formed by many small crystallites aggregated with sizes varying between 8.9 and 40.8 nm with irregular shapes. Moreover, large size hexagonal crystallites were observed

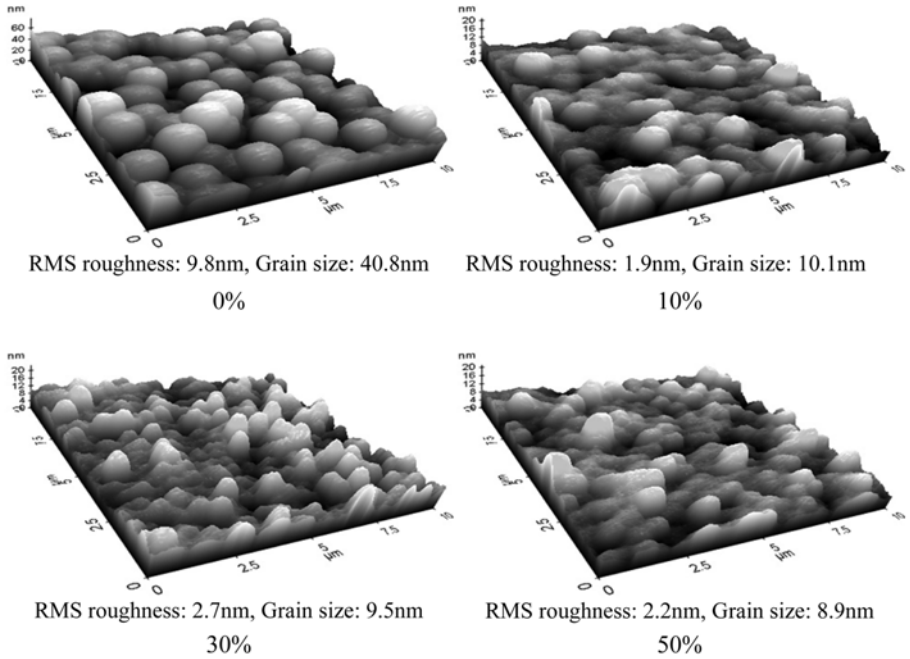

Fig. 2. AFM surface images of AZO films deposited at different oxygen flow contents of 0%, 10%, 30% and 50%.

in the AFM images of the sample grown at an oxygen partial pressure content of 0%. As the content was increased, no obvious grain boundaries could be observed. Results suggest the coexistence of an amorphous Al complex and polycrystalline ZnO in the AZO film.

Electrical properties

Fig. 3 shows the variation of electrical resistivity, carrier concentration, and Hall mobility of the AZO films deposited on glass substrates as a function of various oxygen flow contents. All the films showed n-type conduction. As shown in Fig. 3, the resistivity calculated using the van der Pauw method was 6.9×10^{-4}, 7.7×10^{-3}, 4.4×10^{-2}, and 4.9×10^{-2} Ω cm for the films deposited at oxygen partial pressure contents of 0, 10, 30, and 50%, respectively. The film grown with the content of 0% showed the lowest resistivity of 6.9×10^{-4} Ω cm.

The resistivity was increased rapidly with an increase of the oxygen flow content. On the other hand, the carrier concentration and the Hall mobility were decreased with an increase of the oxygen partial pressure content. The improved electrical conductivity was primarily due to the contributions from Zn, Al interstitial atoms and oxygen vacancies. In addition, the chemisorption of oxygen and the Al complex may lead to an increase in scattering centers which resulted in a decrease in mobility. Besides, the resistivity ρ is proportional to the reciprocal of the product of carrier concentration N and mobility μ as described in the equation [11]:

$$\rho = \frac{1}{Ne\mu} \tag{1}$$

AZO film deposited at an oxygen partial pressure content of 0% showed the lowest resistivity, which probably resulted from the highest product of carrier concentration N and the mobility μ.

In the ZnO film, an oxygen adsorbed on the surface of crystallites not only traps an electron and decreases the carrier concentration, but also decreases the Hall mobility by increasing the potential height at the surface of crystallites [11]. It was also found that the crystallinity was substantially improved with an oxygen partial pressure content of 0% as observed by the larger grain size in Fig. 2. Therefore, it can be concluded that the electrical properties are closely related to the oxygen flow content and the crystallinity during the deposition.

