Different properties of aluminum doped zinc oxide nanostructured thin films prepared by radio frequency magnetron sputtering

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Aluminium doped zinc oxide (AZO) nanostructured thin films are prepared by radio frequency magnetron sputtering on glass substrate using specifically designed ZnO target containing different amount of Al_2O_3 powder as the Al doping source. The optical properties of the aluminium doped zinc oxide films are investigated. The topography of the deposited films were investigated by Atomic Force Microscopy. Variation of the refractive index by annealing temperature are considered and it is seen that the refractive index increases by increasing the annealing temperature.

1. Introduction

ZnO is a II–VI compound semiconductor with a hexagonal wurtzite crystal lattice structure. ZnO transparent conducting films possess very interesting properties in the optical application fields. They have high transparency in the visible wavelength range and aluminium doped zinc oxide (AZO) thin films have a large band gap of about 3.3 eV [1]. These films have many applications such as solar cells, gas and optical sensors, ultrasonic oscillators, transducers, optical waveguides and photo protective coatings [2]. ZnO is naturally an *n*-type semiconductor because of a deviation from stoichiometry due to the presence of intrinsic defects such as O vacancies (VO) and Zn interstitials (Zn_i) [3]. Undoped ZnO shows intrinsic *n*-type conductivity with very high electron densities of about $10^{21}\,cm^{-3}$ [4]. Although it is experimentally known that unintentionally doped ZnO is *n*-type, whether the donors are Zn_i and VO is still controversial [3]. *n*-type doping of ZnO is relatively easy compared to *p*-type doping. Group-III elements Al, Ga, and In as substitutional elements for Zn and group-VII elements Cl and I as substitutional elements for O can be used as *n*-type dopants [3] Doping with Al, Ga, and In has been attempted by many groups, resulting in high-quality, highly conductive *n*-type ZnO films [5–11]. The physical properties of the films depend on the sputtering parameters, such as substrate temperature, different amount of dopant, the rf power and substrate–target distance. We have studied the structural and optical properties of AZO thin films prepared by sputtering technology, when they are submitted to an air annealing treatment in 373–423 K ranges.

We have produced ZnO films with a (0 0 2) preferential orientation onto glass substrate.

2. Experimental

Aluminum doped zinc oxide (AZO) films are prepared by rf magnetron sputtering on glass substrates using specifically designed ZnO-Al_2O_3 target prepared from ZnO-Al_2O_3 nanopowders with different amount of Al_2O_3 as dopant. In order to prepare the target, high purity ZnO (99.99%) and Al_2O_3 (99.99%) powders were used. The composition of the target was $(1-x)ZnO + xAl_2O_3$, where $x = 2.58$ wt%. The powder of ZnO-Al_2O_3 were mixed in ethanol by ultrasonic for 12 h at 323 K. The nanopowders of ZnO-Al_2O_3 is obtained successively by drying the mixture at 373 K. The targets were prepared by pressing the nanopowder under a pressure of 400 MPa in air at room temperature into a pellet with diameter of 120 mm and thickness of 3 mm and they have no conductivity at all.

Corning 2947 glass was used as the substrate and ultrasonically cleaned in distilled water, alcohol and then dried. The glass substrates were fixed parallel to the target with a distance of 4.5 cm. And the shutter was placed between the target and substrate in order to prevent undesirable sputtering.

Before sputtering, the chamber was evacuated to the base pressure of $5 \cdot 10^{-5}$ Torr. The temperature of substrate (T_S) was 273 K and the radio frequency (rf) power (P_{rf}) was 130 W. Sputtering was carried out in Ar plasma. Atomic force microscopy (Nanoscope-IV) in tapping mode was used to study the surface morphology of the deposited films. To find the thickness of the films we used a stylus profilometer [Veeco Dektak 3]. Optical transmittance spectra were recorded by UV-Visible, AGILEN 8453 spectrophotometer in the wave length range of 300–800 nm.

3. Results and discussion

3.1. Surface morphology

The surface topographies of Al-doped ZnO films obtained by AFM are shown in Fig. 1. Surface parameters, such as the maximum peak-to-valley distance ($R_{p\text{-}v}$), Rms roughness and average roughness were analyzed at several regions

Al percentage	$R_{p\text{-}v}$, Å	Rms rough, Å	Ave rough, Å
undoped	148	20.6	16.4
4 wt% Al-doped ZnO film	87.5	9.78	7.49

