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Some physical properties of ZnO thin films prepared by thermal oxidation of metallic Zn

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In this paper, ZnO films were prepared by oxidizing the Zn film deposited by electron beam evaporation on glass substrates. The oxidation process was carried out at three-step of annealing process. At first step, the Zn films were annealed at temperature of 300 ^{0}C for one hour to form ZnO layers on the surface of the Zn films to prevent the diffusion of the metallic Zn from the films during the high-temperature. At second step, the produced films from the first step were annealed at high temperature of 500 ^{o}C for one hour. Finally, the time of oxidation increased from 60 min to 220 min in order to achieve fully oxidized films. The effect of oxidation time on structure, optical and electrical properties of ZnO films were studied. It was found that the films annealed at 300 ^{o}C are opaque and the films annealed at 500 ^{o}C and time 200 min have maximum transmittance of 89% at λ= 600 nm and their corresponding direct optical energy gap are 3.34 eV. The films that heated at low oxidation time represent low relatively resistivity and with increasing the oxidation time these films became more resistive.

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1. Introduction

Zinc oxide (ZnO) which is one of the most important binary II–VI semiconductor compounds has a hexagonal wurtzite structure and a natural n-type electrical conductivity with a direct energy wide band gap of 3.3 eV at room temperature [1]. The resistivity values of ZnO films may be adjusted between 10^{-4} Ω cm and 10^{12} Ω cm by changing the annealing conditions and doping [2]. These features have made ZnO applied in various applications such as transparent conductive film and window materials in solar cell applications due to its high optical transmittance in the visible light region [2,3], gas sensor [4]. Furthermore, ZnO materials have attracted much more interest in the application of optoelectronic devices such as light-emitting diodes (LED), laser diodes, piezoelectric transducer, transistors, bulk acoustic wave devices (SAW), acoustic–optical devices and phosphors [5]. ZnO materials have been prepared by various growth methods such as molecule beam epitaxy (MBE) [6], radio frequency (RF) magnetron sputtering [7], pulsed laser deposition (PLD) [8], metal organic chemical vapor deposition (MOCVD) [9], sol gel technique [10] and chemical vapour transport (CVT) [11].

In this paper, the experimental results regarding some structural, electrical and optical properties of ZnO thin films prepared by thermal oxidation of metallic Zn thin films deposited by electron beam evaporation technique are presented. Such a method is a relatively simple and low-cost procedure that does not require any catalyst or higher-temperature growth.

2. Experimental details

A high purity grains (99.999 %) from metallic Zn was used to prepare the Zn thin films. The deposition process characterized by Edward's high vacuum coating unit model E306A was employed to deposit Zn onto ultrasonically clean glass substrates by electron beam evaporation technique. The deposited samples have been obtained under the conditions: (1) vacuum of 3×10^{-5} Torr; (2) current of 10-15 mA; (3) acceleration voltage of 2.5 kV; and (4) deposition rate of 10-15 nm/min. The film thickness (170 nm) and deposition rate were controlled by means of a digital film thickness monitor model TM200 Maxtek. The oxidation process of Zn films was carried out in a fully controlled furnace in air at three-step of annealing process. At first step, the Zn films were annealed at temperature of 300 ^{0}C for one hour. At the second step, the previous films were annealed at temperature of 500 ^{o}C for one hour. Finally, the films that prepared at the second step were heated at various time values from 60 to 220 min at fixed temperature of 500 ^{o}C. The optical measurements (transmittance and reflectance) of Zn and ZnO thin films have been measured by means of a computer-programmable Jasco V-570 (Japan) double beam spectrophotometer in the wavelength range from 200 to 2500 nm at normal incidence with a scan speed of 1000 nm/min. In the case of reflectivity measurement, an additional attachment model ISN - 470 was provided. From the above parameters (transmittance and reflectance) another parameters can be estimated such as the optical energy gap, refractive index, extinction coefficient, dielectric constants, etc. Measurements of film resistance at room temperature were performed by means of a digital

Keithley 614 electrometer using two-probe technique. Electrical contacts were made by applying silver paste over the surface of the films with a separation of 3 mm. Investigations of the microstructure were carried out using a Phillips PW-1710 Cu-k_α diffractometer (λ = 1.541 838 ˚A) by varying the diffraction angle 2θ from 4 to 70 by a step width of 0.04 in order to evaluate the crystalline phase and crystallite orientation.

