



Highly transparent conductive and near-infrared reflective ZnO:Al thin films

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ABSTRACT

Al-doped ZnO (AZO) thin films have been prepared on glass substrates by pulsed laser deposition. The structural, optical, and electrical properties were strongly dependent on the growth temperatures. The lowest resistivity of $4.5 \times 10^{-4} \Omega\text{cm}$ was obtained at an optimized temperature of 350 °C. The AZO films deposited at 350 °C also had the high optical transmittance above 87% in the visible range and the low transmittance (<15% at 1500 nm) and high reflectance (~50% at 2000 nm) in the near-IR region. The good IR-reflective properties of ZnO:Al films show that they are promising for near-IR reflecting mirrors and heat reflectors.

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1. Introduction

Due to the long-time sun exposure in the tropics, there will be 85% solar energy penetrating through the common glass into our rooms. Along with the popularization of the cars, high temperature in the cars due to the sun exposure is attracting more and more attention. To this issue, there are two main problems. One is that the air-condition will waste too much fuel oil. On the other hand, the sun exposure will cause the aging of the materials in the cars. In this regard, a layer of thin film on the glass is necessary in order to reduce the sunlight radiation. The films should be highly transparent in the visible light region and highly reflective in the near-IR region. Tin-doped indium oxide (ITO) and doped zinc oxide (ZnO) thin films can both satisfy the foregoing characteristics. However, ITO has disadvantages including toxicity, high price, and instability in hydrogen plasma [1]. Accordingly, ZnO has attracted much attention to replace ITO because of high transmittance, non-toxicity, and low cost [2]. Undoped ZnO films are highly resistive. In contrast, doped ZnO such as Al-doped ZnO (AZO) can increase the conductivity by several orders of magnitude [3,4]. AZO thin films can be prepared by many techniques including spray pyrolysis [5], magnetron sputtering [3], sol-gel [6], pulsed laser deposition (PLD) [7], and so on. Among these techniques, PLD seems more advantageous owing to the production of high-quality AZO films at high deposition rates and the similar composition between the films and corresponding targets [7].

To date, the reported reflectance of AZO films on glass was commonly lower than 40% at 2000 nm [8–10]. To meet the

commercial applications, a higher near-infrared reflectance is necessary. In this work, we therefore focus on improving the optical performances in the visible and near-IR regions with high film quality. The influence of growth temperatures on the structural, electrical, and optical properties of AZO thin films has been studied in detail. Highly transparent conductive and near-IR reflective AZO films were deposited by PLD, with a high reflectance of 50% at 2000 nm under optimized growth conditions. To the best of our knowledge, such a high reflectance has not been reported in transparent conducting AZO films before.

2. Experiments

ZnO:Al thin films were deposited by PLD using a ceramic target with the deposition temperatures ranging from room temperature (RT) to 450 °C. The target was fabricated using high-purity ZnO (99.99%) and Al₂O₃ (99.99%) powders with an atomic ratio of Zn/Al of 0.97:0.03. The vacuum chamber was evacuated to a base pressure of 6×10^{-4} Pa firstly. Then, the deposition was carried out in high-purity oxygen ambient at a pressure of 0.5 Pa. All the films were deposited on glass substrates. The substrates were cleaned in an ultrasonic bath using acetone and then ethanol for 30 min, rinsed in de-ionized water, and subsequently dried in a flowing nitrogen gas. A pulsed KrF laser (Compex102, 248 nm, 6 ns) was employed as the ablation source, operating at 280 mJ/pulse and 5 Hz. The target to substrate distance was 45 mm, and the deposition time was kept at 40 min.

The electrical properties were measured by Hall measurements in the van der Pauw configuration (Bio-Rad HL5500PC) at RT. The crystal structure of the films was analyzed by x-ray diffraction (XRD) using a Bede D1 system with a Cu K_α radiation ($\lambda = 0.1541$ nm). The film

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thickness and surface quality was measured using a SIRION field emission scanning electron microscopy (FE-SEM). The chemical bonding states of Al and the contents of Al in the film were analyzed by x-ray photoelectron spectroscopy (XPS) (Thermo ESCALAB 250, Al $K\alpha$ radiation source $h\nu = 1486.6$ eV). The optical transmission and reflection spectra were measured with a UV-4100 spectrophotometer.

3. Results and discussion

3.1. XRD analysis

Fig. 1 presents the XRD patterns (θ - 2θ) of ZnO:Al films deposited at different substrate temperatures. As shown in this figure, the films exhibit highly preferred orientation with their crystallographic c -axis perpendicular to the substrates except the one deposited at RT. The intensity of (002) peak increases with the growth temperature and reaches a maximum at 350 °C, followed by a reduction with the temperature further increasing.

Fig. 2 shows the 2θ values of (002) diffraction peak of the films grown at different temperatures. It can be observed that with the growth temperature increasing, the 2θ values of (002) peaks increase from 33.92 °C to 34.29 °C. Fig. 3 shows the XRD pattern of the used Al-doped ZnO target, where the 2θ values of the (002) peak were determined to be 34.38 °C. Thus, the diffraction angle for the AZO films deposited at this temperature region is smaller than that of bulk Al-doped ZnO crystal. According to the radii of Al^{3+} (0.054 nm) and Zn^{2+} (0.074 nm) [8], it could be assumed that Al^{3+} ions substitute Zn sites in the ZnO lattice, which induces the significant alteration of the d -value. According to Bragg rule, the 2θ value of (002) peak of ZnO:Al thin films should be lower than that of bulk Al-doped ZnO crystal.

