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Effect of Na Concentrations on Microstructure and Optical Properties of ZnO Films

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Abstract: Na-doped ZnO thin films were deposited on the glass substrates using sol-gel method. The effect of Na concentrations on the structural and optical properties of ZnO films was studied. As Na concentration increases from 0.0 at% to 16.0 at%, preferential *c*-axis orientation becomes more and more obvious, and the intensity of the diffraction peaks from (103) increases. The optical band gap E_g value increases from 3.261 to 3.286 eV first and then decreases as Na concentration increases from 0.0 to 2.0 at% and then beyond 2.0 at%. The intensity of all the emissions increases with increasing Na concentration and the origins of the violet emission (wavelength in the 400-407 nm) and the blue emission (wavelength at 473 nm) were discussed in detail.

Key words: Na-doped ZnO thin films; sol-gel method; microstructure; optical properties

1 Introduction

Zinc oxide (ZnO) is a direct wide-band-gap semiconductor material (E_g = 3.37 eV at room temperature). It has a large exciton binding energy of 60 meV which makes the exciton hard to be thermally ionized. Therefore, ZnO is a very promising material for optoelectronic devices, such as ultraviolet light-emitting diodes[1-3], laser diodes[4], photodetectors[5, 6], surface acoustic wave devices[7, 8].

It is well known that chemical doping greatly influences the structural, optical and electrical properties of ZnO. Recently, the fabrications of ZnO thin film doped with the acceptor elements, such as Li[9], K[10, 11], N[12-14], P[15, 16] and As[17], have been reported. Nevertheless, there are relatively less reports of Na-doped ZnO films. Theoretically, Group-I species substituting for Zn possess shallower acceptor levels[18]. However, there are some contradictory understandings of doping group-I species in ZnO. Lee *et al*[19] argued that Li(Na)-H complexes could be helpful to the availability of low resistivity *p*-ZnO, while Wardle *et al*[20] suggested that *p*-type doping would be passivated by the formation of Li-H complexes.

In this paper, ZnO films with different Na concentrations were prepared by sol-gel method. The effect of Na concentration on properties of Na-doped ZnO films has been examined.

2 Experimental

Zinc acetate dehydrate ($Zn(CH_3COO)_2$ $2H_2O$) and sodium chloride(NaCl) were dissolved in ethylene glycol monomethyl ether. Then monoethanolamine(MEA) and methanamide were added under stirring. The molar ratio of MEA to zinc acetate was 1.0 and the concentration of zinc acetate was 0.5 mol/L. The molar ratio of dopant (sodium chloride) in the solution, [Na/Zn], was varied between 0.0 at% and 16 at%. The resultant solution was stirred at 60 ℃ for 2 h to yield a clear and homogeneous solution. The sol-gel coating was made usually 1 d after the solution was prepared. Na-doped ZnO films were prepared on glass substrate by repeated coating. Spin coating was performed at room temperature, with a rate of 3 000 rpm for 30 s. After depositing, the films were preheated in air at 250 ℃ for 10 min. The coating process was repeated after cooling down to room temperature in order to increase the thickness of the coatings. After repeating the coating procedure 15 times for the final film thickness of approximately 497 nm, the films were finally postheated at 550 ℃ for 1 h in air.

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The composition of the film was obtained by means of X-ray photoelectron spectroscopy (XPS, Thermo-VG Scientific ESCALAB250). The crystalline structures of the films were analyzed by X-ray diffractometer (XRD, MACM18XHF) using CuKα radiation at 40 kV and 100 mA. The cross-sectional microstructure of the film was studied by a scanning electron microscope (SEM, JSM-6700F). Optical properties of the films were examined with the normal incident transmittance by a UV-Vis spectrophotometer (UV-2550, SHIMADZU). Photoluminescence (PL) spectra were investigated at room temperature by fluorescence spectrometer (F-4500FL) with a xenon lamp as light source excited at 325 nm.

