

Influence of Al-doping and Oxygen Partial Pressure on the Optical Properties of ZnO Films

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ABSTRACT

Al-doped ZnO (ZnO:Al) thin films were deposited on glass substrates using the radio frequency reactive magnetron sputtering technique. The effects of Al concentrations and oxygen partial pressures on the microstructure and the luminescence properties of the ZnO:Al thin films were studied. The results show that the crystallization of the film is promoted by appropriate Al concentration and oxygen partial pressure. Strong blue peaks located at 436 nm and weak green peaks located at about 495 nm and 530 nm were observed from the photoluminescence spectra of the samples. In addition, absorption properties of the samples were studied by UV spectroscopy. The optical band gaps calculated based on the quantum confinement model are in agreement with the experimental values.

Keywords: ZnO thin films, RF magnetron sputtering, X-ray diffraction, crystal structure, optical properties

1 INTRODUCTION

ZnO has recently gained much interest because of its potential use in many applications, ranging from thin film transistors, and various optoelectronic and piezoelectric applications to surface acoustic wave devices [1-7] because of its wide and direct band gap ($E_g \sim 3.2-3.4\text{eV}$ at 300K [8]), excellent chemical and thermal stability, and specific electrical and optoelectronic property of being a II-VI semiconductor with a large exciton binding energy ($\sim 60\text{meV}$). However, it has been observed that both the structural and optical properties are strongly dependent on the processing conditions, such as the doping agent, the annealing temperature and atmosphere, and even the measurement conditions. In this paper, ZnO:Al thin films were prepared on glass substrates by radio frequency co-reactive magnetron sputtering. The effects of doping levels and oxygen partial pressures on the optical properties of ZnO thin films were studied. The absorption spectra of the samples were measured, and the variation of the optical band gap was analyzed.

2 EXPERIMENTS

ZnO:Al thin films were prepared on glass substrates by radio frequency co-reactive magnetron sputtering. The glass

substrates were ultrasonically cleaned in acetone and rinsed in deionized water. In order to adjust the Al concentrations in the deposited ZnO:Al film, the relative sputtering area of Al-chips, which were attached on a Zn target (99.999% purity, 60 mm in diameter), was varied in the range of 0–3%. The target-to-substrate distance was 50 mm. The base pressure for the system was 2×10^{-4} Pa and film growth was carried out in the growth ambient with partial pressure ratios of oxygen 0.167, 0.375 and 0.500 at a working pressure of 1.0 Pa. ZnO:Al films were deposited on substrates heated at 150 °C with RF power of 100 W used during sputtering for 1 h. The crystal structures were studied by using x-ray diffraction (XRD, D/Max-2400). The photoluminescence measurements were carried out by using a Xe Lamp (RF-5301, wavelength 325 nm). The absorption spectra were measured by using Lambda 35UV/VIS, and all spectra were taken at room temperature in air.

3 RESULTS AND DISCUSSION

The structural properties and optical properties of the ZnO:Al thin films are presented in this section.

3.1 Structural Properties

Fig. 1 and Fig. 2 show XRD patterns of ZnO:Al thin films with different Al concentrations and oxygen partial

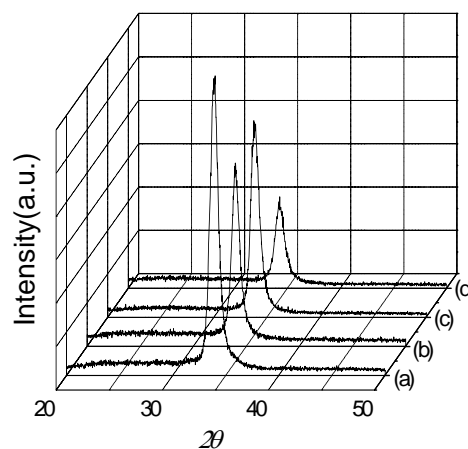


Figure 1: XRD patterns of sample a, b, c and d: (a) pure ZnO, (b) 1% Al, (c) 2% Al and (d) 3% Al.

pressures, respectively. All the samples indicated a preferential c-axis orientation of the ZnO films deposited. The particle sizes of the films were calculated using the Scherrer equation:

$$d = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

where λ , θ and β are the X-ray wavelength (1.5406 Å), diffraction angle and FWHM of the ZnO (002) peak.

