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Optical constants of Na-doped ZnO thin films by sol–gel method

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ABSTRACT

The structural and optical properties of pure and Na-doped ZnO thin films have been investigated by X-ray diffraction (XRD), atom force microscopy and UV–Vis spectrophotometer. The crystal structure of all the thin films is the hexagonal wurtzite. The average grain size and surface roughness increases with the increase of the Na/Zn ratio. The optical band gap of the thin films decreases from 3.26 to 3.12 eV by increasing the Na/Zn ratio from 0.0 to 0.10. Transmittance spectra were used to determine the optical constants of the thin films, and the effect of Na/Zn ratio on the optical constants was investigated. With the increase of Na/Zn ratio, the refractive index decreases and the extinction coefficient increases in the 380–700 nm spectral range.

1. Introduction

Recently, pure and doped ZnO films have received much attention due to their remarkable physical properties and potential applications in antireflection coatings, transparent electrodes in solar cells [1], photodetectors [2], surface acoustic wave devices [3], optoelectronic devices [4], and light emitting diodes [5]. Refractive index is one of the fundamental properties for an optical material, because it is closely related to the electronic polarizability of ions and the local field inside materials. The evaluation of refractive indices of optical materials is considerably important for the applications in integrated optic devices. Therefore, optical constants of pure and doped ZnO films prepared by various methods have been reported, such as filtered cathodic vacuum arc technique [6], sub-molecule doping technique [7], RF magnetron sputtering [8], DC magnetron sputtering [9], and sol–gel method [10,11]. Due to simplicity, safety and low cost, optical constants of ZnO thin films prepared by sol–gel method were studied intensively. Xue et al. [12] reported the effects of Al doping concentration on optical constants of ZnO:Al thin films by analyzing the transmittance spectrum, which showed that the refractive index decreases with the increase of the Al doping concentration. However, there are few reports on the optical constants of Na-doped ZnO film by analyzing the transmittance spectrum.

In this work, pure and Na-doped ZnO thin films were prepared by sol–gel method. The crystalline structure and surface topography of the thin films were investigated by X-ray diffraction (XRD) and atom force microscopy (AFM). The transmittance spectrum was measured by UV–Vis spectrophotometer in the wavelength of 380–700 nm. The effect of the Na/Zn ratio on the surface topography and optical properties were also studied, such as the optical band gap, the refractive index and the extinction coefficient.

2. Experiments and method

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 the dopant (sodium chloride) in the solution, [Na/Zn], was 0, 0.02, 0.06, and 0.10, respectively. The resultant solution was stirred at 60 °C for 2 h to yield a clear and homogeneous solution. The sol–gel coating was made usually 1 day after the solution was prepared. Pure and Na-doped ZnO thin films were prepared on Si (100) or quartz glass substrate by repeated coating. The thin films were obtained by a spin–coating method with 3000 rpm for 30 s. Then, the gel thin films were dried at 150 °C for 10 min, and this procedure was repeated 10 times. After that, these as-coated films were annealed at 800 °C for 60 min in air.

The crystal structure of the thin films deposited on Si substrate was examined by X-ray diffraction (XRD, MACM18XHF) employing Cu Kα radiation. Surface topography of the thin films deposited on the Si substrate was measured by atomic force microscopy (AFM, CSPM4000) operating in contact mode. Composition of the Na-doped ZnO thin film

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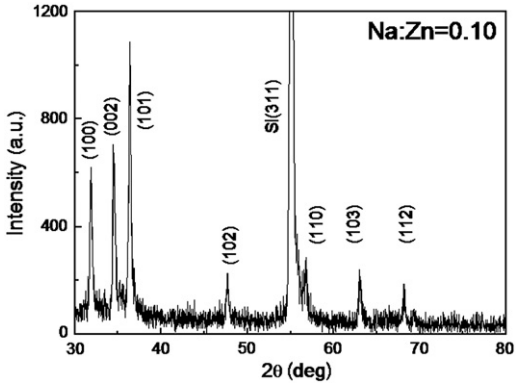

Fig. 1. XRD patterns of ZnO thin films with Na/Zn = 0.10.

with Na/Zn = 0.10 in the solution were investigated by X-ray photoelectron spectroscopy (XPS, Thermo-VG Scientific ESCALAB250). Thin film thickness was investigated by scanning electron microscopy (SEM, S-4800). Transmittance spectrum of the thin films prepared on a quartz glass substrate was obtained with the normal incident transmittance by UV–Vis spectrophotometer (UV-2550, SHIMADZU) in the 380–700 nm spectral range at room temperature in air.

