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Article

Substrate Temperature Effect on Optical property of ZnO Thin Films

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Abstract. The transparent conducting ZnO thin films were deposited on glass substrate by ultrasonic spray technique. The optical, electrical and structural properties of the ZnO thin films were studied as a function of the substrate temperatures in the range of 300 to 400 °C. The as deposited film exhibit a hexagonal structure wurtzite and (101) oriented. The value of grain size G = 28 nm is measured of ZnO film at 350 °C. All the films having high transparency in the visible region, the band gap energy decreased from 3.44 to 3.29 eV with increasing the substrate temperatures from 300 to 400 °C, respectively according to the Burstein-Moss effect (blue shift of E_g). The Urbach energy decreased reaching to minimum at 350 °C; indicating to decrease of the defects. The electrical resistivity of the films at 350 °C is 50 Ω.cm. A systematic study on the influence of the substrate temperatures on the optical, electrical and structural properties of ZnO thin films deposited by ultrasonic spray has been reported.

Keywords: ZnO, thin films, TCO, ultrasonic spray technique.

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1. Introduction

ZnO is one of the most important semiconductor material due to its wide band gap (3.37 eV) and large exciton binding energy (60 meV) at room temperature [1]. Transparent conducting oxides (TCO) are widely used in microelectronic devices, light emitting diodes, thin film, antireflection coatings for transparent electrodes in solar cells, gas sensors in surface acoustic [2–5].

ZnO thin films can be produced by several techniques such as reactive evaporation and thermal annealing [6], molecular beam epitaxy (MBE) [7], magnetron sputtered technique[8], pulsed laser deposition (PLD) [9], the low-temperature solution method [10], the sol-gel technique, chemical vapor deposition, electrochemical deposition [11] and spray pyrolysis [12], have been reported to prepare thin films of ZnO. Among these, we will focus more particularly in this paper on the ultrasonic spray technique that is a low cost method suitable for large-scale production, it has several advantages in producing nanocrystalline thin films, such as, relatively homogeneous composition, a simple and deposition on glass substrate because of the low substrate temperatures involved, easy control of film thickness and fine and porous microstructure [13]. It is possible to alter the mechanical, electrical, optical and magnetic properties of ZnO nanostructures. There are still many factors affecting the physical properties of ZnO thin films. These factors include ZnO sol concentration [14], substrate temperature [15], preheating temperature [16], post-annealing temperature [17], annealing atmosphere [18] and film thickness [19]. Among these factors, the influence of substrate temperature on structural and optical properties of ZnO thin films (especially undoped ZnO thin films) deposited by ultrasonic spray method was less studied. The choice of temperature in range between 300 and 400 °C is important study with deposition the thin films on glass substrate.

In this paper, the undoped ZnO thin films were deposited on glass substrate using ultrasonic spray technique. We have studied the effect of substrate temperature on optical, electrical and structural properties of ZnO films. General study on the effect of substrate temperature from 300 to 400 °C were studied as in others paper [20], around 350 °C. The main goal for this research is to find optimum information on temperature which gives highly semiconducting properties of undoped ZnO thin films.

2. Experimental Procedure

ZnO solution were prepared by dissolving 0.1M ($Zn(CH_3COO)_2$, $2H_2O$) in the solvent containing equal volumes absolute methanol solution (99.95%) purity, then have added a few drops of concentrated HCl solution as a stabilized, the mixture solution was stirred at 30 °C for 4 h to yield a clear and transparency solution. The substrate was R217102 glass in a size of 1×1 cm^2 $\times$ 0.1 cm, prior to pumping; the substrates were cleaned with alcohol in an ultrasonic bath and blow-dried with dry nitrogen gas.

The resulting solutions were sprayed on the heated glass substrates by ultrasonic nebulizer system (Sonics) which transforms the liquid to a stream formed with uniform and fine droplets of 40 μm average diameter (given by the manufacturer). The deposition was performed at different substrate temperatures was 300, 350 and 400 °C with 2 min of deposition time [21].