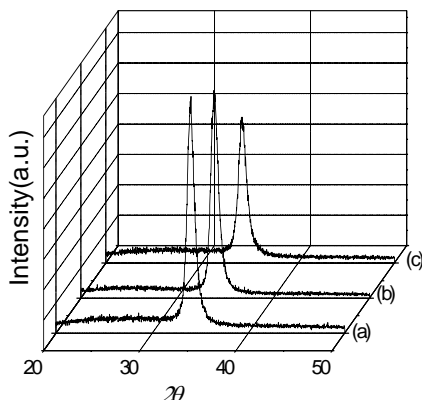


Figure 2: XRD patterns of sample under various oxygen partial pressure: (a) 0.167, (b) 0.375 and (c) 0.500.

The corresponding parameters of the (002) peak are listed in Table 1 and Table 2. It is obvious that the full width at half maximums (FWHMs) of the ZnO (002) peaks increased and particles size decreased after both Al doping and increasing the oxygen partial pressure. As can be seen from Fig. 1 and Fig. 2, the crystallinity of the films decrease with the increasing of the Al concentration (the oxygen partial pressure is kept constant), which indicates that small number of Al atoms may inhibit the c-axis preferential growth of ZnO films. Nevertheless, as the Al concentration further increases, the crystallinity is improved and reaches maximum. The same trend was also observed in Cu-doped ZnO films [9] and the improvement in crystallinity was considered to be due to a moderate number of Al atoms inhabiting interstitial sites and together with Zn atoms sharing oxygen atoms. However, crystallinity of the films decreases when the oxygen partial pressure is increased and Al concentration is kept constant (*i.e.* 2%)

Al Dopant	2θ (°)	FWHM(°)	Size(nm)	E_{opt} (eV)	E_{XRD} (eV)
pure ZnO	34.00	0.90	9.128	3.269	3.275
1% Al	33.96	0.96	8.556	3.308	3.285
2% Al	33.78	0.92	8.924	3.280	3.278
3% Al	34.28	1.02	8.060	3.329	3.296

Table 1: Parameters of the X-ray diffraction pattern of ZnO:Al films with different Al concentrations.

Oxygen Partial Pressures	2θ (°)	FWHM(°)	Size(nm)	E_{opt} (eV)	E_{XRD} (eV)
0.167	34.02	0.88	9.335	3.278	3.271
0.375	33.78	0.92	8.924	3.280	3.278
0.500	34.20	0.98	8.387	3.319	3.288

Table 2: Parameters of the X-ray diffraction pattern of ZnO:Al films under various oxygen partial pressures ratio. Al concentration was kept at 2%.

3.2 Optical Properties

Fig. 3. shows the photoluminescence spectra of ZnO films with different Al doping concentrations. One sharp blue peak located at about 437 nm and two weak green peaks located at about 492 nm and 524 nm were observed. The intensity of the blue peak increased as the Al concentrations in the films increased, and then decreased as the Al concentration further increased. A green luminescence peak centered at 492 nm was observed for all samples, and its relative intensity increased slightly with the increasing of Al concentration in the films. In addition, a weak green peak located at about 524 nm was observed in the pure ZnO film. The intensity of this peak increased as the Al concentrations in the films increased.