3. Results and discussion

Fig. 1 shows the X-ray diffraction (XRD) patterns of Zn films and ZnO films produced by the oxidation of metallic Zn films at various values of temperature and time of annealing. In case of the as-grown Zn, the XRD peaks corresponding to Zn (0 0 2), (1 0 0), and (1 0 1) planes, which are located at 36.32, 39, and 43.23, respectively, indicate that the Zn films have not evident growth orientation. When Zn films oxidized at 300 ^{o}C, ZnO (002) and (100) peaks appeared at 2θ= 34.44 and 31.8 in addition to the existing Zn peaks. As the oxidation temperature was increased to 500 ^{o}C, the intensity of the above ZnO peaks increased and the intensity of the above Zn peaks decreased. When the temperature was fixed at 500 ^{o}C and annealing time increased to 200 min, the Zn peaks completely disappeared and only ZnO peaks were observed, indicating that the Zn were fully oxidized and transformed to ZnO.

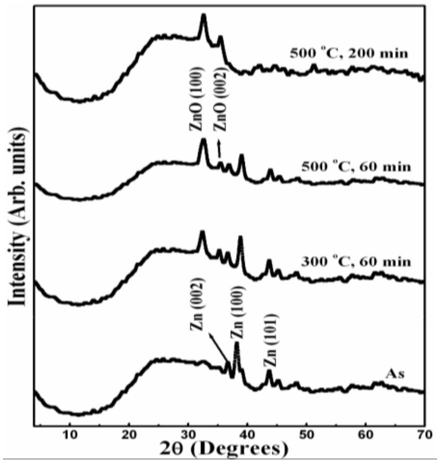

Fig. 1. Fig. 1. XRD patterns of the as-grown Zn and the formed ZnO thin films at different oxidation temperatures and times.

In Fig. 2, the transmission spectra for Zn films that oxidized at 500 ^{o}C for various oxidation times ranged from 60 to 220 min are plotted. As seen, this figure dose not includes the spectra of as deposited films and the films that annealed at 300 ^{o}C where their transmission spectra are close to zero confirming the metallic behaviour of as-deposited and films that heated at low temperature. The Zn films start to oxidize at temperature of 500 ^{o}C for one hour where the transmission spectra can be observed. As may be observed, the increase of the heating time leads to increase the degree of oxidation and hence increasing the transmission. At heating time of 200 min, the films are totally oxidized therefore the transmission records a maximum value of about 9o % in the visible region of spectra. Fig. 3 shows the reflection spectra of as-deposited Zn films and these films treated by three-step annealing process. It is clear that as-deposited films and the films heated at 300 ^{o}C represent high reflection particular at NIR region. According to the classic Drude model [12] correlates between the reflectance R in NIR region and the vibration plasma determined by the carrier concentration. Thus, we can explain the increase of the NIR reflectance of as-deposited and annealed films at 300 ^{o}C in terms of the increase of the free carrier concentrations.

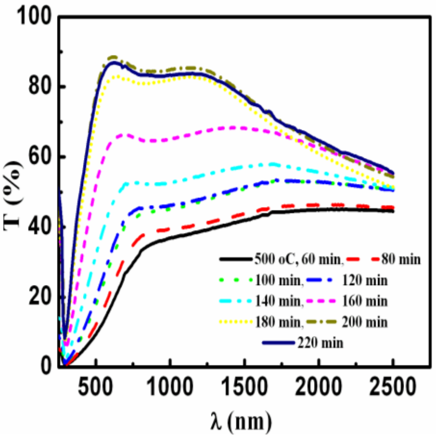

Fig. 2. Transmission spectra (T) of produced ZnO thin films at oxidation temperature 500 ^{o}C and different values of oxidation time.

