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Deposition-Temperature Effects on AZO Thin Films Prepared by RF Magnetron Sputtering and Their Physical Properties

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Transparent conductive thin films have attracted much attention due to their high conductivity and transmittance. In this paper, in order to find the optimal condition for fabricating optoelectronic devices, we investigated aluminum-doped zinc oxide (AZO) thin films prepared by radio-frequency (RF) magnetron sputtering on glass substrates by using a 2 wt.% of Al-doped ZnO target as a function of deposition temperature. The structural, electrical, and optical properties of AZO thin films were studied in terms of the deposition temperature. The crystal structure of AZO thin films had a hexagonal wurtzite structure and the orientation of the sample was along the *c*-axis, regardless of deposition temperature. The deposition temperature had influence on the average grain size and surface roughness, which could be confirmed by means of SEM and AFM. The average grain size increased with increasing deposition temperature. After increasing the deposition temperature, the surface of the AZO thin film improved but the root-mean-square (RMS) value of the surface roughness slightly increased. Also, the average transmittance of AZO thin films in the visible range (400 $\sim$ 800 nm) was above 90 %. The optical band gap was dependent on the deposition temperature, and the value of the band gap of AZO thin films increased with increasing deposition temperature. The experimental results showed that the electrical resistivity of the AZO films deposited at room temperature (RT) and at 500 °C were 8.046 $\times$ 10^{-4} Ω-cm and 1.297 $\times$ 10^{-4} Ω-cm, respectively. Based on this work, we can find the best physical conditions of AZO thin films. Therefore, fabricated AZO thin films can be applied to transparent electrodes of OLEDs.

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I. INTRODUCTION

Zinc oxide (ZnO) is one of the promising wide-band-gap II-VI compound semiconductors for visible and ultraviolet (UV) optoelectronic devices. ZnO can be found easily as *n*-type because of Zn interstitials and oxygen vacancies. Recently, the doping of different elements has been attempted to induce new interesting properties, such as for transparent electrodes [1, 2] and dilute magnetic semiconductors [3, 4]. In particular, transparent conductive oxide (TCO) electrodes using Al-doped ZnO have attracted much attention as powerful candidate materials for ITO transparent electrodes. Transparent electrodes in optoelectronic devices should have high visible transmittance, low resistivity, high infrared reflectance and absorbance in the microwave region [5]. The common transparent electrode material was indium tin oxide (ITO). However, ITO is likely to become unavailable because the fast-growing semiconductor industries are faced with the limitation of indium resources and toxicity in the atmosphere. In view of the depletion

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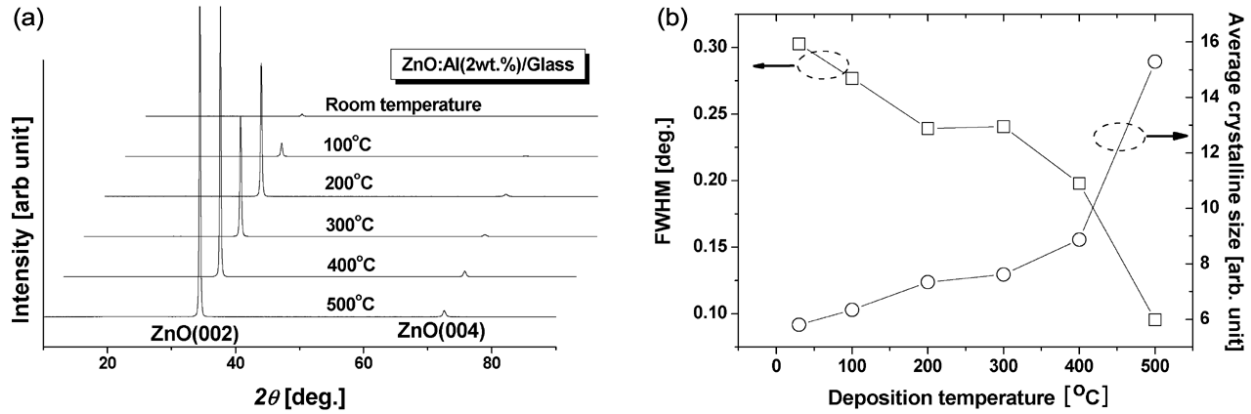