3 Results and Discussion

3.1 XPS spectrum

Typical XPS survey spectrum of the Na-doped ZnO film with 4 at% Na concentration is shown in Fig.1. In survey spectrum, zinc, carbon, oxygen and sodium peaks are observed. Fig.2 shows the high resolution Na1*s* XPS spectrum of 4 at% Na-doped ZnO film. The position of the peak appears at the binding energy of 1 072.02 eV. That is the peak position of the binding energy of Na^+ oxide, which indicates that Na element doped as Na^+ in the Na-doped ZnO film.

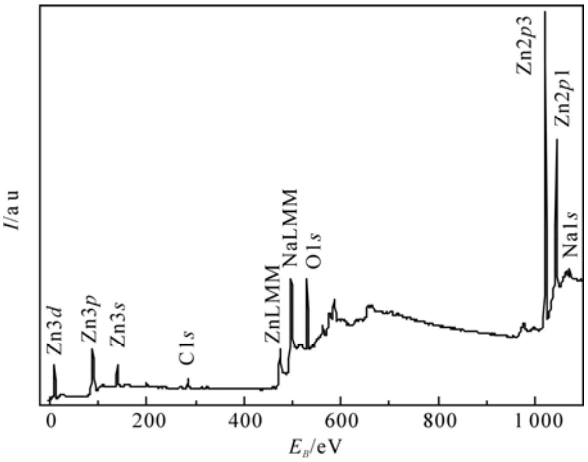

Fig.1 XPS spectrum of 4 at% Na-doped ZnO thin film

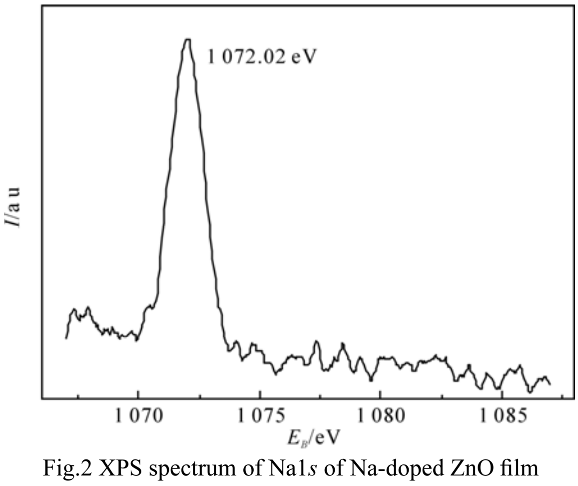

Fig.2 XPS spectrum of Na1*s* of Na-doped ZnO film

3.2 Crystal structure

Fig.3 gives the XRD patterns of undoped ZnO film and Na-doped ZnO films annealed at 550 ℃. It can be seen from the figures that there are not any other phases in Na-doped ZnO films compared with undoped ZnO film. All the films exhibit polycrystalline hexagonal wurtzite structure. No peaks corresponding to either Na metal or any of its oxides are observed in the patterns, which indicate that there is no additional phase present in the Na-doped films. In addition, the undoped ZnO thin film cannot form preferential *c*-axis ((002) crystal plane) orientation. With Na concentration increasing, preferential *c*-axis orientation becomes more and more obvious, and the intensity of the diffraction peaks from (103) increases. It can be seen from the figure that the intensity of the diffraction peaks from (103) is much weaker than that from (002) with 8 at% Na-doped ZnO film. However, the intensity from (103) is similar to that from (002) as Na concentration raises to 16 at%. The relative intensity of the diffraction peaks changes because of the surface energy difference of the ZnO crystal structure, and (002) crystal plane has the lowest surface energy, which suggests that the Na concentration affects the surface energy[21]. However, the transition mechanism is not yet well understood.