3. Results and discussion

Fig. 1 shows the room temperature X-ray diffraction (XRD) pattern of ZnO thin film with Na/Zn = 0.10, which was prepared on a Si substrate . The peaks can be indexed to a hexagonal wurtzite structure apart from that of the Si substrate. No additional phase is observed within the sensitivity of the measurement. Other thin films with Na/Zn < 0.10 also show the similar XRD results. Fig. 2(a)–(d) show the surface topography of pure and Na-doped ZnO thin films. Root mean square (rms) roughness of the different thin films is listed in Table 1, which is obtained by the AFM scanning with a 3 μm range. The AFM study revealed that Na doping enhances the surface roughness of the thin films and increased the average grain size. The surface roughness varies from 7.4 to 44.4 nm when the Na/Zn ratio is 0–0.10. The change

Table 1
Experimental and fitted results obtained for the Na-doped ZnO samples.

Na:Zn ratio	Surface rms (nm)	Thickness by fitting (nm)	Experimental thickness (nm)	Optical bandgap (eV)
0.0	7.4	337	339	3.26
0.02	12.2	351	378	3.22
0.06	15.2	368	372	3.21
0.10	44.4	336	365	3.12

of the average grain size and rms roughness may be attributed to the Na doping in the thin films.

Fig. 3(a) shows the typical XPS survey spectrum of the ZnO thin film with Na/Zn = 0.10. The high resolution scan for C, O, Zn and Na was performed. Fig. 3(b) and (c) give the XPS data of Zn2p3 and Na1s of the thin film. According to the high resolution scan data, the atomic concentrations of elements are computed from the measured peak area together with the sensitivity factors. The obtained atomic concentrations of C, O, Zn and Na are 21.4, 42.2, 35.1 and 1.3 at.%, respectively. The XPS results confirm that the Na element has been doped into the ZnO thin film but the value of the Na/Zn ratio in the thin film surface (0.037) is much smaller than that in the solution (0.10).

Fig. 4 shows the room temperature transmittance spectrum of pure and Na-doped ZnO thin films with the different Na/Zn ratio. It can be seen that the average transmittance in the visible light wavelength range is over 80% for pure ZnO thin film, and decreases with the increase of the Na/Zn ratio. When the Na/Zn ratio increases to 0.02, the average transmittance in the range of 450–700 nm is still beyond 70%, which is important for the applications of Na-doped ZnO thin films to optical devices. The average transmittance in the visible light wavelength range, decreases by increasing the Na/Zn ratio, is about 40% for the thin films with Na/Zn = 0.06 or 0.1.

Optical band gap of the thin films can be obtain by applying the following two formulas (1) and (2) [11]

