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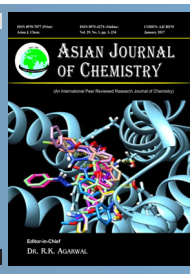

Influence of Annealing Temperature on Properties of ZnO:(Li,N) Thin Films Prepared by Sol-Gel Method

F.C. YU*, J.T. FU, H.S. LI, H.L. HU and L. HE

School of Material Science and Engineering, Lanzhou University of Technology, Lanzhou, Gansu Province, P.R. China

*Corresponding author: Tel: +86 931 2976378; E-mail: yufc72@139.com

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Lithium and N co-doped ZnO thin-film samples were prepared on SiO_2 quartz substrates *via* sol-gel method, followed by thermal annealing at different temperatures (400, 500, 600, 700 and 800 °C). The influence of annealing temperature on the structural, morphological and optical properties of the ZnO:(Li,N) films were discussed. The X-ray diffraction patterns showed that the increase of annealing temperature (400-700 °C) dramatically improves the crystal quality and c-axis orientation. The scanning electron microscope micrographs indicate that the grain size of the films increases significantly with the increase of the annealing temperature. A broad visible emission was observed for each sample at the room temperature photoluminescence spectra that indicates the temperature dependence of defect concentrations. The ultraviolet-visible spectra showed that the average transmittance in visible spectral region decreases with the increasing of annealing temperature.

Keywords: Li-N co-doping, ZnO film, Sol-gel.

INTRODUCTION

With a direct wide band gap (3.37 eV) and a large exciton binding energy (60 meV), ZnO possesses many potential applications in next-generation short-wavelength optoelectronic devices [1]. It is also considered to be a promising material for using in surface acoustic wave filters and sensor devices, solar cells, transparent conductors on liquid crystal displays and short-wavelength light emitting diodes (LEDs) [2-6]. It is necessary to obtain n-type and p-type conductivity of thin-film ZnO material for the development of ZnO based optoelectronics devices. The naturally ZnO film shows n-type conductivity due to the native donor defects, such as zinc interstitials (Zn_i), oxygen vacancies (V_O). The and high quality n-type ZnO thin film materials have been prepared easily by doping method. However, it is difficult to fabricate stable and reproducible p-type ZnO films due to the rise of lattice Madelung energy, low solubility of acceptor doping and self-compensation [7]. Then codoping method is proposed to increase the solubility of acceptor doping [8]. Among the potential p-type acceptor dopants, nitrogen is a popular candidate and Li might also be a good p-type dopant for introducing a shallow acceptor level. Theoretically, Li and N are the best candidates for achieving p-type ZnO film considering the strain effects and energy levels of substitutional Li_{Zn} and N_O acceptors. Duan *et al.* [1] investigated the production of defects in Li, N co-doped ZnO and found that the dual-acceptor complex Li_{Zn}-N_O is unlikely to form, but the additional introduction of N may help compensate the single Li_i donor defect concentration under a certain growth conditions. Many methods were adopted to grow ZnO film, such as pulsed laser deposition (PLD), magnetron sputtering, metal organic chemical vapour deposition (MOCVD), spray pyrolysis, molecular beam epitaxy (MBE) and sol-gel process, *etc.* [9-14]. Compared with other methods, sol-gel process has many advantages like simple facilities, low cost, good uniformity of thickness and controllability of micro-crack and residual stress by optimizing the parameters of the process [15].

Including the above methods, post annealing is a key process in most p-type ZnO film fabrication methods, so that the investigating of the effects of annealing temperature on the micro structure as well as the variation of defect concentrations of doped ZnO crystal becomes necessary. In this work, Li and N co-doped ZnO films were grown on SiO_2 quartz substrates by sol-gel method, followed by thermal annealing at different temperatures. The structural, morphological and optical properties of the samples were investigated to discuss the influence of annealing temperature on the properties of the films.

EXPERIMENTAL

A series of ZnO:(Li,N) thin film samples were synthesized on the SiO_2 quartz substrates by sol-gel method. To prepare

undoped and Li, N co-doped ZnO sols, a certain amount of pure zinc acetate dihydrate with lithium chloride and ammonium nitrate were dissolved in a mixture of 2-methoxyethanol and monoethanolamine, respectively. Here the monoethanolamine, lithium chloride and ammonium nitrate were used as the stabilizer, dopant source of lithium and nitrogen, respectively. The concentration of zinc acetate solution is 0.8 mol/L and the molar ratio of monoethanolamine to zinc is 1:1. The concentrations of lithium chloride and ammonium nitrate are both 15 at. % to zinc acetate in the solution.