Crystallographic and phase structures of the thin films were determined by X-ray diffraction (XRD, Bruker AXS-8D) with CuKα radiation (λ = 0.1541 nm) in the scanning range of (2θ) was between 30° and 60°. The optical transmittance of the deposited films was measured in the range of 300–900 nm by using an ultraviolet-visible spectrophotometer (SHUMATZU 1800), whereas the electrical conductivity of the films and Urbach energy (E_u), which is related to the disorder in the film network, were measured in a coplanar structure obtained with evaporation of four golden stripes on the deposited film surface; the measurements were performed with keithley Model 2400 Low Voltage Source Meter instrument. All transmittance spectra T(λ) and electrical measurements are carry out at room temperature (RT) in air.

3. Results and Discussion

Figure 1 shows the transmission of ZnO films deposited at three different substrate temperatures. As can be seen, an increase in the substrate temperature from 300 to 350 °C improves the films optical transmission. It passes from 50 to 90 % at the wavelength between 400 –800 nm corresponding to (1.55-3.1 eV). The latter is a region of strong transparency. However, the range occurs between 3.25–3.40 eV is the region of the absorption in the layers due to the transition between the valence band and the conduction band [20], as shown in Fig. 2, in this region the transmission decreased because of the onset fundamental absorption. In addition, difference in absorbance can be observed clearly at wavelength shorter than 400 nm. One can note that the substrate temperature effect is clearly observed in the layer quality such as in the average between 370-390 nm; blue shift of the absorption edge was observed as function of substrate temperature until 400 °C revealing Burstein-Moss effect [22] as it mentioned in the inset of Fig. 1, which indicates that the increasing of doping amount can change the lattice structure. We are noting that the temperature effect is clearly observed in the layer quality. These results show that the produced ZnO thin films could be used in solar cells due to the low absorbance in the visible region [15, 21].

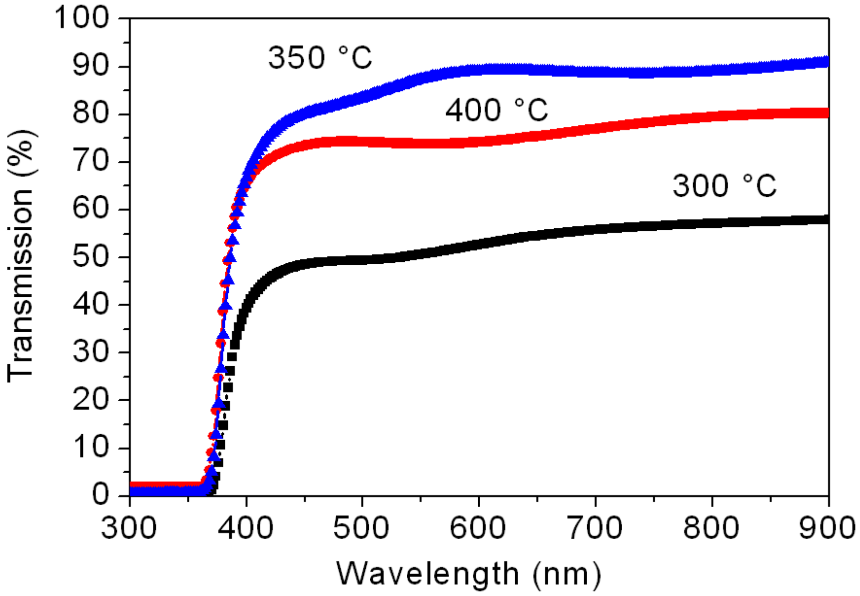

Fig. 1. Transmission spectra of ZnO samples at different substrate temperatures.

