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Effect of Sn dopants on the optical and electrical properties of ZnO films

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The undoped and tin (Sn) doped ZnO films were deposited by a spray pyrolysis method onto the glass substrates. 0.2 M solution of zinc acetate in a mixture of ethanol and deionised water, in a volume proportion of 3 : 1, was employed. Dopant source was tin chloride. The atomic percentage of dopant in solution were Sn/Zn = 1%, 3% and 5%. The effect of tin doping on the optical and electrical properties of ZnO films was studied. The optical transmittance was about 76% in a visible range for Sn-doped ZnO films. The optical band gaps of the films were calculated. This suggests that the absorption edge shifts to the lower wavelengths with Sn dopant. Optical constants of the films were determined. These parameters changed with Sn dopant.

Keywords: ZnO film, optical band gap, optical constant, figure of merit.

1. Introduction

Transparent conducting oxide (TCO) thin films have been extensively investigated since they constitute a major stage of the production of electronic devices both on rigid and flexible substrates. Zinc oxide (ZnO) is a direct bandgap semiconductor having an energy gap of 3.37 eV at room temperature with high exciton binding energy (60 meV). ZnO thin film has been extensively studied because of its potential applications in various fields, for example: solar cells [1], liquid crystal displays, heat mirrors and multilayer photothermal conversion systems [2]. Many techniques have been used to deposit ZnO films on different substrates, including sol–gel processes [3], spray pyrolysis method [4], pulsed laser deposition [5], molecular beam epitaxy [6], and sputtering [7]. Spray pyrolysis, among these methods, is an excellent method for the deposition of thin films of metallic oxides. The ZnO doping is achieved by replacing Zn^{2+} atoms with atoms of elements of higher valance, such as In^{3+}, Al^{3+}, Sn^{4+}, Pb^{4+} [8]. Doping of ZnO thin films with In, Al, Sn, Pb, Ga, and Ge has been reported to improve their electrical and optical properties [9]. In this work, undoped and Sn-doped ZnO (SZO) films have been prepared by using the spray pyrolysis method. The effects of Sn doping on the electrical and optical properties of ZnO films have been reported.

2. Experiment

ZnO and SZO films have been deposited onto the glass substrates at 450 °C substrate temperature. 0.2 M solution of zinc acetate dihydrate diluted in methanol and deionized water (3 : 1) was used for all the films and tin chloride was added to starting solution as a dopant. A few drops of acetic acid were added to improve the clarity of solution. The Sn/Zn ratio was 1% (SZO1), 3% (SZO3) and 5% (SZO5). The starting solution was mixed thoroughly and final solution was sprayed. The nozzle–substrate separation used was of 30 cm. During the spraying process, the substrates were heated electrically by a copper plate. The flow of the solution was 4 ml/min and gaseous nitrogen was used as a carrier gas. Substrate temperature was controlled by means of iron-constantan thermocouple. The thicknesses of the films were determined with Mettler Toledo MX5 microbalance by using a weighing method and found to be approximately 600 nm. Optical transmittance measurements were recorded with a double beam Shimadzu UV 2450 spectrophotometer with an integrating sphere in the wavelength range 190–900 nm. The films were found to be *n*-type by using a hot--probe method. The electrical measurements were carried out using the Van der Pauw configuration and silver paste for the contacts in dark and under a light which has a wavelength of 254 nm. These films were illuminated by a 100 W UV-lamp.

3. Results and discussion

3.1. Optical properties of ZnO and SZO films

The spectral distribution of T and R measured at nearly normal incidence in the wavelength range 350–800 nm for the films is shown in Fig. 1. It could be noted that at longer wavelengths ($\lambda > 400$ nm), all films become transparent and no light is scattered or absorbed as non-absorbing region (*i.e.*, $R + T = 1$). The inequality

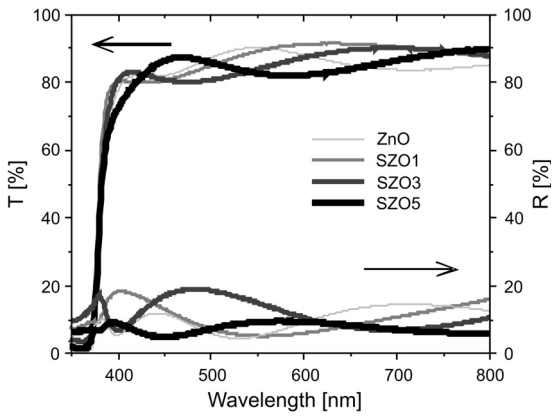

Fig. 1. The transmittance and reflectance spectra of the ZnO and SZO films.

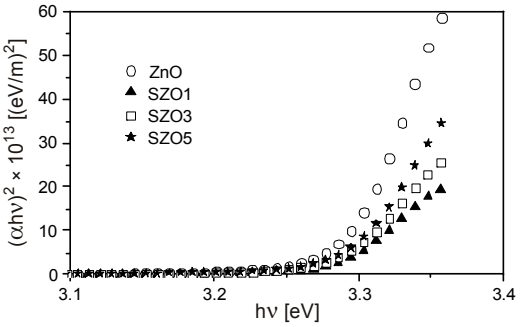

Fig. 2. The plots of $(\alpha h\nu)^2$ vs. photon energy of the ZnO and SZO films.