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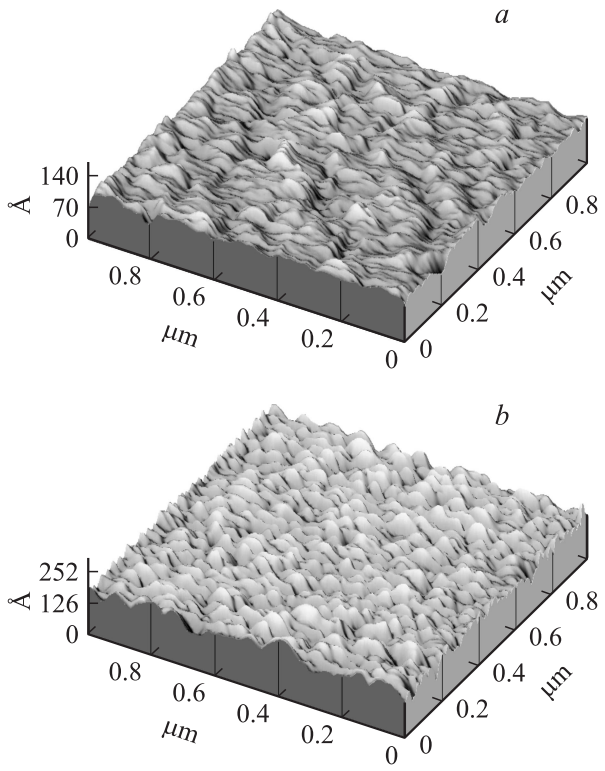

Figure 1. Surface parameters of undoped ZnOfilm (a); 4 wt% Al-doped ZnO film (b).

of the surface. The average values are given in Table. Fig. 1 shows AFM images of the ZAO films prepared with undoped and 4 wt% Al_2O_3 targets, respectively. It shows the large variation of surface roughness and grain size. The grain size of the undoped ZnO film (see Fig. 1, a) is larger than that of 4 wt% Al-doped ZnO film (Fig. 1, b), suggesting that the particles in ZnO films become smaller with increasing Al contents.

3.2. Optical properties

Fig. 2 shows the transmittance spectra of glass substrate (corning 2947). Fig. 3 shows the transmission spectra of AZO thin films (8 wt% Al_2O_3) annealed at 323–373° K in air. An average transmittance of above 90% in the visible range was obtained in both as-deposited and annealed AZO thin films. The films had 90–95% optical transmission in the visible range, which is important for its use in applications such as transparent conductive film.

3.3. Optical transmittance of AZO film as a function of rf power

Optical transmittance of AZO thin film is shown in Fig. 4 by rf power. The average transmittance in the visible range is found to be about 95%. It was found that the optical transmittance of these films was not influenced by rf power.

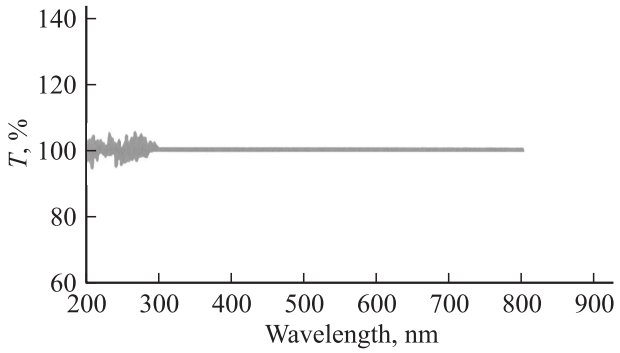

Figure 2. Transmittance spectra of glass substrate (corning 2947).

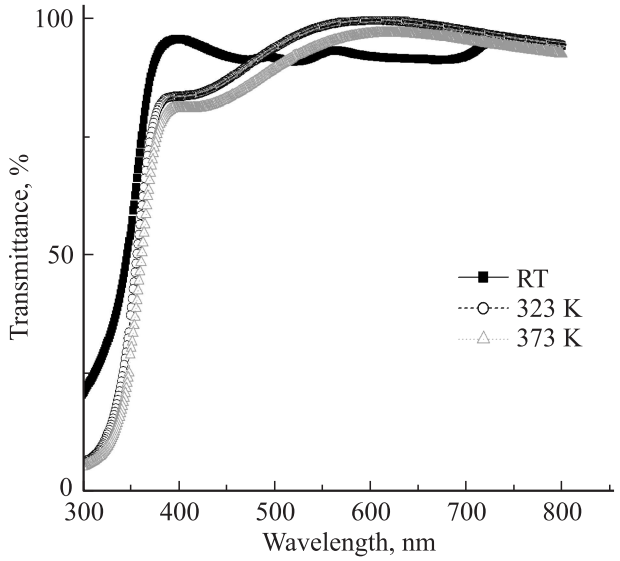

Figure 3. The transmission spectra of AZO thin films annealed at various temperatures in air.