General procedure: All prepared ZnO sols were maintained under continuous magnetic stirring at 70 °C for 2 h to get clear and homogeneous solutions and then standing for 48 h. The quartz substrates were ultrasonically cleaned in distilled water, hydrochloric acid, acetone and ethanol sequentially. The sols were spin coated on the cleaned quartz substrates (3000 rpm for 30 s), then the samples were dried at 150 °C for 10 min to evaporate the solvent. Finally, the thin film samples were annealed at 400, 500, 600, 700 and 800 °C for 1.5 h, respectively.

Detection method: The structural and morphological properties were investigated by an X-ray diffractometer (Bruker, D8 ADVANCE) and a field emission electron microscope (JEOL, JSM-6701F). The UV-visible spectra transmittance and the photoluminescence spectrum were measured at room temperature by a UV-vis-NIR spectrophotometer (Perkin-Elmer) and a fluorospectrophotometer (Lengguang Tech, F97Pro) with an excitation wavelength of 254 nm, respectively.

RESULTS AND DISCUSSION

The XRD patterns of ZnO:(Li,N) thin films annealed under different temperatures (400, 500, 600, 700 and 800 °C) are shown in Fig. 1. All of the patterns show a strong peak corresponding to (002) plane and a weak peak corresponding to (101) plane of ZnO, while the blurry peak corresponding to (100) plane appears only for the sample annealed at 400 °C. The results confirm that ZnO crystal in all the samples exists as a hexagonal wurtzite structure with a preferential orientation along the c-axis. Furthermore, the intensity of (002) peak greatly increases with the increasing of annealing temperature up to 700 °C that indicates increasing annealing temperature (< 700 °C) can significantly improve the crystal quality of the films. Within this temperature range, dopant atoms form new nucleating centers resulted from the decrease of nucleation energy barrier and the grains grow large with the increasing of the temperature, which illustrates that the atoms at high temperature get enough diffuse activation energy to occupy the suitable sites in the crystal. The degeneration of (002) peak intensity for the sample annealed at 800 °C can be understood by the rapid grain growth. The grains with lower surface energy grow rapidly at higher temperature, which restrict the growth of surrounding grains that results in the formation of many big grains and pores in the film.

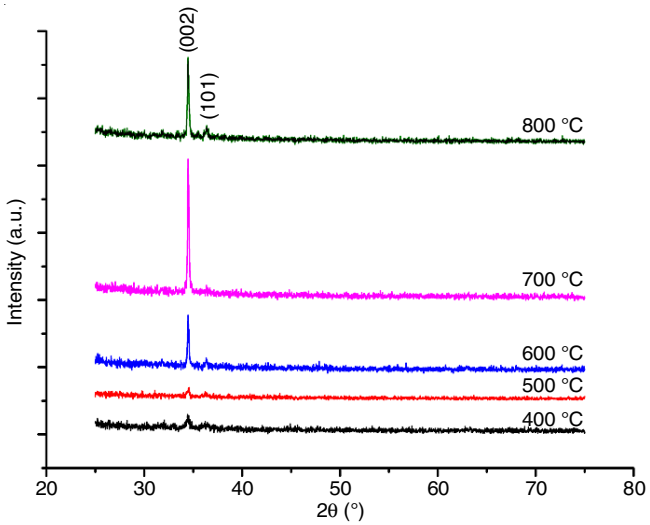

Fig. 1. XRD pattern of the ZnO:(Li,N) thin films annealed under different temperatures

The lattice parameters of a and c and crystallite sizes are listed in Table-1 for the samples annealed at different temperatures, which are calculated from the Bragg relation and the Scherer formula, respectively [9]:

$$n\lambda = 2d \sin\theta \quad (1)$$

where n is the order of diffraction, λ is the wavelength of X-ray and d is the distance between the lattice planes.

The relation of lattice parameters, Miller indices (h, k and l) and d_{hkl} follows the equation [16]:

$$\frac{1}{d_{hkl}^2} = \frac{4}{3}\frac{(h^2+hk+k^2)}{a^2} + \frac{l^2}{c^2} \quad (2)$$

The crystallite size of the ZnO nanoparticles was calculated by the Scherer formula:

$$D = \frac{0.9\lambda}{\beta\cos\theta} \quad (3)$$

where D is the crystallite size, λ is the wavelength of the X-radiation, θ is the diffraction angle and β is the FWHM of the observed peak.

