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ORIGINAL PAPER

Structural and optical properties of ZnO thin films by the spin coating Sol-Gel method

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Abstract ZnO thin films were deposited onto glass substrates by a Sol-gel spin coating method. The structural and optical properties of ZnO thin films were investigated. The molar ratios of the zinc acetate dihydrate to Monoethanolamine were maintained 1:1. The as-grown film was sintered 250 °C for 10 min, then annealed in air at 500 °C for 30 min. The XRD results indicate that ZnO films were strongly oriented to the c-axis of the hexagonal nature. Absorption measurements were carried out as a function of temperature with 10 K steps in the range 10–320 K. The band gap energy was measured 3.275 and 3.267 eV for 0.5 and 1.0 molarity (M) ZnO thin films at 300 K. The steepness parameters were observed between 10 and 320 K and their extrapolations converged at $(E_0, \alpha_0) = 3.65$ eV, 172,819 cm^{-1} and 3.70 eV, 653,436 cm^{-1} for 0.5 and 1.0 M ZnO thin films, respectively.

Keywords ZnO thin film · Sol-gel · Band gap · Steepness parameter

1 Introduction

The films of transparent conductive oxides (TCO) [1] have been extensively studied because of their use in optoelectronic and semiconducting [2] device applications such as light-emitting diodes (LEDs), liquid crystal displays [3], short-wavelength laser diodes, surface acoustic wave devices [4] and ultraviolet (UV) detectors [5]. Among TCOs, there has been a great deal of interest in zinc oxide (ZnO) semiconductor material because it is a wide-band-gap oxide semiconductor with a direct energy gap of about 3.3 eV and a large excitation binding energy (60 meV) at 300 K. These properties of ZnO give assurance of an efficient excitonic emission up to room temperature. [6–8]. Although some optoelectronic applications of ZnO overlap with being another wide-gap semiconductor, GaN, which is widely used for production of green, blue-ultraviolet, and white light-emitting devices, ZnO has some advantages over GaN. Among these advantages are the availability of fairly high-quality ZnO in bulk, and the advantage of a low cost and much simpler crystal-growth technology [9, 10].

Numerous deposition techniques have been studied for preparing thin films including spray pyrolysis [11], pulsed-laser deposition [12], molecular beam epitaxy (MBE) [13], the sol-gel method, etc. Among all these deposition methods, the sol-gel technique [14–16] has reccently been accepted for the growth of ZnO thin films because it is a cost-effective process. It is easily implemented in a laboratory for the deposition of semiconducting thin films of uniform thickness and large area thin film deposition as compared to more complex and expensive techniques requiring vacuums.

In this work, we have performed structural and optical absorption measurements in the range of 10–320 K with 10 K steps. We focused on the band gap energy and steepness parameter calculated from the spectral dependence of the coefficient of absorption in detail.

2 Experimental

ZnO thin films were grown on glass substrates by spin coating the sol-gel method. In order to deposit 0.5 and 1.0

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molarities, zinc acetate dihydrate [$Zn(CH_3COO)_2{\cdot}2H_2O$] was used as a starting material. Monoethanolamine (C_2H_7NO, MEA) and 2-Methoxyethanol ($C_3H_8O_2$) were used as stabilizer and solvent, respectively. The molar ratios of zinc acetate dihydrate to MEA were kept at 1:1. The complex solution was stirred at 60 °C for 2 h until a clear and homogenous sol was obtained. ZnO films were coated onto glass substrates and these substrates were cleaned in acetone and methanol by using an ultrasonic cleaner. Then the substrates were rinsed with de-ionized (DI) water and dried with nitrogen. The precursor solution was dropped onto a glass substrate and spin coated at a speed of 3.000 rpm for 25 s. The as-coated film was sintered at 250 °C for 10 min immediately to evaporate the solvent. This procedure was repeated 10 times to obtain the intended thickness, Then, the film was annealed in air at 500 °C for 30 min. The flowchart is shown in Fig. 1. It was found that the ZnO thin films had n-type conduction by the hot probe technique. The crystalline orientation of the ZnO thin films was investigated by a Rigaku D/Max-IIIC diffractometer with 0.1541 nm wavelength. The X-Ray difraction (XRD) scan was taken between 2θ of 20° and 2θ of 80°. The optical absorption measurements of the ZnO thin film were recorded in the spectral region of 200–400 nm and carried out with 10 K step by using a Perkin Elmer UV/VIS Lambda 2S Spectrometer which works in the range of 190–1,100 nm. The wavelength accuracy of the spectrometer is better than ±0.3 nm. Therefore, energy band gap values can be calculated with an accuracy of better than ±0.001 eV considering the wavelength accuracy of our spectrometer. A closed cycled He cryostat was used to vary the temperature from 10 to 320 K, and energy band gaps were studied as a function of the temperature.