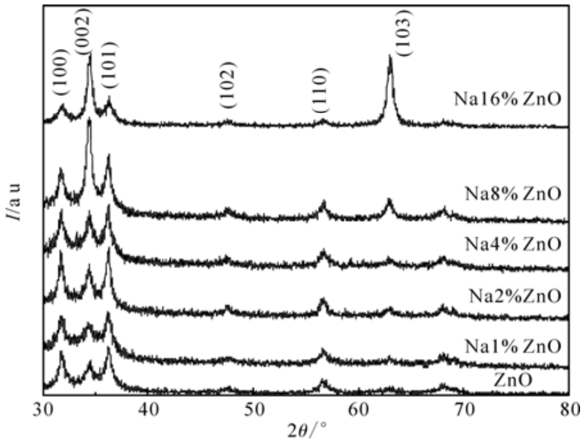

Fig.3 XRD patterns of undoped ZnO film and Na-doped ZnO films annealed at 550 ℃

For analyzing the grain size, Scherrer formula was used as the following:

$$D = k\lambda / \beta \cos\theta$$

where D is the grain size, λ is the X-ray wavelength, β is the peak width at half height of the diffraction peaks, and θ is the diffraction angle. The grain size calculated using Scherrer formula from ZnO (002) peaks has been shown in Table 1. As Na concentration increases, the grain size increases monotonously. Cross-sectional SEM image of 4.0 at% Na-doped ZnO thin film is displayed in Fig.4. The thickness of the film is approximately 497 nm.

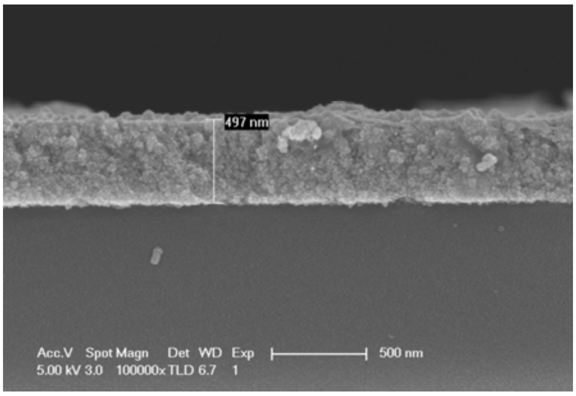

Fig.4 Cross-sectional SEM image of 4 at% Na-doped ZnO thin film

Table 1 The grain size of the Na-doped ZnO films from ZnO (002) diffraction peak

Na concentration/at%	Grain size/nm
0.0	6.2
1.0	6.4
2.0	7.1
4.0	8.2
8.0	12.4
16.0	16.6

3.3 Optical characteristics

Fig.5 shows the transmission spectra of Na-doped ZnO films annealed at 550 ℃ in air for 1 h. The spectra of the films show ripples, which is the characteristic of the interference of light. All films have an average optical transparency over 85% in the visible range. It can be seen from the inset of Fig.5 that the UV absorption edge is blue shifted at first and then red shifted with increasing Na concentration, which is correlated to the change of the optical band gap value. The optical band gap E_g can be determined from the absorption coefficient α, which can be calculated from the transmittance spectra of Na-doped ZnO films. Near the absorption edge, α can be expressed as[22]

$$\alpha = \frac{1}{d}\ln(\frac{1}{T})$$

where d is the film thickness and T is the transmittance. ZnO is a wide band gap semiconductor material with direct band gap. The optical band gap E_g is given by Ref.[22]

$$(\alpha hv)^2 = A(hv - E_g)$$

where A is a constant and hv is photo energy. The functional relationship between $(\alpha hv)^2$ and photon energy hv for Na-doped ZnO films with different Na concentrations is shown in Fig.6. The E_g value can be obtained by extrapolating the linear portion to the photon energy axis. The band gap values determined from Fig.6 are listed in Table 2. It can be shown that the E_g value increase at first and then decreases as Na concentration increases from 0.0 at% to 2.0 at% and then beyond 2.0 at%.

Table 2 Optical bandgap of ZnO films with different Na concentrations

Na concentration/at%	Optical bandgap/eV
0.0	3.261
1.0	3.273
2.0	3.286
4.0	3.282
8.0	3.279
16.0	3.272