TABLE-1
STRUCTURAL PROPERTIES OF ZnO:(Li,N) THIN FILMS ANNEALED UNDER DIFFERENT TEMPERATURES OBTAINED BY XRD PATTERN

Annealing temperature (°C)	a (Å)	c (Å)	c/a	D (nm)
400	3.2234	5.2005	1.6133	26.8017
500	3.2400	5.1959	1.6036	28.1883
600	3.2423	5.1958	1.6025	45.3021
700	3.2491	5.1950	1.5989	48.5780
800	3.2326	5.1970	1.6077	43.6627

Fig. 2 shows the c/a ratios and the crystallite sizes of ZnO:(Li,N) thin films under different temperatures. It is noticed that the c/a ratio decreases with increasing annealing temperature up to 700 °C, but increases under further higher temperature. It is accepted that in the doped ZnO crystals, the changing of c/a ratio indicates deviation of the wurtzite and it is mainly caused by the difference in the electronegativity between the two component elements [17]. Since the electronegativity of Zn, O, Li and N is 1.65, 3.44, 0.98 and 3.04 respectively, the electronegativity difference between Zn and O, Li and O, Zn and N, Li and N corresponds to the value of

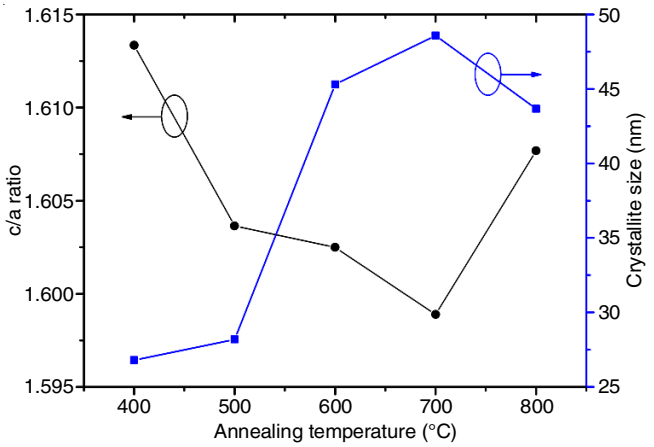

Fig. 2. c/a ratio and crystallite size of the ZnO:(Li,N) thin films annealed under different temperatures

1.79, 2.46, 1.39, 2.06, so it can be deduced that the density of Li_{Zn} and N_O increase with increasing the annealing temperature up to 700 °C. The increase of c/a ratio at higher temperature may be caused by the incorporation of Li_i donor defects which may enhance the formation of neutral Li_{Zn}-Li_i complexes and $(N_2)_O$ donors. The crystallize size increases dramatically from 26 nm to 48 nm with the increasing of annealing temperature from 400 to 700 °C.

Fig. 3 shows the surface morphologies of ZnO:(Li,N) films annealed at different temperatures. The uniform distribution of grains could be seen in each sample through SEM images. The grain size increases dramatically with the increasing of annealing temperature up to 700 °C and many pores appear in the sample annealed at 800 °C, which completely confirm the results obtained by XRD measurements. With the increasing of annealing temperature, the surface roughness of the films also increases. The grain sizes of ZnO:(Li,N) films analyzed by SEM differ from that by XRD, the formers representing the particle sizes while the latters representing the crystallite sizes.

Fig. 4 shows the room temperature photoluminescence spectra of ZnO:(Li,N) films annealed at different temperatures. All the samples display a broad emission in the visible region induced by the deep-level emissions, which is believed to come from the intrinsic defects in ZnO crystal [18]. The strong emission near UV and violet light region at 396 nm (3.13 eV) is attributed to radiative electron transitions from conduction band to intrinsic defects of Zn vacancies (V_{Zn}) [18]. The blue emission centered at 431 nm (2.88 eV) comes from the transitions from near conduction band edge to deep acceptor levels attributed to the defect level produced by Zn interstitials (Zn_i) [19]. The two weak peaks of blue emission in 467 nm (2.66 eV) and green emission in 513 nm (2.42 eV) are ascribed to radiative electronic transitions from conduction band to oxygen

