Structure distortion, optical and electrical properties of ZnO thin films co-doped with Al and Sb by sol–gel spin coating*

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(Received 11 January 2010; revised manuscript received 13 April 2010)

ZnO thin films co-doped with Al and Sb with different concentrations and a fixed molar ratio of $AlCl_3$ to $SbCl_3$ at 1:2, are prepared by a sol–gel spin-coating method on glass annealed at 550 °C for 2 h in air. The x-ray diffraction results confirm that the ZnO thin films co-doped with Al and Sb are of wurtzite hexagonal ZnO with a very small distortion, and the biaxial stresses are 1.03×10^8, 3.26×10^8, 5.23×10^8, and 6.97×10^8 Pa, corresponding to those of the ZnO thin films co-doped with Al and Sb in concentrations of 1.5, 3.0, 4.5, 6.0 at% respectively. The optical properties reveal that the ZnO thin films co-doped with Al and Sb have obviously enhanced transmittance in the visible region. The electrical properties show that ZnO thin film co-doped with Al and Sb in a concentration of 1.5 at% has a lowest resistivity of 2.5 Ω·cm.

Keywords: ZnO thin films co-doped with Al and Sb, sol–gel spin-coating method, structure distortion, optical and electrical properties

PACC: 7360F, 6100M

1. Introduction

Zinc oxide,[1−3] an important member in the II–VI family with a wide band gap (3.37 eV) and a large excitonic binding energy (60 meV), plays a role in various technological domains such as flat-panel displays, solar cells,[4] ultraviolet detectors,[5] and short wavelength light emitting materials.[6] Various methods have now been used to prepare ZnO thin films, such as molecular beam epitaxy (MBE),[7] magnetron sputtering,[8] pulsed laser deposition method,[9] thermal evaporation method,[10] photochemical deposition method,[11] spray pyrolysis,[12] metal–organic chemical vapour deposition (MOCVD)[13] and sol–gel technique.[14] In these techniques, the sol–gel method has been receiving high attention due to its many advantages such as low cost, simple deposition procedure, easier composition control, low processing temperature, easier fabrication of large area films.

In order to reach high-quality optoelectronic device, we need to accumulate a good quality of p-type conduction in ZnO. In addition, it is also rather difficult to achieve low-resistivity, high-hole concentration p-type conduction ZnO films because of its self-compensating effect, deep acceptor level, and low solubility of the acceptor dopants.[15] Yamamoto[16] theoretically predicted that the deliberate co-doping of donors with acceptor is essential for the enhancement of the solubility of the acceptors with the stabilization of the ionic charge distributions and the reduction of acceptor binding energy. Kumar *et al.*[17] reported on ZnO thin films co-doped with Ga and N, grown by radio-frequency magnetron sputtering. The resistivity and the hole concentration were 38 Ω·cm and 3.9×10^{17} cm^{-3}, respectively. Chen *et al.*[18] reported on ZnO thin films co-doped with In and N, grown by direct current reactive magnetron sputtering. The resistivity and the hole concentration were 7.85 Ω·cm and 5.84×10^{17} cm^{-3}, respectively. Furthermore, ZnO thin films are very difficult to be doped with large size ions such as Sb^{3+}. Recently, Limpijumnong, *et al.*[19] proposed a new doping mechanism for Sb impurities

*Project supported by the Innovation Foundation of Beijing University of Aeronautics and Astronautics for PhD Graduates, China (Grant No. 292122), and the Equipment Research Foundation of China (Grant No. 373974).

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in ZnO based on a first-principles calculation. They suggested that Sb would substitute for Zn instead of oxygen and then produce two corresponding Zn vacancies. Ilican *et al.*[20] reported on ZnO thin films doped with Sb grown by a sol–gel method, and they proved that the ZnO thin films doped with Sb is possible. In order to enhance the solubility of the acceptors with the stabilization of the ionic charge distributions and to further validate the co-doping of donors with acceptor, we have recently studied the ZnO films co-doped with Al and Sb in the different concentrations by using a sol–gel spin coating method, and further studied the effects of the concentration of Al and Sb on structure, biaxial stress, optical and electrical properties in detail.