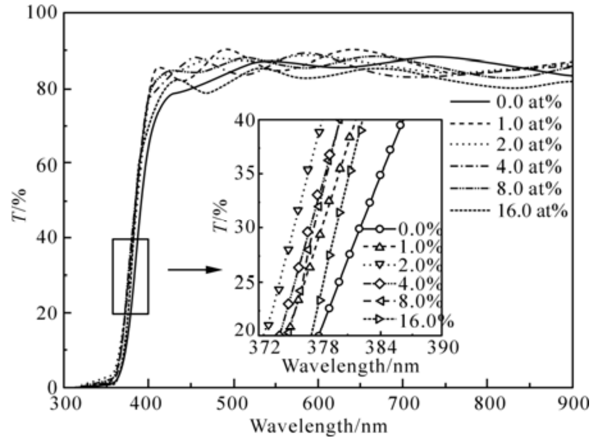

Fig.5 Optical transmittance spectra of ZnO films with different Na concentrations

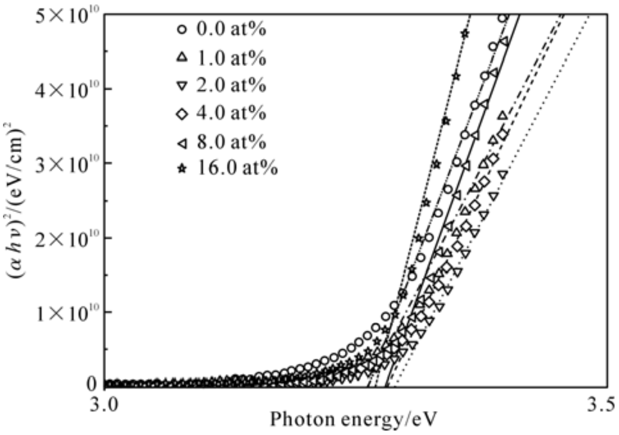

Fig.6 The $(\alpha hv)^2$ *vs* photon energy plot of the ZnO films

The increasing of the band gap value can be explained by means of Moss-Burstein effect. According to the Burstein-Moss theory, in heavily doped zinc oxide films, the donor electrons occupy states at the bottom of the conduction band. Since the Pauli principle prevents states from being doubly occupied and optical transitions are vertical, the valence electrons require extra energy to be excited to higher energy states in the conduction band, which leads to the broadening of optical band gap[23]. The increasing of band gap value by Na concentration suggest an increase in the donor electrons concentration, which indicate that most of the Na ions must be incorporated as interstitial donors into the structure rather than substitutional acceptors. The red shift of the optical band gap for doped ZnO films may be associated with the hybridization between the orbital of Al dopant and of ZnO matrix[24], the doping concentration[25] and the defects of films[22, 26]. The red shift of the optical band gap of ZnO film can be explainend as follows: With the Na concentration increases from 2 at% to 16 at%, there are more chance for the Na atoms to occupy substitutional sites and to generate Na acceptor. Substitutional incorporation of Na atoms neutralizes the donor electrons in ZnO.

The PL spectra of undoped and Na-doped ZnO thin films are given in Fig.7. It can be seen that there are a violet light (wavelength in the 400-407 nm) and two deep-level emissions in visible regions (wavelength near the 454 and 473 nm) for all films and the intensity of the emission peak increases with the increasing of Na concentration. It is believed that the intensity of the emission peak may be connected with (002) preferred orientation. There are five main intrinsic defects in ZnO films, such as zinc vacancy, oxygen vacancy, interstitial zinc, interstitial oxygen, and anti-site oxygen[27].