Optical properties

Fig. 4 shows optical transmittance spectra of the AZO films as a function of different oxygen flow contents. The average transmittance of the films was higher than 80% in the visible region from 300 to 1100 nm with a sharp fall in the transmittance at the absorption edge, which indicated good crystallinity in the sputter-deposited films. In Fig. 4, the optical absorption edge was shifted towards the shorter-wavelength region for the films deposited at an oxygen partial pressure content of 0% and shifted to a longer wavelength for the films deposited at the oxygen partial pressure content of 50%. The shift of the absorption edge to the shorter-wavelength region is attributed to the Burstein-Moss shift [12], which is due to an increase in the carrier concentration.

Such a behavior was expected as a result of substitutional doping of an Al^{3+} at the Zn^{2+} site creating one extra free carrier in the process. Burstein [12] pointed out that an increase in the Fermi level in the conduction band of degenerate semiconductors leads to a band gap widening effect, which is consistent with our experimental results. The maximum transmittance was observed from the film deposited with an oxygen partial pressure content of 0%. According to the XRD spectra shown in Fig. 1, we can

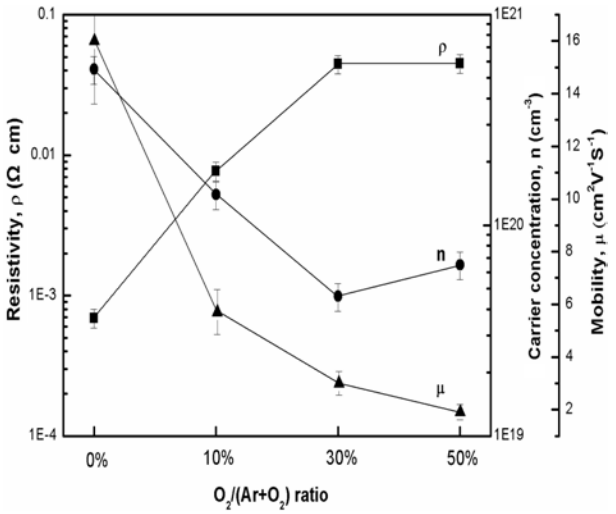

Fig. 3. Electrical properties of AZO films prepared at several oxygen flow contents.

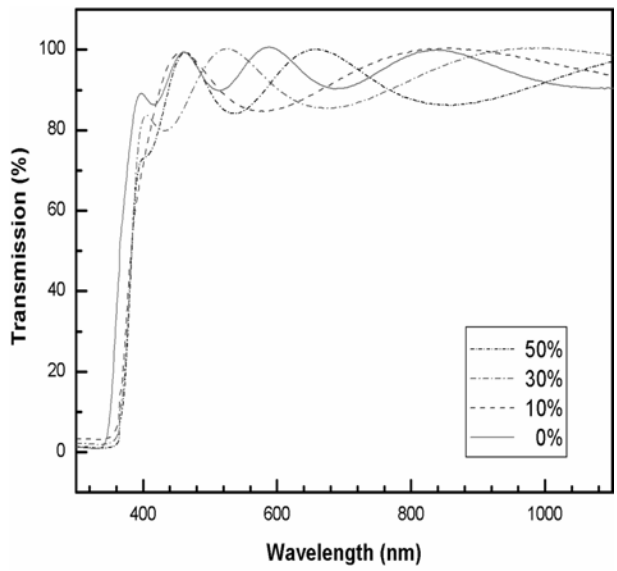

Fig. 4. Optical transmittance spectra of AZO films grown at various oxygen flow contents.

conclude that the AZO film deposited in an oxygen flow content of 0% had the best crystallinity. Therefore, the AZO film prepared at this same condition also had the best transmittance in the visible region. The results indicate the optical properties of the AZO films are significantly affected by the oxygen flow content.

The relation between the absorption coefficient (α) and the incident photon energy hv can be written as:

$$ahv = A(hv - Eg)^m \quad (2)$$

Where A is a constant and m = 1/2 and 2 for direct and indirect allowed transitions, respectively. The $(\alpha hv)^2$ versus hv plots for the AZO films fabricated on glass substrates is shown in Fig. 5. The graphs of $(\alpha hv)^2$ versus hv were found to be straight lines over the whole optical absorption spectra, thus supporting the interpretation of a direct rather than an indirect band gap for all AZO films. The direct energy band gaps were found to be 3.45, 3.38, 3.36, and 3.33 eV for the films deposited at various oxygen flow contents of 0, 10, 30, and 50%, respectively.

Fig. 6 shows the room-temperature PL spectra of the AZO films grown with different oxygen flow contents. It is noted that all samples show a strong violet emission centering about 419 nm (2.96 eV) without any accompanying deep-level emission and UV-band emission, indicating non-stoichiometric AZO films. Also, results show that the violet emission peak position shifted slightly from 419 nm to 439 nm when the oxygen flow content was increased from 0% to 50% and then the intensity of the violet emission peaks were decreased with an increase of the oxygen flow contents.