In order to investigate the effect substrate temperatures on ZnO films further, the optical band gap energy E_g was measured from the transmission spectra using the following relations [23]:

$$(Ah\nu) = B(h\nu - E_g)^n \tag{1}$$

where A is the absorbance, B is a constant, $h\nu$ is the photon energy, E_g the band gap energy of the semiconductor and n can have values 1/2, 3/2, 2 and 3 depending up on the mode of inter band transition, i.e. direct allowed, direct forbidden, indirect allowed and indirect forbidden transition respectively. For n = 1/2 the transition data provide the best linear curve in the band edge region, implying the transition is direct in nature. The band gaps of the films have been calculated using Tauc's plot by plotting $(Ah\nu)^2$ versus photon energy $h\nu$ as shown in Fig. 2 and by extrapolating the linear portion of the absorption edge to find the intercept with energy axis of $(Ah\nu)^2 = 0$ on $h\nu$ at higher photon energies indicates that the films are essentially direct transition n-type semiconductors.

Table 1. Optical, structural and electrical characteristics of ZnO thin films obtained at different substrate temperatures.

Ts (°C)	E_g (eV)	E_u (meV)	Grain size
300	3.292	112.84	
350	3.317	98.29	28
400	3.441	100.26	

Besides, we have used the Urbach energy (Table 1), which is related to the disorder in the film network, is expressed as [23]:

$$A = A_0 \exp\left(\frac{h\upsilon}{E_u}\right) \tag{2}$$

where A is the absorbance, A_0 is a constant and E_u is the Urbach energy.

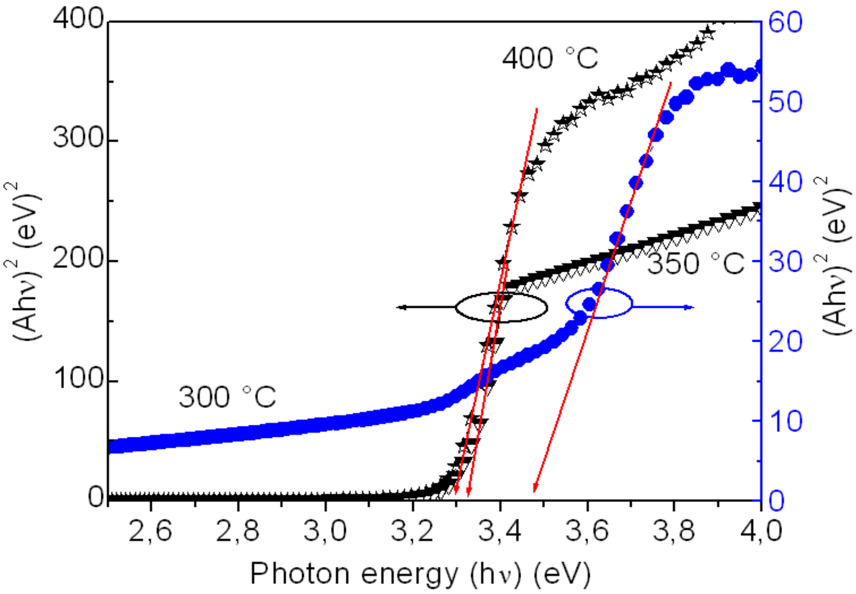

Fig. 2. The typical variation of $(Ah\upsilon)^2$ as a function of photon energy of undoped ZnO film.

As clearly seen in Fig. 3, the variations of both E_g and E_u correlate very well, the optical gap energy decreased with increasing of substrate temperature from 3.44 to 3.29 eV, the band gap is narrowing due to the decrease in the transition tail width and shift effect [15, 21]. Witch explained by increasing in carrier concentration. Generally, defects are accumulated at the grain boundaries. However, our optical band gap results indicate that the Burstein–Moss effect is weak. According to Brustein–Moss effect, raising the Fermi level into the conduction band of a degenerate semiconductor leads to energy band broadening [22]. Therefore the shrinkage effect is dominant over the Burstein–Moss effect, since the E_g values decreases with the increase of substrate temperature.