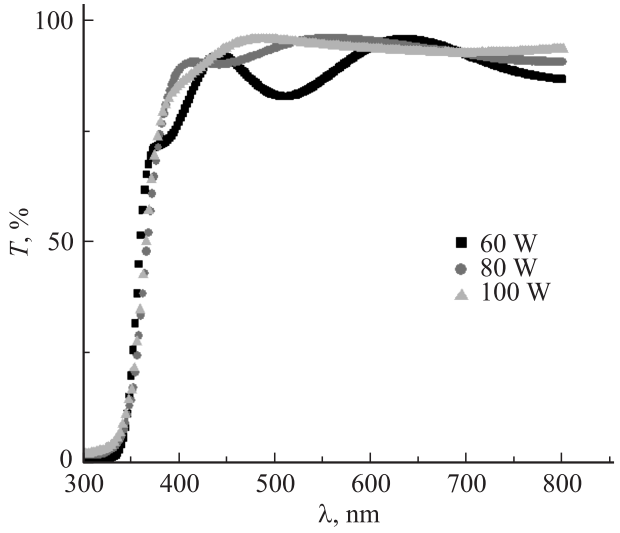

Figure 4. Dependence of optical transmittance of AZO thin film on rf power.

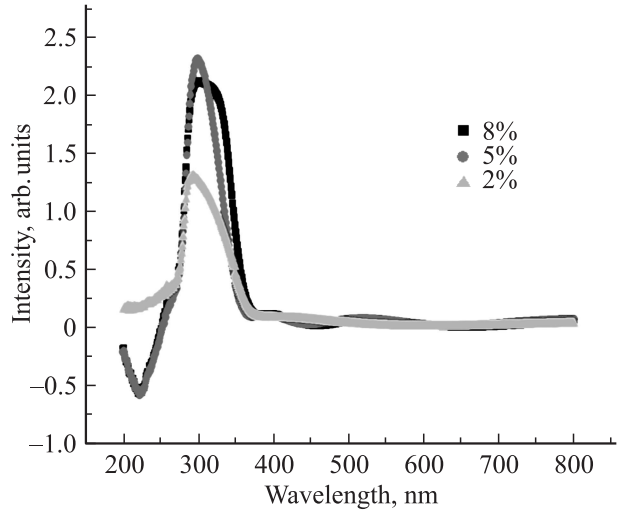

Figure 5. Absorption spectra of different Al content.

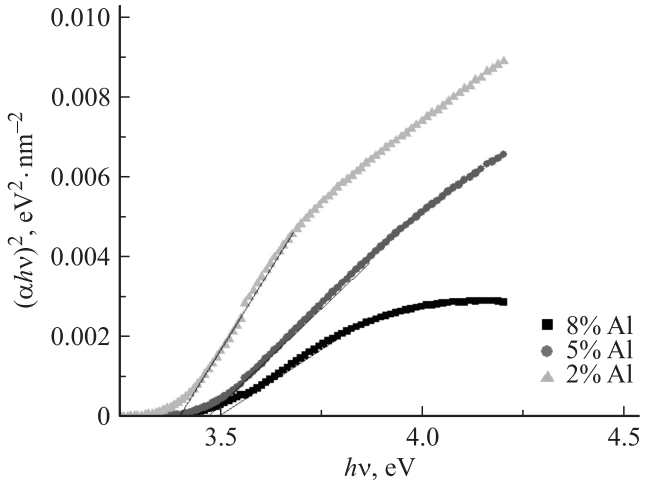

Figure 6. Variation of optical bandgap as a function of Al content.

3.4. Optical band gap of AZO as a function of Al content

Fig. 5 shows absorption spectra of different Al content. The variation of optical band gap as a function of Al content is shown in Fig. 6. It shows that the band gap widens (blue shift) with increasing Al content. It has the similar result investigated by Fukumura et al. [12]. As the Mn content in $Zn_{1-x}Mn_xO$ films with different Mn contents is increased, the midgap absorption around 3 eV develops and the absorption edge blueshifts. This broadening effect can be understood based on the Burstein effect [13]. Burstein pointed out that an increase in the Fermi level in the conduction band of degenerate semiconductors leads to widening of the energy band (blue shift). It shows that the band gap widens with increasing Al contents The reason is that the density of electrons decreased after the Al^{+3} ion was substituted into the Zn^{+2} ion site in the films. This means that the valence level was lowered.

4. Conclusion

We have successfully grown nanocrystalline AZO thin films by reactive rf-magnetron sputtering. The AFM result shows that the grain size of the un-doped ZnO film is larger than that of 4 wt% Al-doped ZnO film, suggesting that the particles in ZnO films become smaller with increasing Al contents. It was found that the optical transmittance of AZO thin films was not influenced by rf power. A clear blue shift in the optical absorption edge of AZO as compared to bulk ZnO has been observed with the resultant band gap in the range of 3.24–3.32 eV. The study shows the potential of nanocrystalline AZO thin films for optoelectronic devices in the UV region.

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