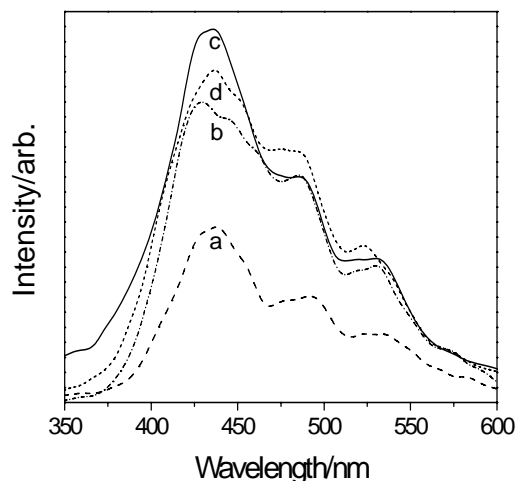


Figure 3: Photoluminescence spectra of Al doped ZnO thin films with different Al doping concentrations: (a) pure ZnO, (b) 1% Al, (c) 2% Al and (d) 3% Al.

Kohan *et al.* [10] have calculated the energy levels of defects in ZnO thin films by the full-potential linear muffin-tin orbit method and they have shown that the energy interval between the Zn interstitial levels to the top of the valence band was about 2.9 eV. The luminescence center (~2.84 eV) observed in this work agrees quite well with Kohan's theoretical calculation. Therefore, the blue

emission band was assigned to the electron transition from the Zn interstitial levels to the top of the valence band.

Fig. 4. shows the photoluminescence spectra of ZnO films under various oxygen partial pressures with an Al doping concentration of 2%. A strong blue peak at 436 nm was observed with a oxygen partial pressure of 0.375. The possible reason is that the growth behavior of the sample is mainly influenced by the density of oxygen in the space where the sample was deposited. When the oxygen gas flow rate was lower (0.167), the oxygen poor environment would tend to increase the concentration of the oxygen vacancy defects, so the intensity of blue peak decreased. When the oxygen gas flow rate was 0.500, some Zn vacancies might appear in the deposited films and they would affect the concentration of the Zn interstitial, which led to the blue band's relative weakness. In order to calculate the direct optical band gap of ZnO:Al films; we used the Tauc relationship [11] as follows:

$$\alpha h\nu = A(h\nu - E_g)^n \quad (2)$$

where α is the absorption coefficient, A is a constant, h is Planck's constant, ν is the photon frequency, E_g is the optical band gap, and n is 1/2 for direct band gap semiconductors.

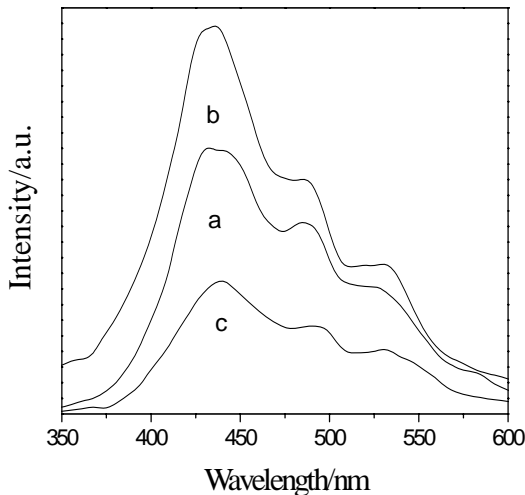


Figure 4: Photoluminescence spectra of Al doped ZnO thin films under various oxygen partial pressure: (a) 0.167, (b) 0.375 and (c) 0.500.

Fig. 5 and Fig. 6 show the graph of $(\alpha h\nu)^2$ vs. photon energy $h\nu$ for ZnO:Al thin films with various Al doping concentrations and oxygen partial pressure, respectively. The linear dependence of $(\alpha h\nu)^2$ on $h\nu$ at higher photon energies indicates that the ZnO:Al films are essentially direct-transition-type semiconductors. The straight-line portion of the curve, when extrapolated to zero, gives the optical band gap E_{opt} .