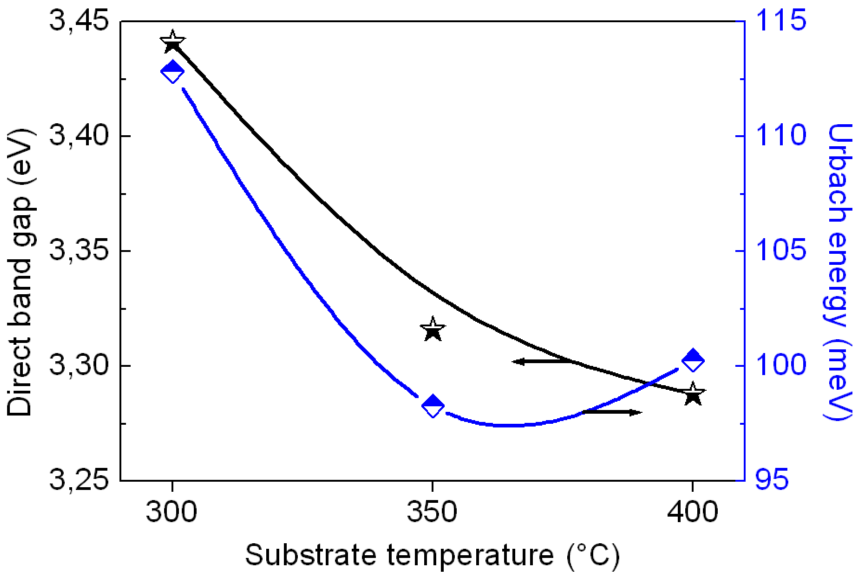

Fig. 3. The variation of optical band gap and Urbach energy of undoped ZnO films with the substrate temperature.

In Fig. 3, it is worth to bear in mind that the Urbach tail energy is closely related to the disorder in the film network. One can see that a minimum Urbach energy was reached at 350°C, which means the adequate temperature for less disorder, which may be attributed to the similar ionic radius between O^{2-} and Zn^{2+}, as it was expressed in the literatures [23–26].

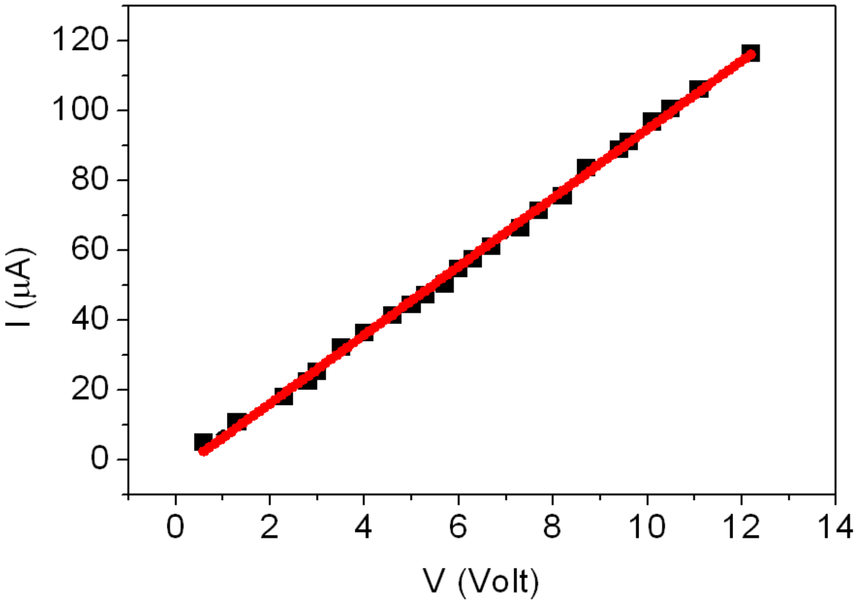

Fig. 4. Variation of I–V characteristic of ZnO thin film deposited at a substrate temperature of 350 °C.