Fig. 1. (a) X-ray diffraction patterns for AZO thin films at different deposition temperatures, and (b) temperature effects on the full width at half maximum (FWHM) and crystalline size.

of ITO, AZO will be emerging as an alternative transparent electrode. In comparison with ITO, AZO thin films have a variety of advantages such as good electrical conductivity and transmittance, abundance as a raw material, a nontoxic nature, and high stability in hydrogen gas [6]. It has been reported that ZnO can be deposited by various techniques including radio-frequency (RF) magnetron sputtering [7, 8], direct-current (DC) sputtering [9], spray pyrolysis [10], pulsed laser deposition (PLD) [11], and chemical vapor deposition (CVD) [12]. The specific growth techniques are a crucial factor to control physical properties of AZO thin films such as structural, optical, and electrical characteristics. RF magnetron sputtering has advantages in target fabrication, deposition speed, and control of gas pressure. There are numerous reports dealing with oxygen pressure, target-to-substrate distance, post-deposition annealing, and hydrogen effects on the quality of AZO thin films [8,13–15].

In this study, we investigate the thermal effects of AZO thin films on glass substrates as a function of the deposition temperature with low oxygen pressure. In order to provide the best condition for applying the AZO electrode to the optoelectronic device, the structural, optical, and electrical properties are also examined in this paper.

II. EXPERIMENTS

AZO thin films were deposited on glass substrates (Corning 1737, Samsung) by employing the RF magnetron sputtering technique. 2 wt.% of Al-doped ZnO target was the optimum composition to achieve the minimum resistivity [16]. Therefore, a 2 wt.% target of Al-doped ZnO was used to deposit AZO thin films in this work. The AZO target was specially designed by sintering a mixture of high-purity zinc oxide (ZnO, Aldrich Chemical Company, 99.9 %) and aluminum oxide (Al_2O_3, Aldrich Chemical Company, 99.9 %). The sputtering system was pumped down to 4×10^{-6} Torr by using a rotary pump and a turbo molecular pump. The working pressure was 1×10^{-2} Torr. Before sputtering, the Corning glasses were ultrasonically cleaned sequentially in distilled water, acetone, alcohol, and distilled water, and finally dried with nitrogen gas. After 5 minutes' pre-sputtering with Ar plasma, AZO thin films were deposited on the glass by using 2 wt.% of Al-doped ZnO target with RF power of 120 W according to the different deposition temperatures (room temperature ∼500 °C). Since high transparency and low resistivity are essential factors to fabricate high-performance optoeletronic devices, the crystallinity, crystal structure, and growth orientations were investigated by X-ray diffraction (XRD), and the surface morphology was studied by using a scanning electron microscope (SEM) and an atomic force microscope (AFM). The electrical properties were also studied by resistivity measurement. The optical properties were also studied in the visible range by employing UV/VIS/NIR spectroscopy and by analyzing the relationship of the widening of the optical band gap with changes in the deposition temperature.

III. RESULTS AND DISCUSSION

Figure 1 shows XRD spectra of AZO thin films prepared with different sputtering temperatures. As shown in Figure 1(a), the peak of ZnO(002) was observed at $2\theta \sim 34.45°$. The peak of ZnO(004) was $2\theta \sim 72.57°$ as indicated in Figure 1(a). This indicates that the AZO thin films have a good *c*-axis orientation, that is the vertical growth to the substrate. At lower deposition temperature, we can find a slight peak shift of the position toward 34°. However, with increasing deposition temperature, perfect *c*-axis-orientation growth at the position of ZnO(002) was achieved. For all samples, the peak in-