This means that the intensity of PL peak is related to the oxygen vacancies in the ZnO film. Bachari *et al.* [13] studied the effect of the oxygen partial pressure on the stoichiometry of ZnO films deposited by R.F. magnetron

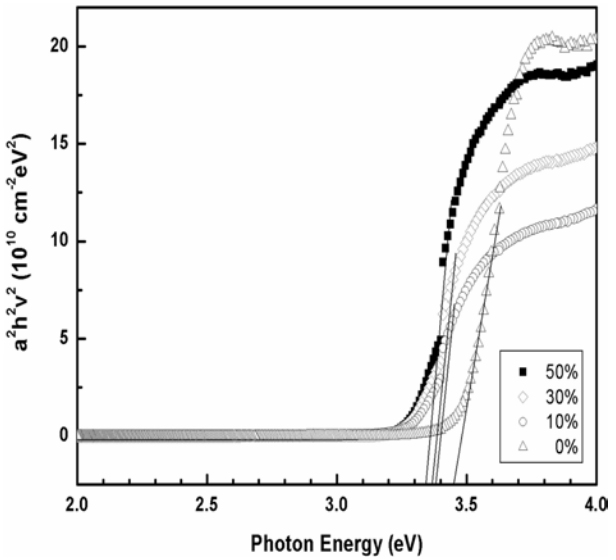

Fig. 5. Plots of $(\alpha hv)^2$ vs photon energy for AZO films deposited at various oxygen flow contents.

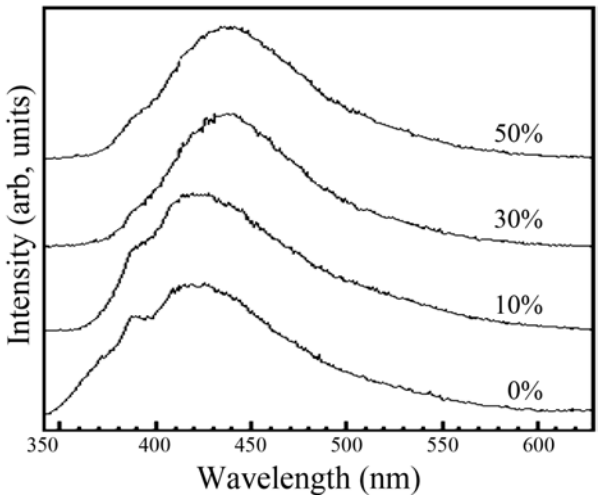

Fig. 6. Room temperature PL spectra of AZO films deposited at various oxygen flow contents.

sputtering and found that the stoichiometry of the films could be further improved by increasing the oxygen partial pressure. With an increase in the oxygen partial pressure, the deficiency of the oxygen vacancies leads to a decrease in PL intensity.

Generally, UV emission originates from crystal defects or (002) oriented ZnO films. Different defects in ZnO films contribute to different emissions of the PL spectra [14]. Sun calculated the energy levels of various intrinsic defects in ZnO by applying the full-potential linear muffin-tin orbital method [15]. According to Sun's calculated results, the calculated energy interval from the interstitial zinc (Zn_i) level to the valence band was 2.9 eV, which was well consistent with the violet emission peaks centered around 419 nm (or 2.96 eV) of the AZO films deposited at various oxygen flow contents in this study. Therefore, it could be deduced that the violet emission of PL spectra of the AZO films was attributed to the energy transition of electrons from the interstitial zinc (Zn_i) level to the valence band [16-17].

Conclusions

In this study, AZO films were prepared by changing the oxygen flow contents. The structural, electrical and optical properties of the films were analyzed. As the oxygen flow content in the sputtering ambience was increased, the (002) diffraction peak intensity was decreased and led to poorer crystallinity. Moreover, large size hexagonal crystallites were observed in the AFM images of the sample grown at an oxygen flow content of 0%. The resistivity was increased with an increase of the oxygen flow content. This is attributed to the fact that the amount of oxygen vacancies as donors was reduced as a result of introducing oxygen into the films. In addition, the conductivity of the AZO films was closely connected with the crystallinity, carrier concentration and mobility. The AZO film deposited

in an oxygen flow content of 0% had an excellent transmission in the visible region and showed a typical violet luminescence behavior. Therefore, increasing the oxygen flow content had negative effects on the structural, electrical and optical properties of the AZO films.

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