$$\alpha = \frac{1}{d}\, ln\left(\frac{1}{T}\right) \tag{1}$$

$$(\alpha h\nu)^2 = A\left(h\nu - E_g\right) \tag{2}$$

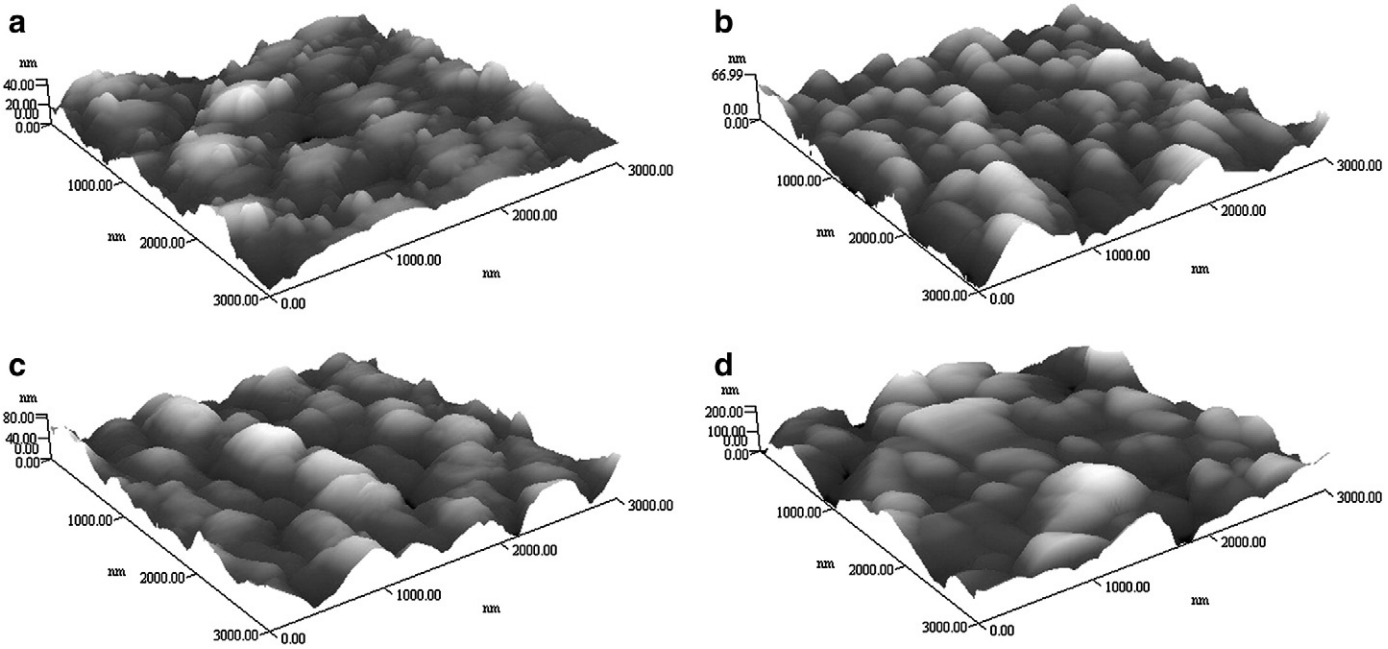

Fig. 2. AFM images of the ZnO thin films with different Na/Zn ratios (a) 0, (b) 0.02, (c) 0.06, and (d) 0.10.

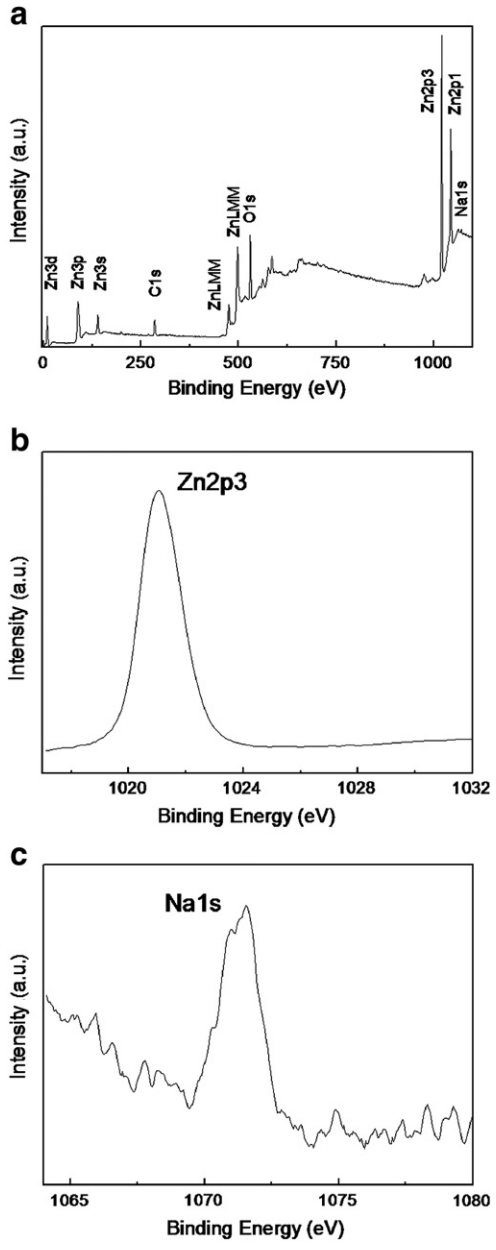

Fig. 3. XPS survey spectrum (a), high resolution scan data of Zn2p3 (b) and Na1s (c) for the ZnO thin film with Na/Zn = 0.10.