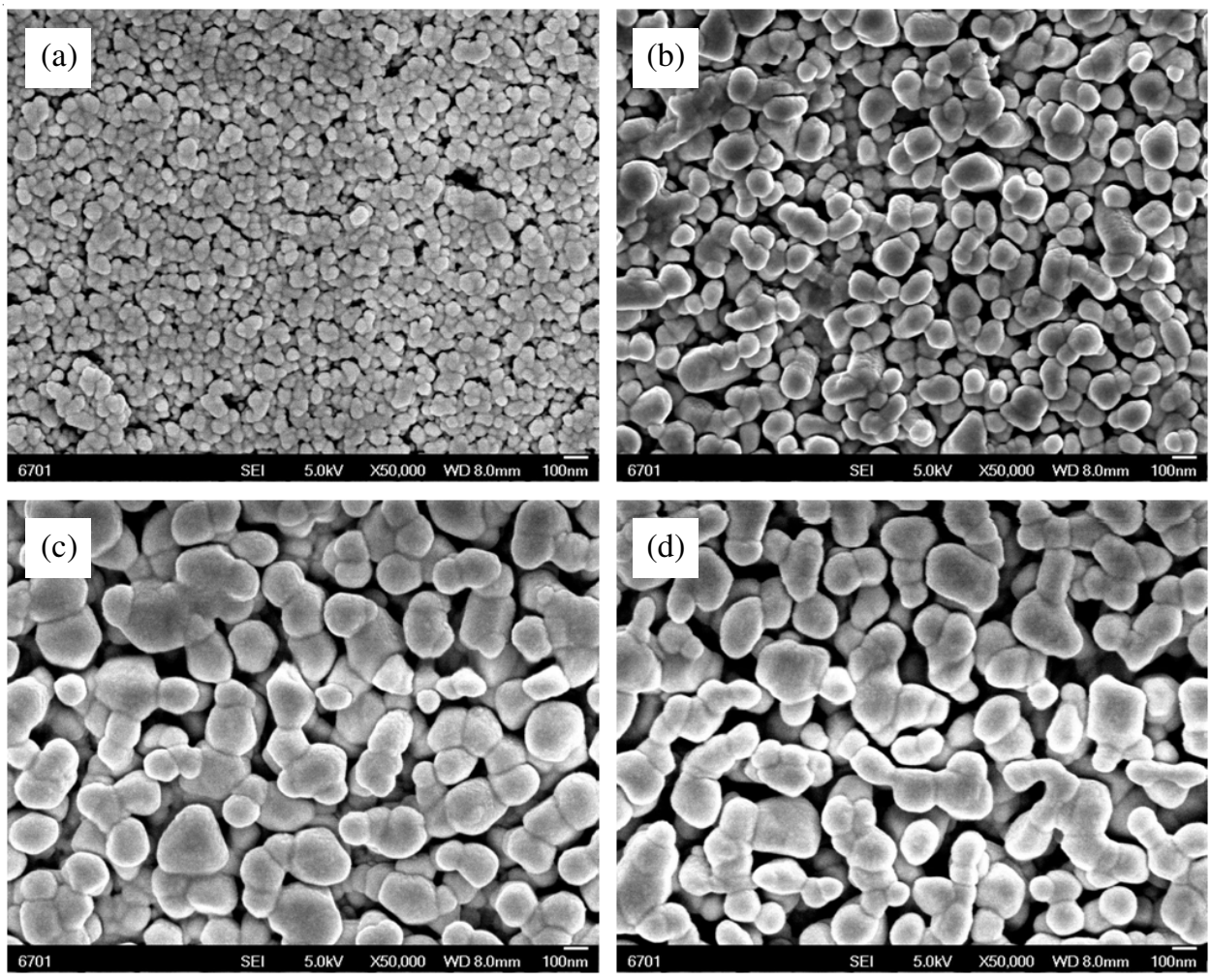

Fig. 3. SEM images of ZnO:(Li,N) films annealed at different temperatures: (a) 500 °C; (b) 600 °C; (c) 700 °C; (d) 800 °C