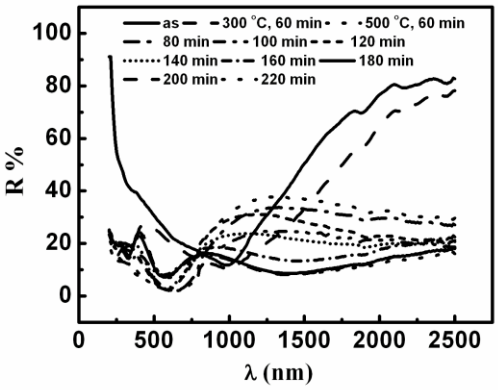

Fig. 3. Reflection spectra R(%)of the as-grown Zn and produced ZnO thin films at different values of oxidation temperature and time.

Fig. 4 shows the absorbance spectra of ZnO samples obtained by oxidized metallic zinc at temperature 500 ^{o}C and various values of annealing time. It is clear that, the absorbance at wavelength higher than 650 nm is low and its value decreased with increasing the annealing time. The films annealed at 500 ^{o}C and time 220 min show lower absorption at lower wavelength. In addition, difference in absorbance can be observed clearly at wavelength shorter than 650 nm. These results show that the produced ZnO materials could be used in photovoltaic applications due to the sharp increase of absorbance in strong absorption region [13].

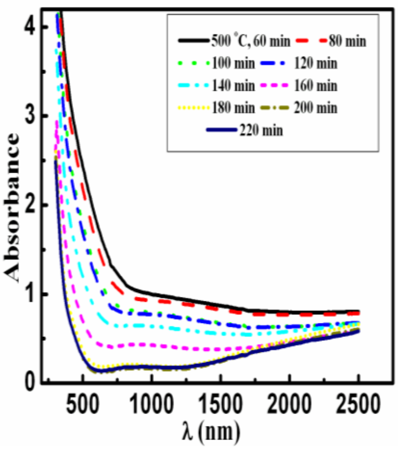

Fig. 4. Absorbance spectra of produced ZnO thin films at oxidation temperature 500 ^oC and different values of oxidation time.

The direct optical band gap, E_g, of the ZnO thin films was determined by extrapolation of the linear portion of α^2 versus $h\nu$ plots using the flowing equation [14]

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

where α is absorption coefficient, $h\nu$ is the photon energy, E_g the optical band-gap energy and A is a constant, depending on the electron–hole mobility, having a value between 10^5 cm^{-1} and 10^6 cm^{-1}. The $\alpha h\nu$ versus $h\nu$ plots for ZnO films annealed at various oxidation times are shown in Fig. 5. It can be seen that, with increasing the thermal oxidation time from 60 to 220 min, the direct optical energy gap increase. The fully oxidized films have direct optical gap of 3.34 eV which is very close to the band gap of intrinsic ZnO powder [9] and are in good agreement with the literature reports [15,16].

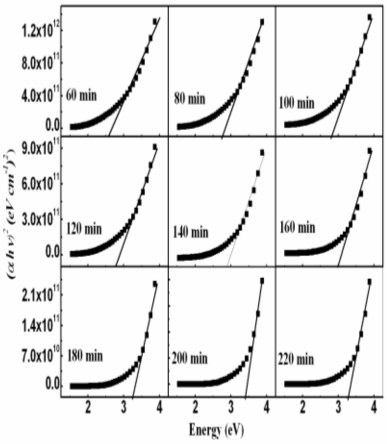

Fig. 5. Graph of $(\alpha h\nu)^2$ versus photon energy of ZnO thin films at oxidation temperature 500 ^oC and different values of oxidation time.

Refractive indexes of the ZnO thin films produced at various values of thermal oxidation time were calculated using the following equation [17]

$$\frac{n^2-1}{n^2+1} = 1 - \sqrt{\frac{E_g}{20}} \tag{2}$$

where n is the refractive index of the ZnO thin films and E_g is the band gap energies of the produced ZnO thin films. As shown in Fig. 6, the refractive index of the ZnO transparent thin film changes from 2.54 to 2.32 due to increasing band energies. These refractive index values are in good agreement with experimental data given in ref [18]. Besides, using Taus model [19], the variation of refractive index with wavelength was calculated using the equations:

$$n = \frac{1+R}{1-R} \pm \left[\left(\frac{R+1}{R-1}\right)^2 - \left(1+k^2\right)\right]^{1/2} \tag{3}$$