R. E. Marotti *et al.* [12] suggested that the band gap and the absorption edge of nanostructure materials shift due to quantum size effects (QSE). Accordingly, the band gap values of nanocrystalline films can be calculated from the following equation [13]:

$$E = E_g^0 + \frac{h^2}{8\mu R^2} - \frac{1.8e^2}{\epsilon R} \quad (3)$$

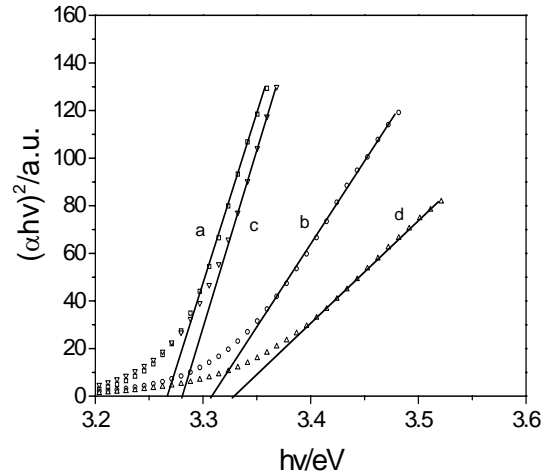


Figure 5: $(\alpha h\nu)^2$ versus $h\nu$ of ZnO films with various Al concentrations: (a) pure ZnO, (b) 1% Al, (c) 2% Al and (d) 3% Al

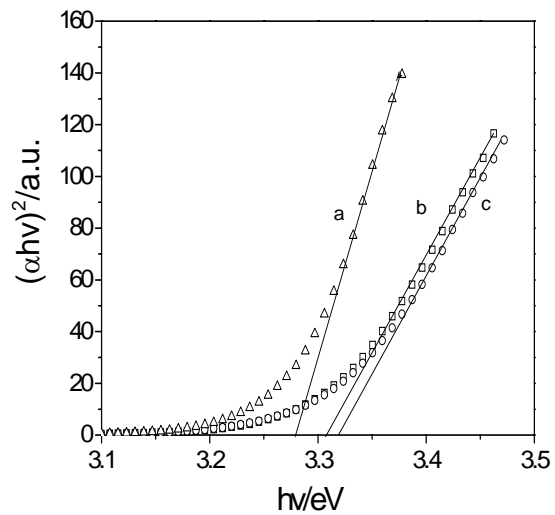


Figure 6: $(\alpha h\nu)^2$ versus $h\nu$ of ZnO:Al films under various partial pressure ratio of oxygen: (a) 0.167, (b) 0.375 and (c) 0.500.

where E_g^0 is the energy gap for bulk materials, h is the Planck's constant, e is the electron charge, R is the radius of ZnO nanocrystallites, ϵ is the dielectric constant of ZnO,

and μ is the reduced exciton mass. The crystal sizes of our samples are in the range of the weak confinement limit, so the band gap values of the samples can be calculated by using the following equation [14]:

$$E = E_g^0 + \frac{\hbar^2}{8\mu R^2} \quad (4)$$

As can be seen from Table 1 and Table 2, the change trend of E_{opt} and E_{XRD} are totally consistent, *i.e.*, both of them shift to a shorter wavelength first and then to a longer wavelength region when Al concentration is increased.

4 CONCLUSIONS

In this paper we studied the effect of Al concentrations and oxygen partial pressure on the microstructure and the luminescence properties of the ZnO:Al thin films. The structural properties studied using XRD were in agreement with the results obtained by optical properties. The band gap calculated from the optical data was found to be comparable to that calculated from the XRD data (particle size). During the growth of the ZnO:Al thin films, oxygen poor or rich environments affected the concentration of Zn interstitials, which led to blue band weakness. The strongest blue peak was observed in PL spectra when the Al concentration was 2% and the partial pressure ratio of oxygen is 0.375. The appearance of the blue peak is important for the development and application of ZnO-based blue emission devices.

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