2. Experiment

The ZnO thin films co-doped with Al and Sb were prepared onto glass substrates by the sol–gel spin-coating method. Zinc acetate [$Zn(CH_3COO)_2{\cdot}2H_2O$] was used as a starting material. Ethylene glycol monomethyl ether ($C_3H_8O_2$), ethanolamine (C_2H_7NO), aluminium chloride ($AlCl_3$) and antimony trichloride ($SbCl_3$) were used as solvent, stabilizer, doping source, respectively. According to the co-doping result,[16] the molar ratio of ethanolamine to zinc acetate and that of $AlCl_3$ to $SbCl_3$ were always kept at 1:1 and 1:2, respectively. Required quantities of $SbCl_3$ were added into zinc acetate to obtain sols with Sb–Zn molar ratios of 1.0, 2.0, 3.0, 4.0 at%, respectively. The obtained mixture was stirred at 60 °C for 4 h to yield a clear and homogeneous solution, which then served as the coating source after cooling down to room temperature. The glass substrates were first cleaned by a detergent, then in methanol and acetone each for 30 min by using an ultrasonic cleaner. Finally, the gas substrates were rinsed with deionized water and dried in oven. The coating solution was dropped onto a glass substrate, which was rotated at 3000 rpm for 30 s using KW-4A spin coater. After the spin coating, the film was dried at 350 °C for 20 min in a furnace to evaporate the solvent and to remove organic residuals. This coating/drying procedure was repeated for five times before the film was inserted into a tube furnace and annealed at 550 °C for 2 h in air. This coating process was applied to all samples.

The crystal graphic interpretations were performed on Rigaku D/MAX-RB x-ray diffractometer (XRD) using Cu Kα wavelength (λ = 1.54059 Å, 1 Å=0.1 nm) and scanning in a 2θ range from 20° to 80°. Surface morphology and thickness of the film were studied using an FEI-SIRION scanning electron microscope (SEM). Optical transmittance was recorded with a double beam TU-1901 UV-V that is a spectrophotometer in a wavelength range of 280–850 nm. The conductivity measurements were performed with the four probe method.

3. Results and discussion

3.1. Structure and morphology of the ZnO thin film

Figure 1 shows x-ray diffraction patterns of the Al and Sb co-doped ZnO thin films with different concentrations, annealed at 550 °C for 2 h in air and prepared on glass substrates by the sol–gel spin-coating method.

From Fig. 1, one can see that all peak positions of the ZnO films correspond to the standard diffraction pattern of wurtzite hexagonal ZnO (JCPDS 76-0704). However, the (002) peaks of the diffraction patterns of ZnO films are quite different for different concentrations, the intensity of the (002) peak decreases with the increase of concentration of Al and Sb, which indicates that the doping concentration of Al and Sb plays an important role in suppressing the crystalline behaviour. According to XRD data, average crystallite size is approximately calculated from Scherrer formula

$$D = K\lambda/\beta\cos\theta, \tag{1}$$

where D is crystallite size, K is a constant of 0.89, λ is the x-ray wavelength (0.15406 nm), β is the full width at half maximum, and θ is diffraction angle.

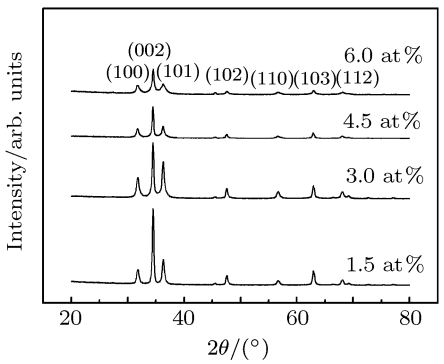


Fig. 1. XRD patterns of the Al and Sb co-doped ZnO thin films.

The calculated average crystallite sizes are 13.324, 14.336, 14.819, and 15.897 nm, corresponding to those of the Al and Sb co-doped ZnO thin films with concentrations of 1.5, 3.0, 4.5, 6.0 at%, respectively. Grains

with smaller sizes have higher surface areas and can cause more band bending effect.

According to the hexagonal symmetry, the lattice constant can be calculated from the following formula:

$$d = \frac{1}{\sqrt{\dfrac{4(h^2+hk+k^2)}{3a^2} + \dfrac{l^2}{c^2}}}, \tag{2}$$

where d is the interplanar distance, h, k, l are crystal plane indices, and a, b, c are cell parameters, respectively.