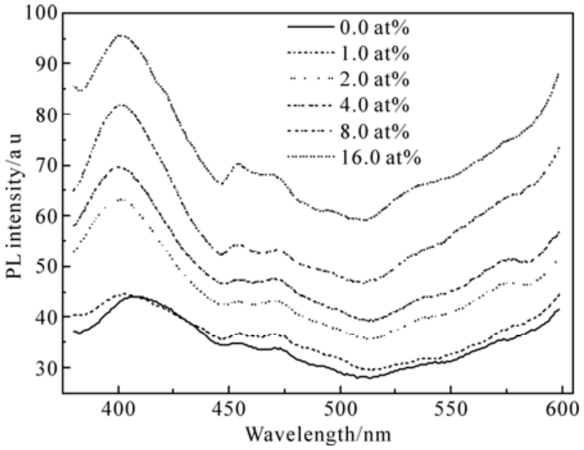

Fig.7 Photoluminescence (PL) spectra of the ZnO films

The violet emission may be originated from the electron transition from the bottom of the conduction band to the Zn vacancy (V_{Zn}) level[28]. Fig.7 shows the change of the violet emission peak. The peak of violet emission of ZnO films shifts from 407 nm to 400 nm with increasing Na concentration ranging from 0 at% to 2.0 at%, then has a redshift at higher Na concentration, which were attributed to Burstein-Moss effect that the energy of conduction band electron increase first and then decrease with increasing the Na concentration. The results are in agreement with the observation from the optical transmittance measurement. The 473 nm blue emission may be originated from the electron transition from the shallow donor level of zinc interstitials to that of Zn vacancy[28]. The intensity of the 473 nm blue emission increases with increasing Na concentration, indicating more zinc interstitials or zinc vacancy was produced with increasing Na concentration.

4 conclusions

The component, structural and optical properties of ZnO films were investigated by means of X-ray photoelectron spectroscopy, X-ray diffractometer, UV-Vis spectrophotometer and fluorescence spectrometer. XPS results reveal that Na element doped as Na^+ in the Na-doped ZnO film. XRD analysis show that preferential *c*-axis orientation becomes more and more obvious, and the intensity of the diffraction peaks from (103) increases with the enhancement of Na concentration. The transmittance spectra indicate that as increasing the Na concentration below 2.0 at%, the optical band gap of the ZnO film blueshifts while redshifts when the Na concentration exceeds 2.0 at%. The PL spectra show that there is a violet emission (wavelength in the 400-407 nm), and the peak of violet emission shifts from 407 nm to 400 nm with increasing Na concentration ranging from 0 at% to 2.0 at% then has a redshift at higher Na concentration. This phenomenon can be explained by Burstein-Moss effect.

References

[1] S S Lin, J G Lu, Z Z Ye, *et al*. P-type Behavior in Na-doped ZnO Films and ZnO Homojunction Light-emitting Diodes[J]. *Solid State Communications*, 2008, 148: 25-28

[2] D Y Wang, S X Gao. Influence of Annealing Condition on the Structure and Optical Properties of Na-doped ZnO Thin Films Prepared by Sol-gel Method[J]. *Journal of Alloys and Compounds*, 2009, 476: 925-928

[3] Z Z Zhang, Z P Wei, Y M Lu, *et al*. P-type ZnO on Sapphire by Using O_2–N_2 Co-activating and Fabrication of ZnO LED[J]. *Journal of Crystal Growth*, 2007, 301-302: 362-365

[4] D C Look, B Claflin. P-type Doping and Devices Based on ZnO[J]. *Physics Status Solid B*, 2004, 241: 624-630

[5] K J Chen, F Y Hung, S J Chang, *et al*. Optoelectronic Characteristics of UV Photodetector Based on ZnO Nanowire Thin Films[J]. *Journal of Alloys and Compounds*, 2009, 479: 674-677

[6] K Wang, Y Vygranenko, A Nathan. Optically Transparent ZnO-based n–i–p Ultraviolet Photodetectors[J]. *Thin Solid Films*, 2007, 515: 6 981-6 985

[7] W C Shi, H Y Su, M S Wu. Deposition of ZnO Thin Films on SiO_2/Si Substrate with Al_2O_3 Buffer Layer by Radio Frequency Magnetron Sputtering for High Frequency Surface Acoustic Wave Devices[J]. *Thin Solid Films*, 2009, 517: 3 378-3 381

[8] S Krishnamoorthy, A A Iliadis. Properties of High Sensitivity ZnO Surface Acoustic Wave Sensors on SiO_2/(100) Si

Substrates[J]. *Solid State Electronics*, 2008, 52: 1 710-1 716

[9] L L Chen, H P He, Z Z Ye, *et al*. Influence of Post-annealing Temperature on Properties of ZnO:Li Thin Films[J]. *Chemical Physics Letters*, 2006, 420: 358-361

[10] J Wu, Y T Yang. Deposition of K-doped P-type ZnO Thin Films on (0001) Al_2O_3 Substrates[J]. *Material Letters*, 2008, 62: 1 899-1 901