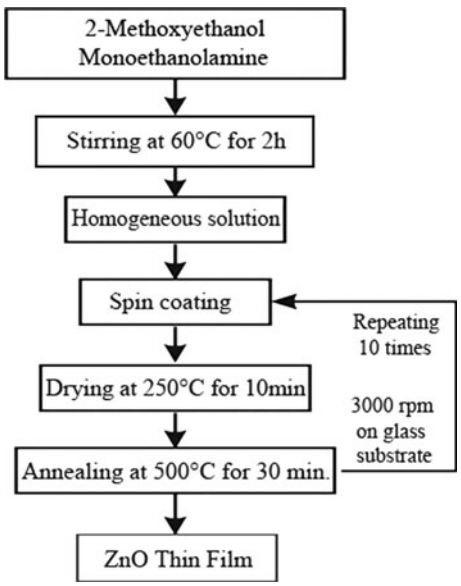

Fig. 1 Flowchart for the deposition of ZnO thin films by the sol-gel method

3 Results and discussion

Figure 2 shows the XRD patterns of the samples deposited on glass substrates. The diffraction peaks around 33.70 degrees being (002) plane, indicate the growth of ZnO with a higher degree of preference along the *c*-axis perpendicular to the substrate. Shan et al. [17] reported that the growth temperature had played a role in determining the crystal quality. By comparison of ZnO grown at a different molarity, it can be said that (002) peak appears in both films and by a increase of the molarity, the intensities of the (002) peak begin to drop and other planes begin to appear indicating that the quality of the films changes from single crystalline to polycrystalline [18].

The absorption coefficients were obtained from the transmission data using the relationship [19, 20]:

$$T = (1-R)^2 \exp(-A) = (1-R)^2 \exp(-\alpha d) \quad (1)$$

where R is the reflectivity, A is the absorbance, α is the optical absorption coefficient in cm^{-1} and d is the sample thickness. The optical absorption coefficients were determined for all temperatures using the values of R at room temperature by

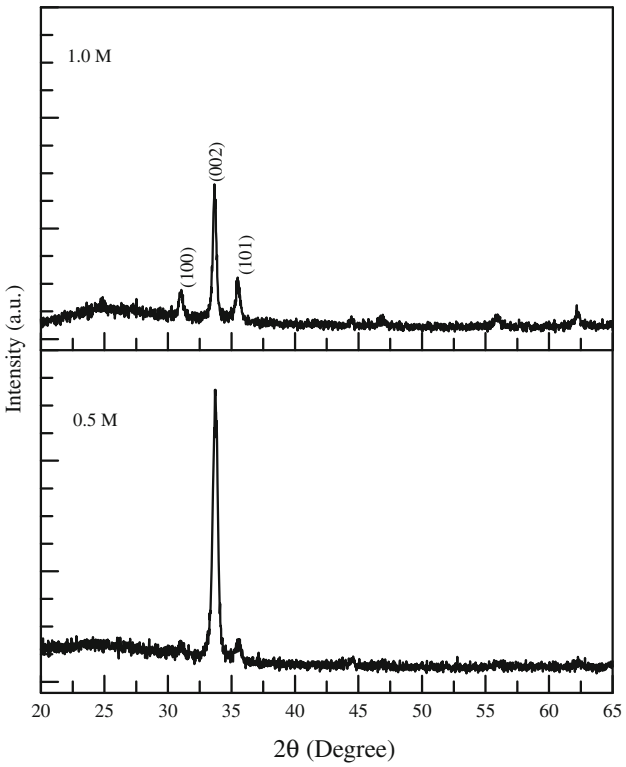

Fig. 2 XRD patterns of the ZnO films prepared with two different molarities

assuming that the temperature change from 10 to 320 K produces a small change in R [21]. The multiple reflection and the interference fringes of the samples were put with a small angle with respect to the incident beam. The fundamental absorption edge in most semiconductors follows the exponential law. Above the exponential tail, the absorption coefficient of the semiconductor was observed to obey the equation