The biaxial stress along the c axis was calculated by using the following formula:[21]

$$\sigma = -453.6 \times 10^9[(c - c_0)/c_0], \tag{3}$$

where c is the lattice parameter of the strained ZnO film calculated from x-ray diffraction data, and c_0 is the strain-free lattice parameter (c_0 = 0.5206 nm). From formulae (2) and (3), the calculated biaxial stresses are 1.03×10^8, 3.26×10^8, 5.23×10^8, 6.97×10^8 Pa, corresponding to those of the Al and Sb co-doped ZnO thin films with concentrations of 1.5, 3.0, 4.5, and 6.0 at%, respectively. The biaxial stress is enhanced with the concentration of Al and Sb increasing, which indicates that the atoms of Al and Sb bring on the distortion of ZnO lattice.

Figure 2 shows SEM photographs of the Al and Sb co-doped ZnO thin films at different concentrations (the molar ratio of Al to Sb is always kept at 1:2), prepared on glass substrates by sol–gel spin-coating method and annealed at 550 °C for 2 h in air. It is found that surface particles of thin films become more uneven with the doping concentration increasing. The crystallite sizes of thin films are about 50 nm. For comparison, the grain sizes of ZnO films, analysed by SEM, are much larger than those calculated by XRD data. This difference might be that because the grain size measured from SEM is the size related to the surface morphology rather than the size of the single crystal grain, and the grain size measured from XRD is the size of single crystal along the thickness direction of the thin film.

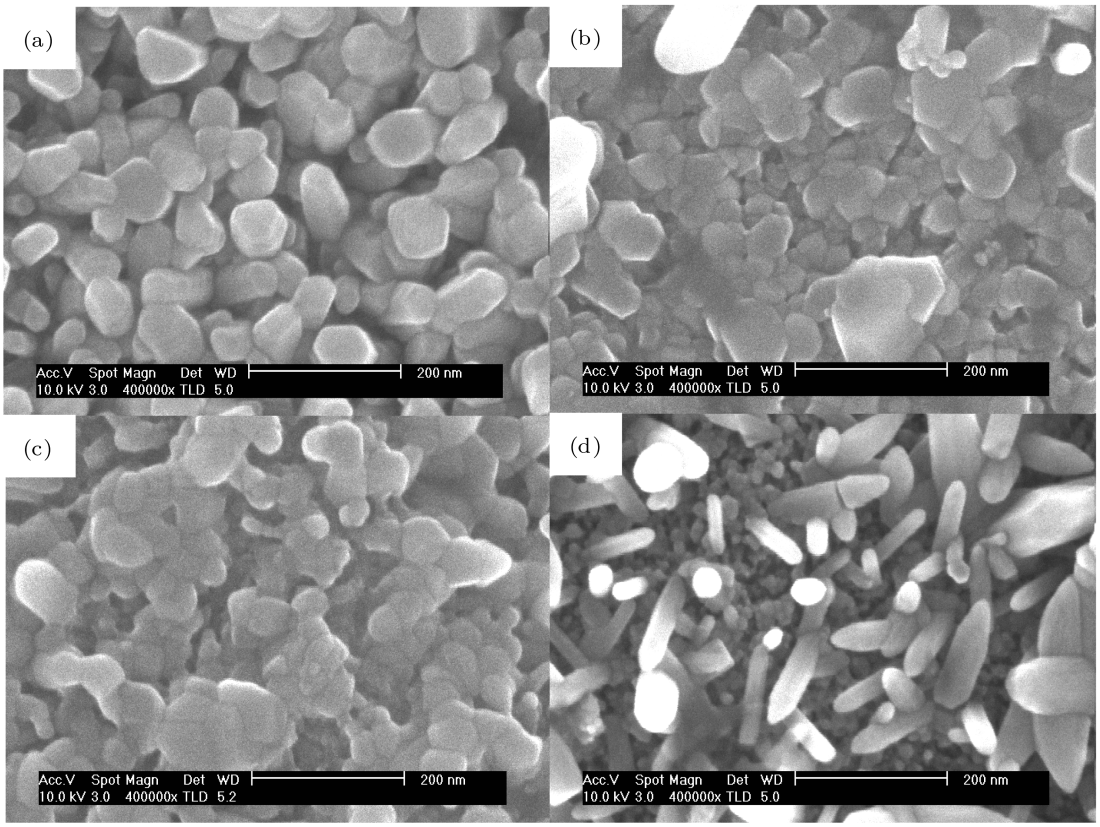


Fig. 2. SEM micrographs of the ZnO thin films with different doping concentrations of (a) 1.5 at%, (b) 3.0 at%, (c) 4.5 at%, (d) 6.0 at%.