[11] L H Xu, X Y Li, J Yuan. Effect of K-doping on Structural and Optical Properties of ZnO Thin Films[J]. S*uperlattices and Microstructures*, 2008, 44: 276-281

[12] M L Tu, Y K Su, C Y Ma. Nitrogen-doped P-type ZnO Films Prepared from Nitrogen Gas Radio-frequency Magnetron Sputtering[J]. *Journal Applied Physics*, 2006, 100: 053 705-053 708

[13] Y J Zeng, Z Z Ye, W Z Xu, *et al*. Study on the Hall-effect and Photoluminescence of N-doped P-type ZnO Thin Films[J]. *Material Letters*, 2007, 61: 41-44

[14] B Yao, L X Guan, G Z Xing, *et al*. P-type Conductivity and Stability of Nitrogen-doped Zinc Oxide Prepared by Magnetron Sputtering[J]. *Journal of Luminescence*, 2007, 122-123: 191-194

[15] G X Hu, H Gong. Unexpected Influence of Substrate Temperature on the Properties of P-doped ZnO[J]. *Acta. Materialia*, 2008, 56: 5 066-5 070

[16] V Vaithianathan, Y H Lee, B T Lee, *et al*. Doping of As, P and N in Laser Deposited ZnO Films[J]. *Journal of Crystal Growth*, 2006, 287: 85-88

[17] D C Look, G M Renlund, R H Burgener, *et al*. As-doped P-type ZnO Produced by an Evaporation/Sputtering Process[J]. *Applied Physics Letters*, 2004, 85: 5 269-5 271

[18] C H Park, S B Zhang, S H Wei. Origin of P-type Doping Difficulty in ZnO: The Impurity Perspective[J]. *Physical Review B*, 2002, 66: 073 202-073 204

[19] E C Lee, K J Chang. Possible P-type Doping with Group-I Elements in ZnO[J]. *Physical Review B*, 2004, 70: 115 210-115 213

[20] M G Wardle, J P Goss, P R Briddon. Theory of Li in ZnO: A Limitation for Li-based P-type Doping[J]. *Physical Review B*, 2005, 71: 155 205-155 214

[21] X C Wang, W B Mi, S Dong, *et al*. Microstructure and Optical Properties of N-incorporated Polycrystalline ZnO Films[J]. *Journal of Alloys and Compounds*, 2009, 478: 507-512

[22] S W Xue, X T Zu, W L Zhou, *et al*. Effects of Post-thermal Annealing on the Optical Constants of ZnO Thin Film[J]. *Journal of Alloys and Compounds*, 2008, 448: 21-26

[23] B E Sernelius, K F Berggren, Z C Jim, *et al*. Band-gap Tailoring of ZnO by Means of Heavy Al Doping[J]. *Physics Review B*, 1988, 37: 10 244-10 248

[24] M Gabás, S Gota, J R Barrado, *et al*. Unraveling the Conduction Mechanism of Al-doped ZnO Films by Valence Band Soft X-ray Photoemission Spectroscopy[J]. *Applied Physics Letters*, 2005, 86: 042 104-042 106

[25] H P He, F Zhuge, Z Z Ye, *et al*. Strain and Its Effect on Optical Properties of Al-N Co-doped ZnO Films[J]. *Journal of Applied Physics*, 2006, 99: 023 503-023 505

[26] X Y Gao, Q G Lin, H L Feng, *et al*. Study on the Structural, Electrical, and Optical Properties of Aluminum-doped Zinc Oxide Films by Direct Current Pulse Reactive Magnetron Sputtering[J]. *Thin Solid Films*, 2009, 517: 4 684-4 688

[27] L P Peng, L Fang, X F Yang, *et al*. Effect of Annealing Temperature on the Structure and Optical Properties of In-doped ZnO Thin Films[J]. *Journal of Alloys and Compounds*, 2009, 484: 575-579

[28] P S Xu, Y M Sun, C S Shi, *et al*. Electronic Structure of ZnO and Its Defects[J]. *Science in China* (*Series A*), 2001, 44: 1 174-1 181