$$K = \frac{2.303\,\lambda}{4\pi\ \ d}\log_{10}\left(\frac{1-R}{T}\right) \tag{4}$$

where T is the transmittance, R is the reflection, k is the extinction coefficient and d is the film thickness. Fig. 7 shows the variation of refractive index (n) and extinction coefficient (k) with wavelength in the visible region of totally oxidizing Zn films (500 ^oC, 200 min). It is noted that, both n and k follow the same trend. Where they decrease with increasing wavelength up to λ = 600 nm and then they start to increase with further increase in wavelength. This behaviour of variation of n and k with wavelength was observed by Caglar et al [20]. In addition, the average refractive index calculated by Taus model is 2.2 while the calculated by equation (2) is 2.3.

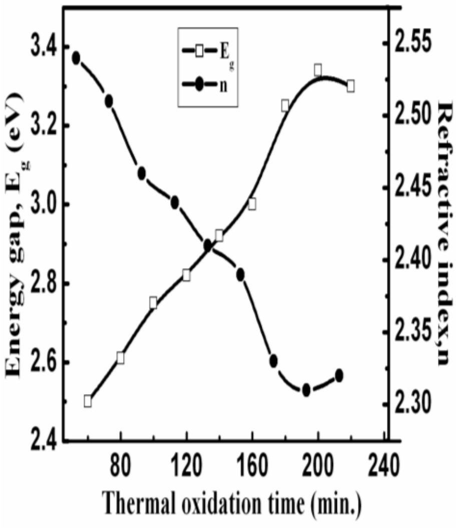

Fig. 6. Dependence of the refractive index (n) and energy gap (E_g) on the oxidation time of ZnO films prepared at oxidation temperature 500 ^oC.

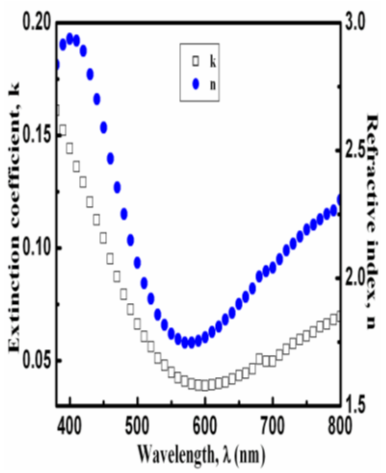

Fig. 7. Variations of the refractive index (n) and extinction coefficient (k) with the wavelength of ZnO films formed at oxidation temperature 500 °C and time 200 min.

The fundamental electron excitation spectrum of the film is described by means of a frequency dependence of the complex electronic dielectric constant. The dielectric constant is defined as, $\varepsilon(\omega) = \varepsilon_1(\omega) + i\,\varepsilon_2(\omega)$ and real (ε_1) and imaginary (ε_2) 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 [21],

$$\varepsilon_1 = n^2 - k^2, \qquad \varepsilon_2 = 2nk \tag{5}$$

Fig. 8 shows ε_1 and ε_2 values dependence of wavelength (photon energy) of totally oxidizing Zn films (500 °C, 200 min). It can be seen that, the real and imaginary parts of dielectric constant decrease with increasing wavelength in the visible region up to certain wavelength (λ = 600 nm) and then they increase with further increase in wavelength. The values of real part are higher than imaginary part of dielectric constant.

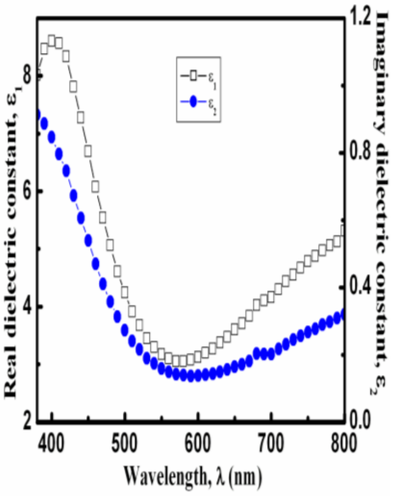

Fig. 8. Variations of the real (ε_1)and imaginary (ε_2)dielectric constant with the wavelength of ZnO films formed at oxidation temperature 500 °C and time 200 min.