Fig. 2 also shows the full width at half-maximum (FWHM) of (002) diffraction peak of the films grown at different temperatures. It is seen that the FWHM first decreases from 0.441 at 250 °C to 0.404 at 350 °C and then increases to 0.422 at 450 °C. The FWHM value is influenced by many factors such as grain size, stress distribution, and crystal imperfection [3]. Regardless of the influencing factor, the FWHM value is widely used as a negative indicator of film quality. From this point of view, we could also draw the conclusion that the optimal growth temperature is 350 °C, since the corresponding AZO film has the best crystal quality considering its smallest FWHM value.

3.2. SEM observations

Fig. 4 shows the surface morphologies of the ZnO:Al films deposited at different temperatures. The surface is rather rough for

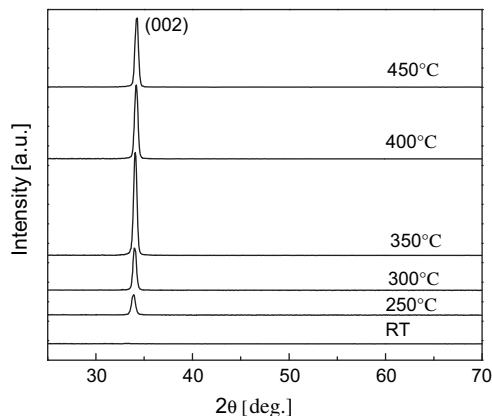


Fig. 1. X-ray diffraction (θ - 2θ) patterns as a function of growth temperatures for ZnO:Al films.

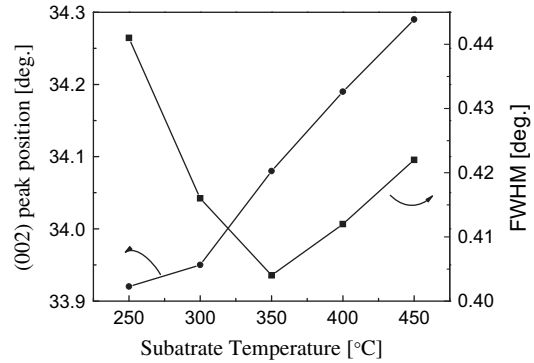


Fig. 2. Dependence of FWHM and 2θ value of (002) peak of ZnO:Al films on growth temperatures.

the AZO film grown at room temperature. In contrast, the surface becomes smooth for the AZO films grown above 250 °C. From 250 to 400 °C, the surface is not very different, except that there are some large AZO particles on the surface of the AZO film at 450 °C. The AZO film is very dense and the crystal grain cannot be clearly observed.

Fig. 5 shows the cross-sectional SEM image of the ZnO:Al thin film grown at 350 °C. The film exhibits a columnar crystal structure, with a thickness of about 730 nm. The thicknesses of the films deposited at different temperatures are shown in Table 1. As can be seen, the film thickness first increases and then decreases as the temperature increases. The tendency is the same as that reported by Bae *et al* [11]. At low temperature, it is hard to deposit. As the temperature increases, the film deposition becomes easy. But, when the temperature is too high, the film thickness decreases. It is noted that the thickness of the AZO film deposited at 350 °C is much thicker than those deposited at other temperatures, which also indicates that the temperature of 350 °C is suitable for film growth.

3.3. XPS analysis

Fig. 6 shows the $\text{Al}2p$ XPS spectra of the Al-doped ZnO films grown at the different temperatures. The $\text{Al}2p$ peak energies at different temperatures are located at between 73.8 and 74.1 eV, which are assigned to Al–O bond. Table 2 shows the Al contents in the films at different temperatures according to XPS measurements.

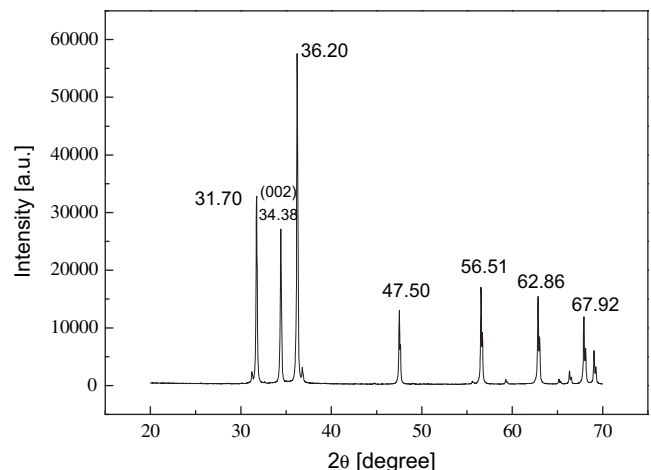


Fig. 3. The x-ray diffraction (θ - 2θ) pattern of the used Al-doped ZnO target.

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