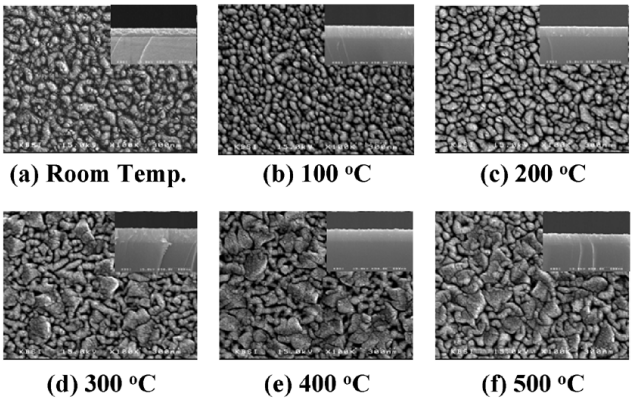

Fig. 2. Scanning electron micrographs of AZO thin films at different deposition temperatures.

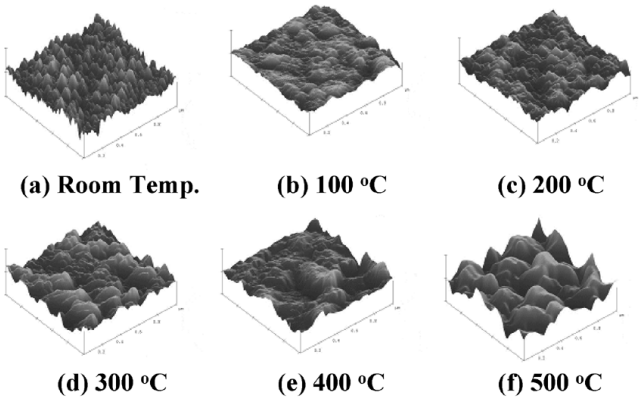

Fig. 3. AFM images of AZO films at different deposition temperatures.

tensity increased and the detected noises decreased with increasing deposition temperature. In order to investigate the effect of the deposition temperature on the crystallinity and the average grain size, the full width at half maximum (FWHM) was calculated from the XRD spectra, and the average grain size can be deduced by the Scherrer formula:

$$t = \frac{0.9\lambda}{\Delta\theta \cos\theta_B}, \quad (1)$$

where t is the grain size, $\Delta\theta$ is the FWHM, and θ_B is the Bragg angle as shown in Figure 1(b). Depending on the deposition temperature, the crystalline size varied from 5.8 to 15.3 nm. FWHM shrank, which was evidence of the improvement of the crystal quality, and the grain size of the as-grown AZO film increased on increasing the deposition temperature.

Since the surface properties of the AZO thin films can affect electrical and optical properties and characteristics of the optical devices, it is very important to investigate the surface morphology of AZO thin films. Figure 2 shows SEM surface micrographs of AZO films prepared at various deposition temperatures. As the deposition temperature increased, the grain size increased and the surface roughness decreased. These results, in agreement with the XRD analysis, indicated that the diffusion probability of ZnO and Al atoms on the surface can be controlled by the deposition temperature. A higher temperature enhances the occupation probability of Al ions on Zn sites, as well as oxygen vacancies and Zn interstitial atoms. In other words, Al atoms can diffuse to the surface, dependent upon the deposition temperature. An increase in crystalline size would be strongly related to a decrease in resistance for free electrons, because of lower grain and grain-boundary scattering. At higher temperatures, cracks were observed in the AZO films, and the formation of cracks probably originated from the different thermal expansion coefficients of the films and substrates.

The average grain size of AZO films was checked by AFM images (1 μm $\times$ 1 μm) at different substrate deposition temperatures as indicated in Figure 3. As we can see from Figure 3, the surface was very flat and no very sharp peak appears in the domain. AZO film deposited at RT had an average grain size of 3.29 nm, and for a sample deposited at 500 °C was 15.03 nm. For all samples, the average grain size was in the range from 3.29 nm to 15.03 nm. We also measured surface roughness of the AZO thin films. It can be seen that the root-mean-square (RMS) roughness of the thin film increases with increasing deposition temperature. The RMS value of RT-deposited AZO was 1.38 nm, whereas the RMS value of AZO thin film deposited at 500 °C was 4.66 nm. Increasing the deposition temperature made the surface roughness larger. The larger values of the grain size also influenced the increasing RMS value of the samples. The result was in good agreement with XRD data in Figure 1.