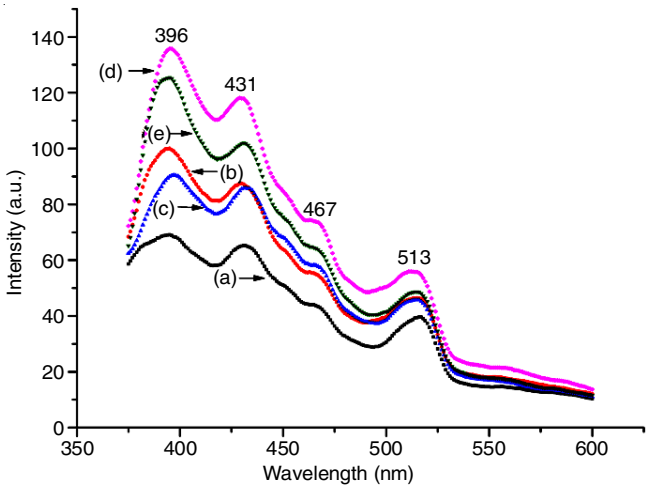

Fig. 4. Room temperature photoluminescence spectra of ZnO:(Li,N) films annealed at different temperatures: (a) 400 °C; (b) 500 °C; (c) 600 °C; (d) 700 °C; (e) 800 °C

vacancy (V_O) and Zn_i to V_O, respectively [16,19]. With the annealing temperature increasing up to 700 °C, the emission intensity in the visible region increases, indicating the temperature dependence of intrinsic defects concentration. Li atoms in interstitial sites may replace Zn atoms in the lattice and enhance the formations of Li'_{Zn}, $Zn_i^{\cdot}$ and V_O^{+} as follows [20]:

$$Li_i^{+} + Zn_{Zn} + e^{-} \longrightarrow Li_{Zn}^{\cdot} + Zn_i^{+} \quad (or) \qquad (4)$$

$$Li_i^{+} + e^{-} \longrightarrow Li_{Zn}^{\cdot} + V_O^{+} \qquad (5)$$

where Li_i^{+} represents lithium in interstitial position, Zn_{Zn} zinc in zinc site, Li'_{Zn} lithium on Zn lattice size, Zn_i^{+} zinc in interstitial position and V_O^{+} oxygen vacancy on lattice site. So it can be deduced that with annealing temperature increasing, more Li atoms replace Zn atoms and form Li'_{Zn}, Zn_i^{+} and V_O^{+}, which is well agree with the XRD measurements.

Fig. 5 shows the transmittance spectra of the ZnO:(Li,N) thin films annealed at different temperatures. As seen from the spectra, with the increasing of annealing temperature, the average transmittance in visible spectral region decreases, which may be caused by both of the temperature dependence of the surface roughness and the intrinsic defect concentrations.

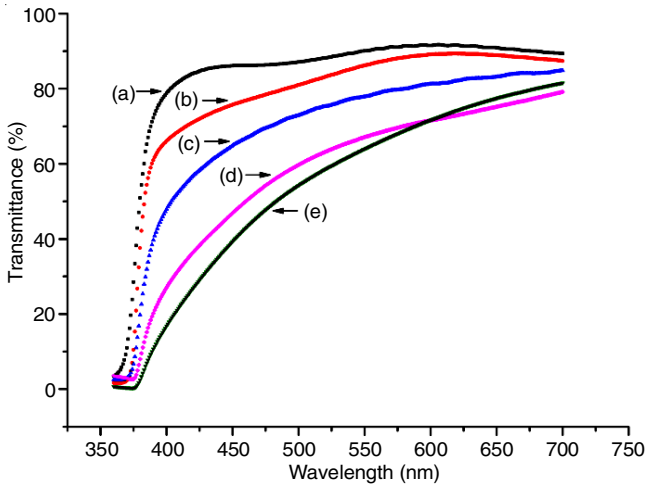

Fig. 5. Transmittance spectra of the ZnO:(Li,N) films annealed at different temperatures: (a) 400 °C; (b) 500 °C; (c) 600 °C; (d) 700 °C; (e) 800 °C

That is well confirmed the results of SEM measurements and photoluminescence measurements.

Conclusion

ZnO:(Li,N) thin film samples were grown on SiO_2 quartz substrates by sol-gel method annealed under different temperatures (400, 500, 600, 700 and 800 °C). The influence of annealing temperature on structural, morphological and optical properties of the ZnO:(Li,N) films were investigated. With the increasing of annealing temperature up to 700 °C, the crystalline quality of ZnO:(Li,N) films are improved and the average grain size in the samples increases dramatically, simultaneously, the concentration of intrinsic defects increases and the transmittance in visible spectral region decreases. Further higher temperature annealing results in a degeneration of crystal quality and induces a change of additional defect concentration. Both of temperature dependence of surface roughness and defect concentration affect the transmittance. Based on those results, the annealing temperature of 700 °C is suggested to be the optimal value for ZnO:(Li,N) thin films grown on SiO_2 quartz substrates by sol-gel method.

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