The volume energy loss (VELF) and the surface energy loss (SELF) functions are considered quantities of interest in studying the rate of energy loss for electrons passing through a material. They are relate to the real and imaginary parts of the dielectric constant by the following relations [22, 23]:

$$VELF = \frac{\varepsilon_2^2}{\varepsilon_1^2 - \varepsilon_2^2}, \tag{6}$$

Fig. 9 shows the variation of VELF and SELF with the photon energy of fully oxidized Zn films that annealed at 500 °C and 200 min. From this figure, it is clear that the energy loss by the free charge carriers when traversing through the bulk material has approximately the same behaviour as when they traverse the surface. It is also clear that there is no significant difference between them particularly at higher photon energies but the VELF increases more than SELF at photon energy 3.5-4 eV. The same behaviour was obtained by Ziabari and Ghodsi [24] for CdO-ZnO films and by El-Nahass et al [22] for CoPc films.

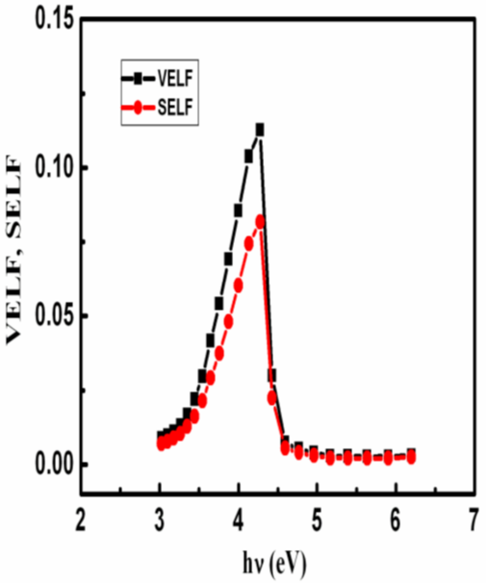

Fig. 9. Plots of VELF and SELF versus hν of ZnO films produced at oxidation temperature 500 °C and time 200 min.

The thermal oxidation time dependence of the electrical resistivity of the ZnO films measured at annealing temperature 500 °C is shown in Fig. 10. It is seen that, up to a oxidation time of 160 min, the film resistivity varied in a relatively narrow range. Then, the electrical resistivity begins to increase quickly and the films become more resistive at high time where the measured resistivity is about 10^6 Ω cm. This fact reveals that, beginning with increasing of the oxidation time, some important structural changes take place in the film due to the Zn oxidation. These results confirmed those revealed by the XRD patterns presented in Fig. 1.

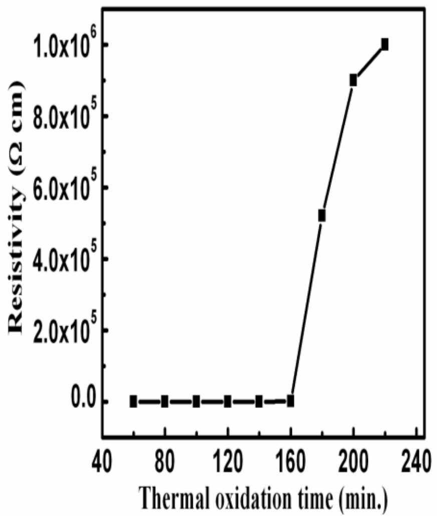

Fig. 10. Plots of electrical resistivity as a function of oxidation time of ZnO films prepared at oxidation temperature 500 °C.

4. Conclusions

Polycrystalline ZnO thin films have been prepared on glass substrates by oxidation of metallic Zn at various values of oxidation temperature and time. Zn films start to transform to ZnO at temperature of 500 °C and time of 60 min, and change completely to ZnO at 500 °C and 200 min. The fully oxidized films represent transmission of 89 % in the visible region and direct energy gap of 3.34 eV. With increasing the oxidation time, the formed ZnO films become more resistive and change from metal to semiconductor. Other important optical parameters such as refractive index; extinction coefficient; dielectric constants, and volume and surface energy loss functions of totally oxidized Zn films were estimated and discussed in this work.

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