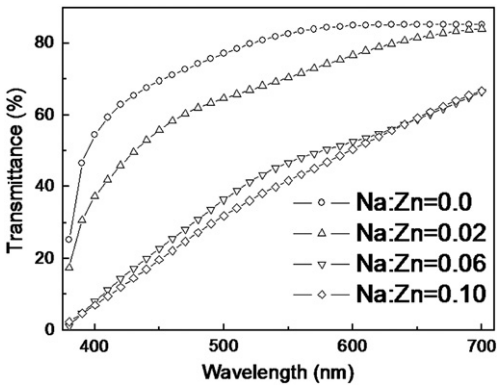

Fig. 4. Optical transmittance spectra of pure and Na-doped ZnO thin films.

In the formula (1), α is the absorption coefficient, d is the film thickness and T is the transmittance of the thin films. In the formula (2), A is a constant, $h\nu$ is the photo energy and E_g is the optical band gap. According to formulas (1) and (2), we calculated the absorption coefficient $\alpha \sim \ln(1/T)$ as well as $(\alpha h\nu)^2 = A(h\nu - E_g)$. Then the plot of $(\alpha h\nu)^2$ versus the photon energy $h\nu$ can be obtained. The E_g value was determined by the extrapolation method. The photon energy at the point where $(\alpha h\nu)^2 = 0$ is E_g. The optical band gaps determined by transmittance spectra are listed in Table 1. It can be seen that the optical band gap decreases monotonically when the Na/Zn ratio increases from 0.0 to 0.10. Li et al. [7] reported that as the Al content increases from 4 to 6 wt.%, the optical band gap of Al-doped ZnO (AZO) films decreased from 3.32 to 3.20 eV. Xu et al. [13] investigated the effect of K content on the optical band gap of K-doped ZnO thin films by the sol–gel method, which shows that the optical band gap of the K-doped ZnO thin films increases at first and then decreases with the increasing K content. Kim et al. [14] verified that the doped K in ZnO contributes differently with a criterion of 2 mol%. For our heavy Na-doped ZnO thin films, the ratio of substitutional doping of Na in Zn site increases by increasing the Na content. Conclusively, the carrier concentration in the Na-doped ZnO thin films decreases as the Na content increases [14]. So, the decrease of the optical band gap of the thin films can be interpreted by Moss–Burstein effect, where the decrease is the result of a decrease in the carrier concentration, and the corresponding downward shift of the Fermi level to below the band edge [15,16].

The optical constants play an important role in the optical communication and designing of the optical devices, because they are closely related to the electronic polarizability of ions and the local field inside materials. [17] In the normal spectroscopic ellipsometry (SE) analysis system, usually based on the reflection type, substrates with high reflectivity are required. In this work, ellipsometric parameters ψ and Δ were measured by using the transmittance spectrum of the thin films deposited on quartz glass substrates. The transmittance spectrum, which was converted to target files by programming, can be used to extract the optical constants of the thin films. Then, in the analysis process, the analysis software identified the target files and executed the calculation relationship between transmittance data and ellipsometric parameters. If the dispersion relation was properly employed and the initial parameters were set suitably, the simulation results can be successfully obtained [18].

The contribution of conduction band to valence band transitions can be taken into account by a combination of Lorentzian oscillators. For pure and Na-doped ZnO thin films, the free carrier are electrons and the free-electron contribution is described in terms of the Drude model. Therefore, a general parameterized equation can be expressed as [19]:

$$\varepsilon(\omega) = \varepsilon_\infty \left(1 + \sum_{j=1}^{m} \frac{A_j^2}{(E_{center})_j^2 - E(E - i\nu)} - \frac{\omega_p^2}{E(E + i\nu)}\right) \quad (3)$$

where ε_∞ is the high-frequency lattice dielectric constant. j is the number of oscillators. E_{center} is the center energy of each oscillator. A_j is the amplitude of oscillator. ν is the electron collision frequency. ω_p is the plasma frequency. Fig. 5 shows the typical fitting result of the transmittance spectrum for the ZnO thin film with Na/Zn = 0.06. It is found that the calculated data is consistent with the experimental data. Other thin films can be fitted similarly (not shown). The fitted thickness of all thin films is listed in Table 1, which is consistent with those obtained by the SEM measurement (shown in Table 1). Based on the results mentioned above, it is found that the Lorentzian oscillators + Drude model is suitable to describe the spectral of the thin films.