$$\alpha \hbar w = B(\hbar w - E_g)^n \quad (2)$$

where α is the absorption coefficient and $w = 2\pi v$ is angular frequency, B is a constant and n is an index which can be assumed to have values of 1/2, 3/2, 2 and 3, depending on the nature of electronic transition responsible for the absorption. $n = 1/2$ for the direct allowed transition (high energy part of the spectra), $n = 3/2$ for forbidden direct transition, $n = 2$ for the indirect allowed transition (low energy part of the spectra) and $n = 3$ for forbidden indirect transition [22].

An exponentially increasing absorption edge in a number of insulators, including ionic crystals, semiconductors, and organic crystals follows the empirical expression [23]:

$$\alpha = \alpha_0 \exp\left[\frac{\sigma(\hbar w - E_0)}{k_B T}\right] \quad (3)$$

where α_0 and E_0 are characteristic parameters of the material, σ is the steepness parameter, k_B is the Boltzmann constant and T is the temperature.The steepness parameter σ, which characterizes the steepness of the straight line near the absorption edge, is expressed empirically as a function of temperature [24]:

$$\sigma = \sigma_0\left(\frac{2kT}{\hbar w_p}\right)\tanh\left(\frac{\hbar w_p}{2k_B T}\right) \quad (4)$$

where σ_0 is a temperature-independent but material dependent parameter. Some of the researchers stated that $\hbar w_p$ corresponded to the energy of phonons associated with Urbach tail. The following empirical expression is often used to describe the temperature dependence of the energy gap [25]:

$$E_g(T) = E_g(0) - \delta\frac{T^2}{T+\beta}, \quad (5)$$

where $E_g(T)$ is the energy gap, $E_g(0)$ is the energy gap at 0 K, δ and β are constants depending on the material. The constant (β) is approximately equal to the Debye temperature θ_D.

4 Conclusions

This paper presents the results of the structural, optical absorption experiments and steepness parameter in ZnO thin films grown the by sol-gel method for two different molarities over the temperature range from 10 to 320 K. The absorption spectra of both 0.5 and 1.0 M ZnO crystals are used to study the energy gap. The absorption coefficient spectra were obtained from the experimental absorbance values at different sample temperatures using Eq. (1). The typical spectra obtained at 10, 80, 160, 240, and 320 K for the ZnO thin films prepared at two various molarities of the precursor solutions are shown in Fig. 3a and b, respectively. The absorption coefficients and are between 2.500 and 18.000 cm^{-1} for 0.5 M ZnO and 5.000 and 39.000 cm^{-1} for 1.0 M ZnO, respectively, in the temperature range of 10 to 320 K**.** The absorption edges of both investigated thin films shifted to lower energy values considerably as the temperature was changed from 10 to 320 K. As seen in Fig. 3a and b, the absorption coefficients of ZnO (0.5 M) are smaller than those of ZnO (1.0 M).