3.2. Optical properties of the ZnO thin film

Figure 3 shows the transmittance spectra of the Al and Sb co-doped ZnO thin films with different concentrations, prepared on glass substrates by sol–gel spin-coating method and annealed at 550 °C for 2 h in air.

For all the films, they have high transmittances in the visible region and show sharp absorption edges in the UV region except for the case of 6.0 at%. The ZnO thin film co-doped with Al and Sb in a concentration of 1.5 at% has the highest transmittance, and the ZnO thin film co-doped with Al and Sb in a concentration of 6.0 at% has the lowest transmittance in the visible region.

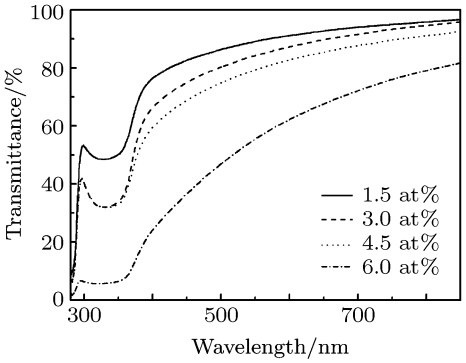


Fig. 3. Optical transmittance spectra of the Al and Sb co-doped ZnO thin films.

Optical band gap of the ZnO thin films can be obtained by applying the following two formulae (4) and (5):[22]

$$T = (1-R)^2 \exp(-\alpha d), \tag{4}$$

$$\alpha h\nu = D(h\nu - E_{\rm g})^{1/2}. \tag{5}$$

In formula (4), T is the transmittance of the ZnO thin film, R is its reflectivity, α is the absorption coefficient, and d is the film thickness. In formula (5), $h\nu$ is the photon energy, D is a constant, and $E_{\rm g}$ is the optical band gap. According to formulae (4) and (5), we calculate the absorption coefficient $\alpha \sim \ln T$ as well as $\alpha h\nu \sim (h\nu - E_{\rm g})^{1/2}$.

Figure 4 shows the plot of $(\alpha h\nu)^2$ versus photon energy $(h\nu)$ obtained from the data of Fig. 3. Extrapolation of linear portion to the energy axis at $(\alpha h\nu)^2 = 0$ gives the $E_{\rm g}$ value. The $E_{\rm g}$ values obtained by the above process are 3.18 eV, 3.22 eV, 3.00 eV and 2.95 eV, which are corresponding to the Al and Sb co-doped ZnO thin films with concentrations of 1.5 at%, 3.0 at%, 4.5 at%, and 6.0 at%, respectively. We believe that the change of $E_{\rm g}$ originates from the co-doping of Al and Sb.

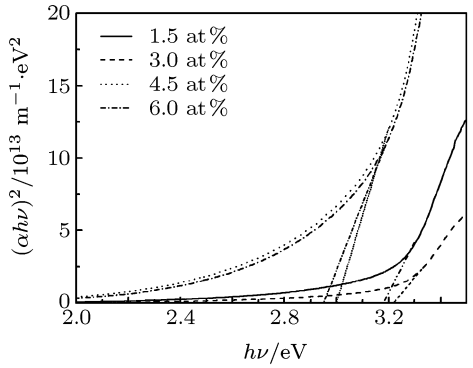


Fig. 4. Plots of $(\alpha h\nu)^2$ versus $h\nu$ of the Al and Sb ZnO co-doped thin films.