($R + T < 1$) at shorter wavelengths ($\lambda < 400$ nm) known as absorbing region is due to the existence of absorption. The transmittance is over 76% for the visible region. It can be seen that in the visible region, the transmittance is limited only by the surface reflectance of about 7.5%.

In the direct transition, the absorption coefficient can be expressed by [10],

$$\alpha h\nu = A\left(h\nu - E_g\right)^{1/2} \tag{1}$$

where A is a constant, $h\nu$ is the photon energy and E_g is the optical bandgap. Figure 2 shows plots of $(\alpha h\nu)^2$ versus $h\nu$. These films show that the optical bandgap values are about 3.37, 3.26, 3.25 and 3.18 eV for ZnO, SZO1, SZO3 and SZO5, respectively. The optical band gaps of the films decreased with the Sn concentration. This shift in the optical band gap may be attributed to the band shrinkage effect because of increasing carrier concentration [11]. A similar result was found in different dopant atoms [12].

In the exponential edge region, Urbach rule is expressed as [13]

$$\alpha = \alpha_o \exp\left(h\nu / E_U\right) \tag{2}$$

where α_o is a constant, E_U is the Urbach energy, which characterizes the slope of the exponential edge. Equation (2) describes the optical transition between the occupied states in the valence band tail to the unoccupied states of the conduction band edge. Figure 3 shows Urbach plots of the films. The Urbach energy values of ZnO, SZO1, SZO3 and SZO5 films were calculated to be 0.055, 0.054, 0.058 and 0.058 eV, respectively.

The refractive index is an important parameter for optical materials and applications. Thus, it is important to determine optical constants of the films, and the complex optical refractive indexes of the films are described by the following relation [14]

$$n' = n(\omega) + ik(\omega) \tag{3}$$

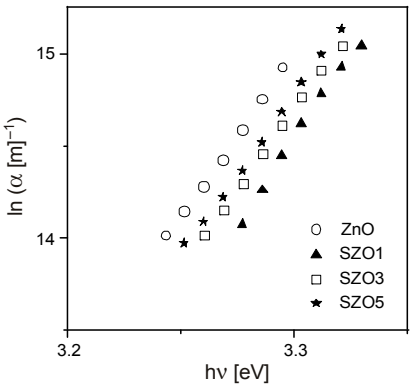

Fig. 3. The Urbach plots of the ZnO and SZO films.

where n is the real part and k is the imaginary part (extinction coefficient) of complex refractive index. The refractive index of the films was determined from the following relation [15]

$$n = \frac{1+R}{1-R} + \sqrt{\frac{4R}{(1-R)^2} - k^2} \tag{4}$$

where $k = \alpha\lambda/4\pi$ is the extinction coefficient. The n and k values dependence on wavelength is shown in Figs. 4**a** and 4**b**, respectively. As seen in Fig. 4**a**, these films show that the average refractive index values are about 1.96, 1.94, 2.04 and 1.76 for ZnO, SZO1, SZO3 and SZO5 films, respectively. The change in the refractive index is a result of the Sn content. As seen in Fig. 4**b**, the extinction coefficient values decrease up to a certain value of wavelength and then, increase.

The fundamental electron excitation spectrum of the film was described by means of a frequency dependence of the complex electronic dielectric constant. The real and imaginary parts of the dielectric constant are related to the n and k values. The ε_1 and ε_2 values were calculated using the formulas [16]

$$\varepsilon_1(\omega) = n^2(\omega) - k^2(\omega) \tag{5}$$

$$\varepsilon_2(\omega) = 2n(\omega)k(\omega) \tag{6}$$

The ε_1 and ε_2 values dependence on wavelength is respectively shown in Figs. 5**a** and 5**b**. As seen in these figures, the ε_1 values are higher than ε_2 values.

3.2. Electrical conductivity of ZnO and SzO films

Physical properties of chemically sprayed ZnO films can be modulated mainly by *i*) the substrate temperature, *ii*) the nature of the dopant, *iii*) the amount of absorbed oxygen that appears during the deposition process, and *iv*) the annealing process in controlled environments [17]. In this respect, in order to improve and control

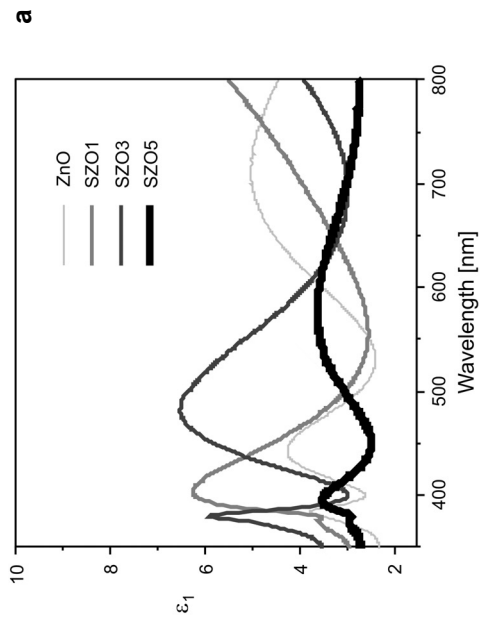

Fig. 5. The variation of real parts (**a**) and imaginary parts (**b**) of dielectric constant of the ZnO and SZO films with wavelength.