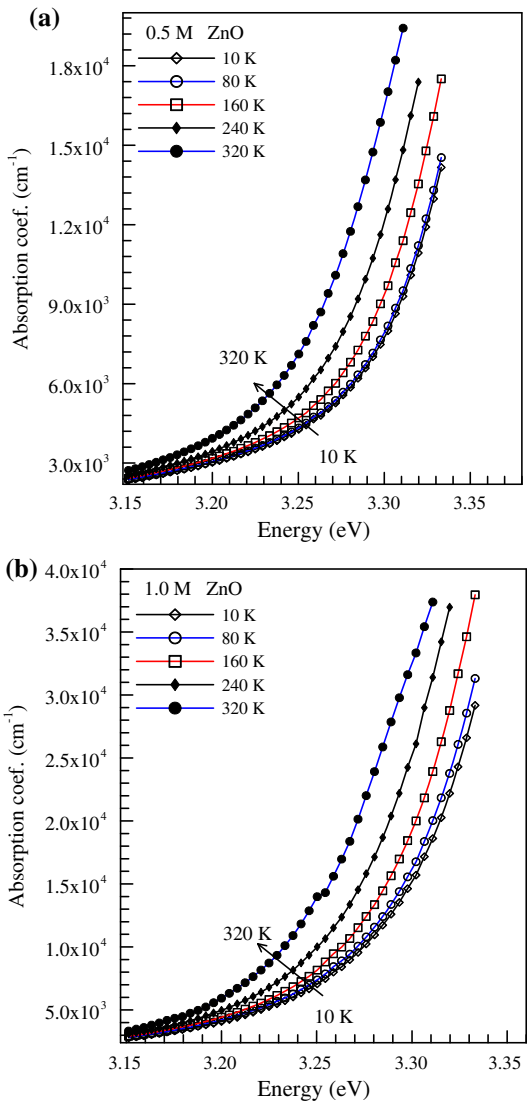

Fig. 3 Typical absorption spectra obtained at 10, 80, 160, 240 and 320 K for (**a**) ZnO (0.5 M), (**b**) ZnO (1.0 M) thin films

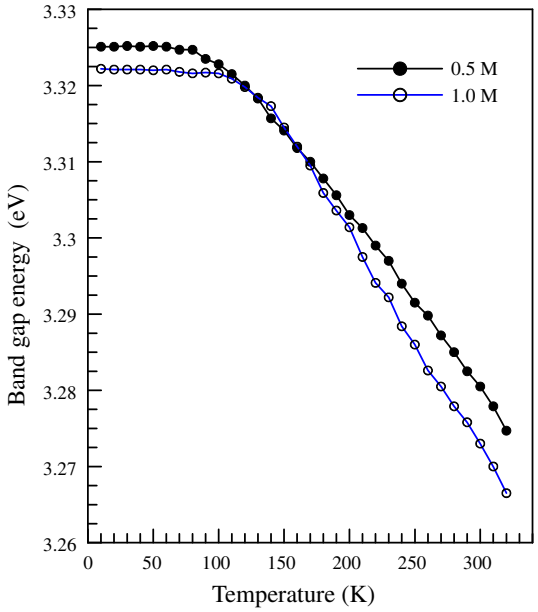

Fig. 4 The temperature dependence of optical band gap values for ZnO thin films

The energy gaps values for both 0.5 and 1.0 M ZnO thin films were obtained from the dependencies (α^2 vs. ($\hbar$w)) by extrapolation of the dashed straight lines to $\alpha^2 = 0$. The temperature dependence of the band gap values of these films in the temperature range 10 to 320 K is shown in Fig. 4. The energy gaps values for both 0.5 and 1.0 M ZnO thin films are given in Table 1 for different temperatures. At 320 K, the band gaps values of 0.5 and 1.0 M ZnO are 3.275 and 3.267 eV, respectively. These results agree with the investigation carried out by [26–29]**.** It is evident that the energy band gap values decrease with increasing temperature. As seen in Fig. 4, the temperature dependence of the energy band gap values does not follow the conventional linear relationship. The temperature variations of the energy band gap values are most probably caused by variations of the lattice parameters rather than by the electron- phonon coupling [30]. α values were found to be 3.5×10^{-4} eV K^{-1} for 0.5 M and 3.8×10^{-4} eV K^{-1} for 1.0 M ZnO thin films, respectively. Once these values are used, the curves given in Fig. 4 closely fit the experimental values. Both samples have negative temperature coefficients calculated from a satisfactory fitting of the