Figure 4(a) shows the optical transmittance curve of AZO deposited on glass substrates at different deposition temperatures. The transmittance spectra as a function of wavelength were in the range of 300 $\sim$ 800 nm for the samples (thickness 450 nm). It was found that the average optical transmittance in the visible range (400 $\sim$ 800 nm) was above 90 % for all deposition temperatures, in comparison with the transmittance of ITO film (85 %), which is obtained by commercial means. This means that the deposition temperature does not have a significant effect on the transparency of the films over the visible light range. However, the shift in short wavelength was strongly related to the deposition temperature of the AZO films. Also, the peak oscillation in the curve was due to the irregular surface of the AZO films.

Figure 4(b) shows plots of the optical band gap for AZO thin films with different deposition temperatures. The optical band gap can be determined by plotting $(\alpha h\nu)^2 vs.\ h\nu$ and extrapolating the straight line portion of the energy axis. The optical absorption coefficient α

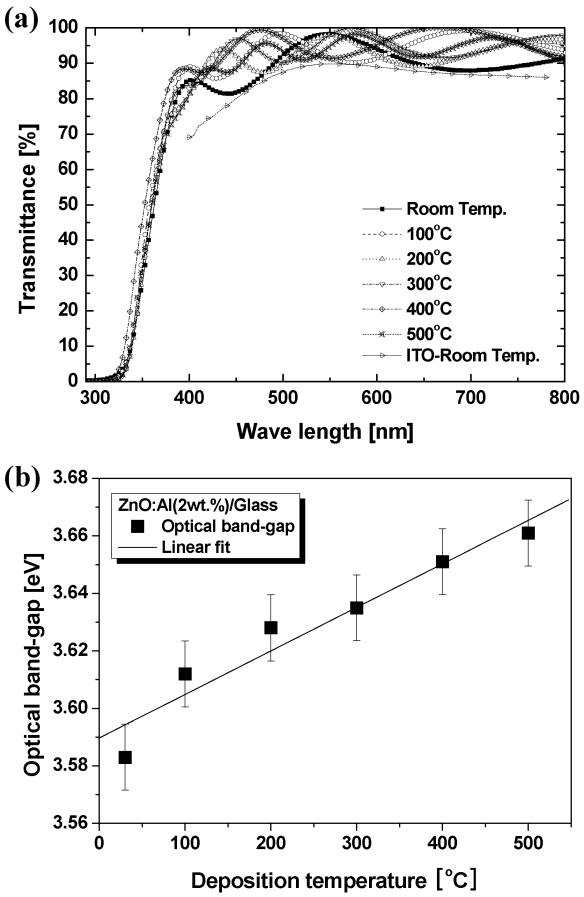

Fig. 4. (a) Optical transmittance of AZO thin films in the visible range, and (b) optical band gap of AZO films deposited at different deposition temperatures.

is defined as

$$I = I_0 e^{-\alpha t}, \tag{2}$$

where I is the intensity of transmitted light, I_0 is the intensity of incident light, and t is the thickness of the AZO thin film (450 nm). The transmittance T is defined as I/I_0, so we can obtain α from Eq. (2). Similarly to the structure of ZnO, the AZO thin films have a direct band gap. The absorption edge for direct interband transition is given by [17] as follows:

$$\alpha h\nu = C(h\nu - E_g)^{1/2}, \tag{3}$$

where C is a constant for a direct interband transition, and α is the optical absorption coefficient. The photon energy at the point where $(\alpha h\nu)^2$ is zero is E_g and can be determined by extrapolation of the curve. From Figure 4(b), E_g was 3.583 eV for deposits at RT, 3.635 eV for 300 °C, and 3.661 eV for 500 °C, respectively. The optical band gap decreased in accord with a decrease in the deposition temperature on the substrate. This can be explained by the Burstein-Moss effect that an increase