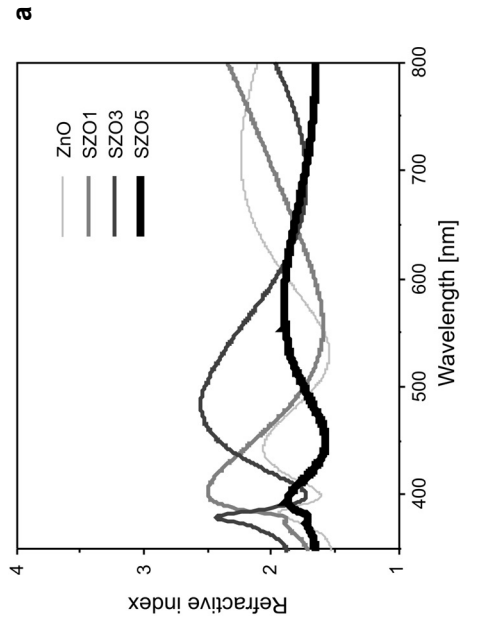

Fig. 4. The variation of refractive index (**a**) and extinction coefficient (**b**) of the ZnO and SZO films with wavelength.

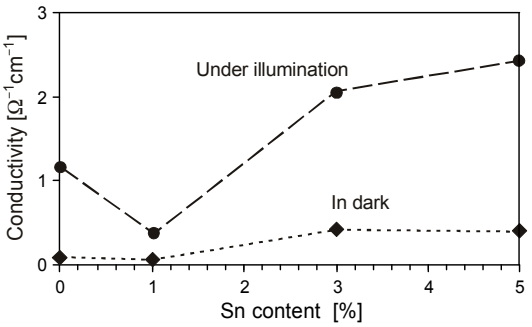

Fig. 6. The variation of conductivity of the ZnO and SZO films with dopant.

the electrical properties of *n*-type ZnO films, they have been doped with different kinds of impurities. The incorporation of these impurities into the ZnO lattice can increase the electrical conductivity.

The electrical properties of the ZnO and SZO films were investigated by using Van der Pauw method. The variation of conductivity depending on the Sn content is shown in Fig. 6 in both dark and illumination. In the dark measurements, the conductivity increases slightly depending on the Sn doping [18]. This increase in conductivity is related to the improvement of crystallinity [19]. But in the illumination, the conductivity decreases at first doping ratio and then it increases with doping content. This result shows that the ZnO and SZO films are sensitive to the UV light.

3.3. Figure of merit for ZnO and SZO films

For applications as transparent contacts, the films must have a low resistivity and a low absorption coefficient in the visible region. A way for evaluating this compromise is by means of the figure of merit (FOM) [20], defined as:

$$\text{FOM} \equiv \frac{1}{\alpha\rho} \tag{7}$$

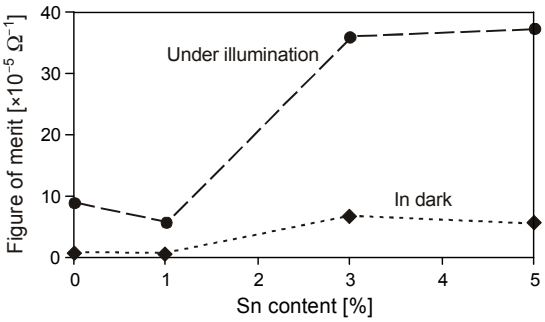

Fig. 7. Variation of figure of merit with the dopant concentration.

where α and ρ are the visible absorption coefficient and the electrical resistivity, respectively. As the visible absorption coefficients of all the films were similar, the figure of merit was strongly dependent on electrical resistivity. As shown in Fig. 7, the variation of FOM shows the same trend with that of electrical conductivity, due to the variation observed in the electro-optical properties of ZnO films. The highest figure of merit value under illumination was $37.2\times10^{-5}\ \Omega^{-1}$, which was obtained for the SZO5 film. This result is in good agreement with literature [21].

4. Conclusions

The undoped and Sn-doped ZnO films were produced by the spray pyrolysis method. The optical and electrical properties of these films have been investigated. The average optical transmittance, optical band gaps, Urbach energy and optical constants (refractive index, extinction coefficient and dielectric constants) values of the films were calculated. The conductivity and figure of merit values of the films were calculated. The SZO5 film has the highest conductivity and figure of merit values under illumination.

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