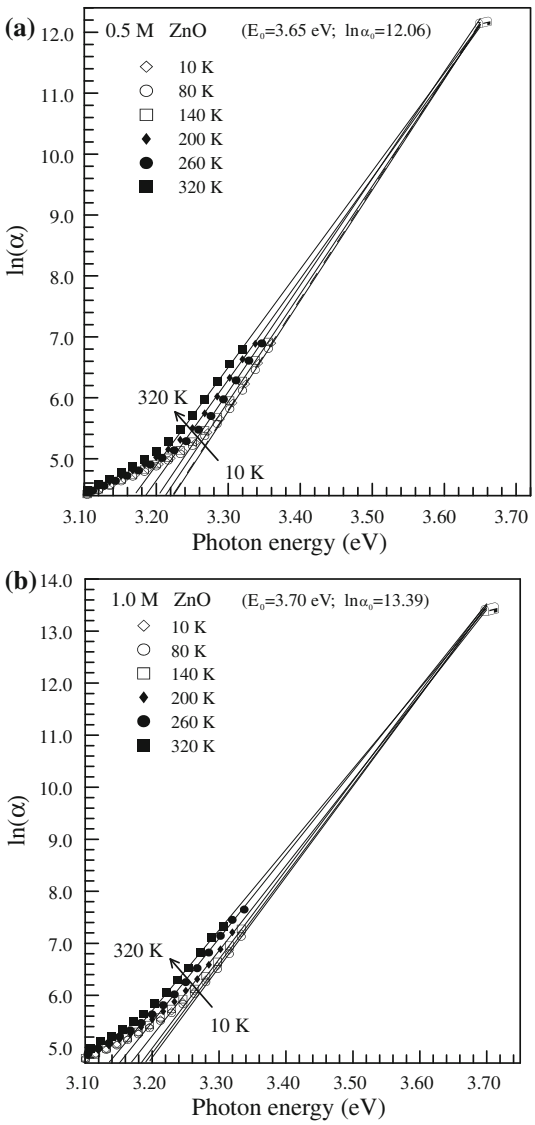

Fig. 5 The Urbach plots obtained at 10, 80, 160, 240 and 320 K versus photon energy for (**a**) 0.5 M ZnO, (**b**) 1.0 M ZnO. *Solid lines* are the fitting results with Eq. (3)

experimental curve using the above Eq. (5). These results are in good agreement with results obtained by Park and Hong [31]. The steepness parameters were observed for both ZnO thin films between 10 and 320 K. The typical steepness parameters for various temperatures are shown in Fig. 5a and b. It is found that all extrapolations of the

Table 1 The band gap values and steepness parameter of 0.5 and 1.0 M ZnO thin films at different temperatures

	0.5 M ZnO					1.0 M ZnO				
	Temperature (K)					Temperature (K)				
	10	80	160	240	320	10	80	160	240	320
E_g (eV)	3.325	3.325	3.312	3.294	3.275	3.322	3.322	3.312	3.288	3.267
Steepness parameter	0.065	0.513	0.938	1.437	1.312	0.017	0.132	0.275	0.412	0.352

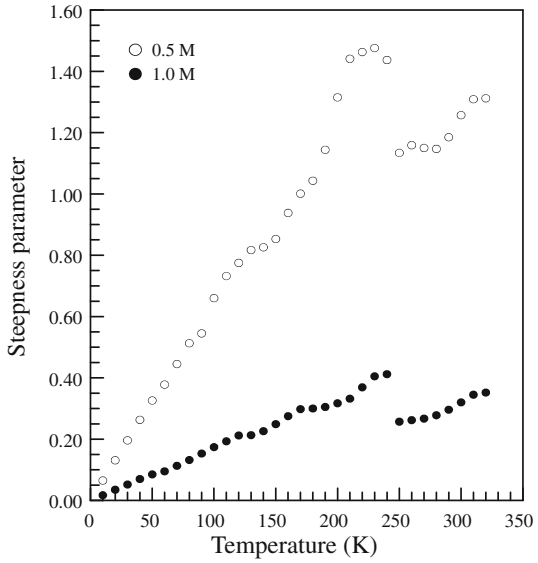

Fig. 6 The steepness parameters versus temperature for 0.5 and 1.0 M ZnO thin films

steepness parameters were converged at (E_0, α_0)=3.65 eV, 172,819 cm^{-1} and 3.70 eV, 653,436 cm^{-1} for 0.5 and 1.0 M ZnO thin films, respectively. These results show that absorption spectra of all samples obey steepness parameters. All of the points, in Fig. 5, intersect the same (E_0, α_0) point. Figure 6 shows steepness parameters (σ) of both ZnO thin films as a function of temperature. Steepness parameters for both 0.5 M ZnO and 1.0 M ZnO increase with increasing sample temperature in the range 10–220 K, decrease in the range of 220–250 K and again increase after 250 K. These parameters are given in the Table 1 for different temperatures.

In conclusion, structural, optical absorption and steepness parameter in ZnO thin films grown by sol-gel method are performed. The results of the XRD peaks around 33.70 degree indicate that ZnO is highly oriented to the *c*-axis perpendicular to the substrate. The band gap energy and the steepness parameter are calculated from the spectral dependence of the coefficient of absorption in the temperature range of 10–320 K. The steepness parameters of both ZnO thin films increased with increasing sample temperature in the range 10–220 K, decreased in the range of 220–250 K and again increased after 250 K.

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