3.3. Electrical properties of ZnO thin film

ZnO exhibits a wide range of conductivity. Its behaviour varies from metallic to insulating. Its electrical characteristics can be controlled by doping with ternary elements or by adjusting process conditions. The resistivity of the films is calculated from the following equation:[23]

$$\rho = \frac{\pi t}{\ln 2}\frac{V}{I}, \tag{6}$$

where t is the thickness of the sample, V is the voltage and I is the current. Figure 5 shows the electrical resistivities of the Al and Sb co-doped ZnO thin films with different concentrations.

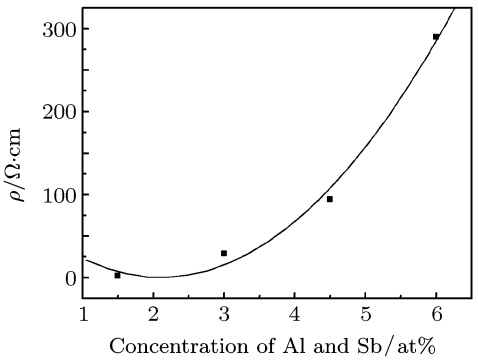


Fig. 5. Electrical resistivity versus concentration of the Al and Sb co-doped ZnO thin film.

In Fig. 5, the dots denote experimental data, and the line represents the fitting. The results indicate that the resistivities of the ZnO thin films are enhanced with the concentration of Al and Sb increasing. One can see from Fig. 5 that the ZnO thin film co-doped with Al and Sb in a concentration of 1.5 at%

has a lowest resistivity of 2.5 Ω·cm. The relation between resistivity (ρ) of the film and concentration (x) of Al and Sb is fitted by least square fitting method:

$$\rho = 83.88 - 79.42x + 18.83x^2, \tag{7}$$

where x is the concentration of Al and Sb, and ρ is the resistivity. It is a fitting formula. From formula (2), we can know that the theoretical lowest resistivity is about 0.14 Ω·cm when the co-doping concentration with Al and Sb is about 2.1 at%.

The resistivity of the ZnO film is dependent on the carrier concentration of electrons and holes. And it can be described by the following equation:[24]

$$np = 6.30 \times 10^{38} \left(\frac{m_n m_p}{m_0}\right)^{3/2} \left(\frac{T}{300}\right)^3 \times \exp\left(-\frac{E_g}{k_B T}\right), \tag{8}$$

where n is the electron concentration, p is the hole concentration, m_n is the electron effective mass, m_p is the hole effective mass, m_0 is the electron mass, T is the temperature, E_g is the band gap width, and k_B is the Boltzmann's constant. As can be seen from Eq. (8), the resistivity of the Al and Sb co-doped ZnO thin film is dependent on band gap width. The band gap width can be adjusted by doping, and the deliberate co-doping of donors with acceptor is essential for the enhancement of the solubility of the acceptors with the stabilization of the ionic charge distribution and the reduction of acceptor binding energy.[16] Limpijumnong, *et al.*[19] proposed a new doping mechanism for Sb impurities in ZnO based on a first-principles calculation. They suggested that Sb would substitute for Zn instead of oxygen and then produce two corresponding Zn vacancies. Saliha Ilican, *et al.*[20] experimentally proved the existence of Sb_{Zn}–$2V_{Zn}$ complexes. Therefore, we also consider that the conducting mechanism of the ZnO thin film co-doped with Al and Sb could be that the Sb substitutes for Zn instead of oxygen, thereby producing two corresponding Zn vacancies.

4. Conclusions

The Al and Sb co-doped ZnO thin films with different concentrations have been prepared by a sol–gel spin-coating method and annealed at 550 °C for 2 h in air. The molar ratio of $AlCl_3$ to $SbCl_3$ was always kept at 1:2 in our experiment. Structure, biaxial stress and surface morphology are characterized by XRD and SEM, and the results confirm that the Al and Sb co-doped ZnO thin films are of wurtzite hexagonal ZnO with a very small distortion. The optical band gaps of the Al and Sb co-doped ZnO thin films are 3.18 eV, 3.22 eV, 3.00 eV and 2.95 eV, corresponding to the concentrations of 1.5 at%, 3.0 at%, 4.5 at%, 6.0 at%, respectively. The electrical resistivities are measured by four probe method, and the results show that the Al and Sb co-doped ZnO thin film with a concentration of 1.5 at% has a lowest resistivity of 2.5 Ω·cm

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