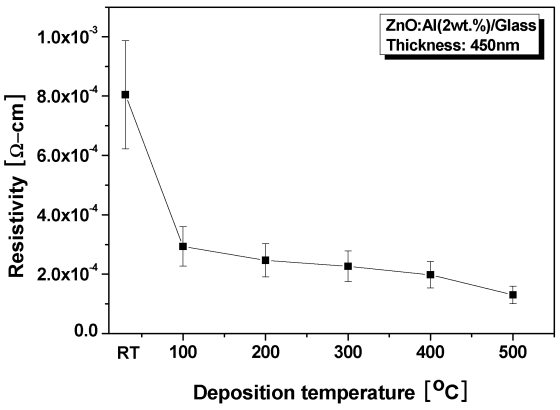

Fig. 5. Resistivity measurements of AZO thin films at various deposition temperatures.

of the Fermi level in the conduction band of a degenerate semiconductor leads to an energy band-widening effect, a "blue shift" [18]. Otherwise, the absorption edge of a degenerate semiconductor is shifted to high energies with increasing carrier concentration [18–20]. An increase of carrier concentrations with increasing deposition temperatures implies that more Al atoms diffuse into the ZnO layer and partially replace the Zn^{2+} sites at elevated temperature [21].

The conductivity of zinc oxide thin films was primarily dominated by electrons which were generated by the oxygen vacancies and Zn interstitial atoms. The electrical resistivity in AZO films was much lower than in pure ZnO films, due to the contribution from Al ions on the substitutional site of Zn ions and Al interstitial atoms as well as from oxygen vacancies [13]. Figure 5 shows the resistivity measurement of AZO thin films as a function of deposition temperature. The other experimental conditions were kept constant on each AZO thin film, except for the deposition temperature. The resistivity of AZO thin film decreased from 8.046×10^{-4} Ω-cm to 1.297×10^{-4} Ω-cm as the deposition temperature was increased from RT to 500 °C. The resistivity decreased with an increase in the deposition temperature. In particular, slight decreases in the resistivity were found above a deposition temperature of 200 °C. The decrease in resistivity with an increase in deposition temperature was due to the fact that the increasing deposition temperature can influence the growth of average grain size, thereby reducing the grain boundary scattering and decreasing the resistivity. The value of minimum resistivity of AZO thin film was 1.297×10^{-4} Ω-cm at a deposition temperature of 500 °C. From the experimental results mentioned above, we can find the optimum condition of AZO thin films for fabricating OLED devices. The best conditions of Al doping weight and deposition temperature for fabricating OLEDs were 2 wt.% and 500 °C, respectively. If we can apply the AZO thin films to the transparent electrodes

in OLEDs as a replacement for ITO electrodes, we can expect that the use of AZO will significantly contribute to an improvement in the performance of OLEDs.

IV. CONCLUSION

In this work, we found that the deposition temperature significantly affects structural, optical, and electrical properties of AZO films. Low resistivity and high transparency can be achieved by adjusting the substrate deposition temperature with 2 wt.% of Al-doped ZnO target. The average transmittance of AZO films was about 90 % in the visible range, and minimum resistivity was 129.7 $\mu\Omega$-cm at a deposition temperature of 500 °C when using 2 wt.% of Al-doped ZnO target. The FWHM decreased and crystalline size increased with an increase in substrate temperature. The optical band gap of AZO shifted to shorter wavelength with an increase in deposition temperature. This can be explained by the Burstein-Moss effect. The experimental results revealed that the best conditions for AZO thin films for OLEDs were 2 wt.% of Al-doped ZnO and 500 °C deposition temperature. Thus, fabricated AZO thin films are suitable for the application of transparent electrodes as an alternative to ITO.

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