The derived value of the refractive index n is shown in Fig. 6(a), which has a comparable value of the ZnO single crystal measured by Yoshikawa et al. [20] using spectroscopic ellipsometry. It can be seen

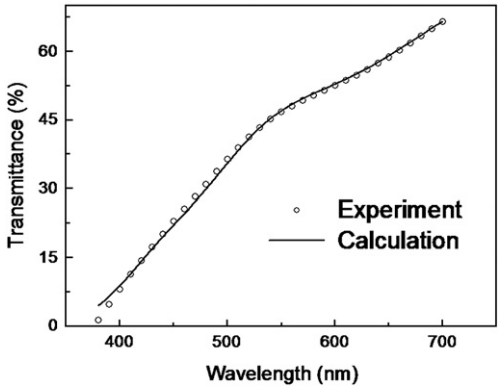

Fig. 5. Typical fitting result of the transmittance spectrum for the ZnO thin film with Na/Zn = 0.06.

that, for the pure and Na-doped ZnO thin films, with increasing wavelength, the refractive index decreases in the wavelength range from 380–700 nm. A pure ZnO thin film has a higher refraction index *n* compared with the ZnO crystals. This difference may be due to the different structures or density of the thin films and the different fitting approaches. Besides, the value of refractive index of the thin films decreases with the increasing of the Na/Zn ratio. Liu et al. [6] considered that the increase in the volume fraction of the "voids" on the surface of the ZnO films is responsible for the reductions in the refractive index. Other researchers suggested that the decrease of the refractive index is attributed to the increase of the carrier concentration [7,12]. In our work, the decrease of the refractive index with the increase of the Na content can be mainly attributed to the increase of the volume fraction of the "voids" on the surface of the thin films. In addition, Fig. 6(b) shows the dependence of the extinction coefficients of the thin films on the wavelength in the range of 380–700 nm. It can be seen that the extinction coefficient increases when the Na content is increased.

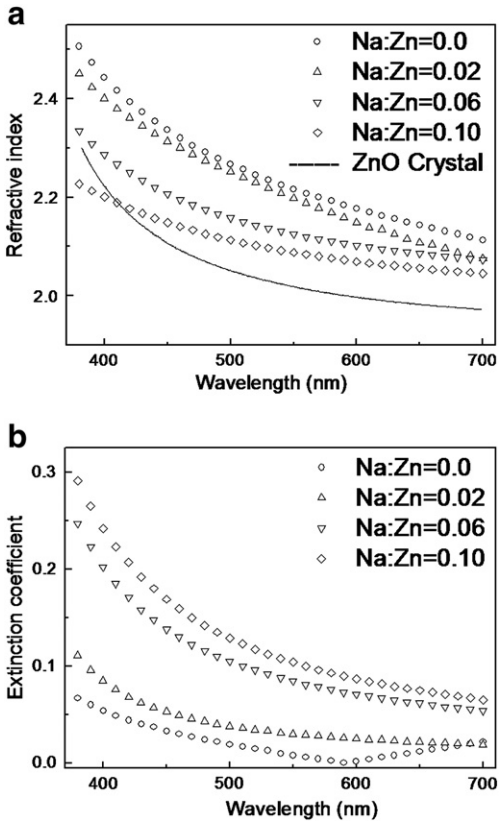

Fig. 6. Effects of Na/Zn ratio on the refractive index (a) and the extinction coefficient (b) of pure and Na-doped ZnO films.

4. Conclusion

Pure and Na-doped ZnO thin films were deposited on Si or quartz glass substrate by sol–gel method. It is clearly observed that the average grain size, surface roughness and "voids" on the surface of the thin films increase with the increasing of the Na/Zn ratio. The optical band gap decreases from 3.26 to 3.12 eV by increasing the Na/Zn ratio. The refractive index of the Na-doped ZnO thin films can be controlled by varying the Na content, which is important for the applications in designing integrated optic devices.

Acknowledgements

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