The I–V characteristic of ZnO thin film is shown in Fig. 4, where two diverse types of I–V characteristics are observed. The ZnO film is grown at a substrate temperature of 350 °C; this letter is optimal value was obtained as in others paper [22], we have studied the effect of substrate temperature on physical properties of undoped and Co doped Zno thin films. As can be seen from Fig. 4, the current is small, which is analogous to that of the n-type semiconductor. The curve of I–V is linearly, which the current increase with increasing of tension. The film show low resistivity is suggested to transparent conductive was measured by following formula:

$$\rho = \left(\frac{\pi}{\ln 2} \frac{V}{I} \right) d = R_S d \tag{3}$$

The X-ray diffraction pattern of undoped ZnO thin films is presented in Fig. 5. The thin film was deposited at a substrate temperature of 350 °C, as it can be seen the diffraction peaks were observed at = 31.8°, 34.5°, 36.4°, 47.5° and 56.55° which are related to the following plans (100), (002), (101), (102) and (112) respectively. The obtained XRD spectra matched well with the space group P63mc (186) (No. 36-1451) of the wurtzite ZnO structure [23]. Moreover, single significant (100) diffraction peak, with height intensity, was observed for the ZnO film which indicate that the ZnO film have preferential a-axis orientation perpendicular to the crystallographic plans (100). These results can be explained as it was expressed in the literatures [20, 23, 24, 27].

The average grain size (G = 28 nm) can be calculated from the full width at half maximum (FWHM = 0.29 °) value of the ZnO (100) diffraction peak (θ = 31.81°) using Scherrer's formula [28]:

$$G = \frac{0.9\lambda}{\beta \cos\theta} \tag{4}$$

Where G, λ, β and θ denote the grain size, the X-ray wavelength, FWHM and the Bragg angle of (100) peak, respectively. The observed value of grain size is relatively approach to the value of ZnO thin films (29.71 – 33.28 nm) [20], we have obtained that the crystalline quality of thin films enhanced at a substrate temperature of 350 °C.

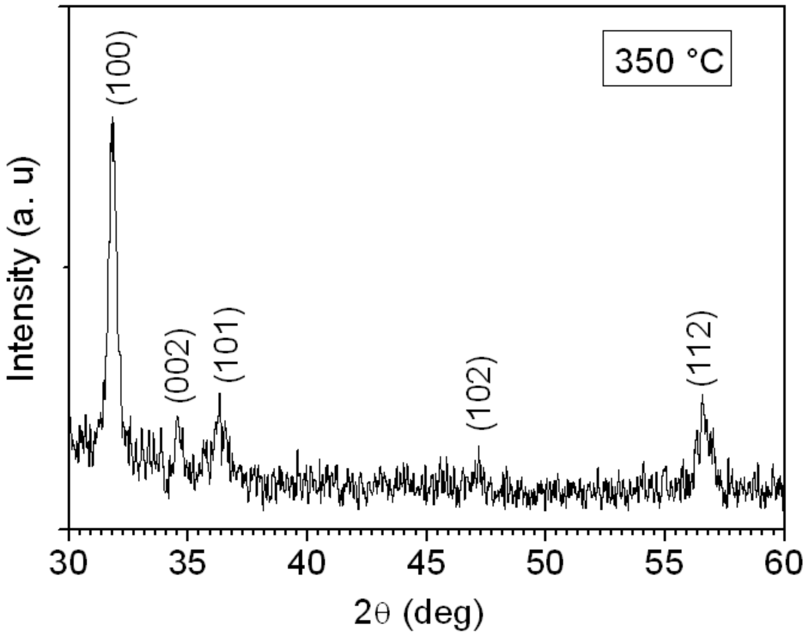

Fig. 5. X-ray diffraction spectra of ZnO thin films deposited on glass substrate at T_s = 350 °C.

4. Conclusion

In conclusion, highly transparent conductive of undoped ZnO thin films have been deposited on glass substrate by Ultrasonic spray at different substrate temperatures between 300 and 400 °C. The optical, electrical and structural properties were investigated, the film is nanoycrystalline structure wurtzite and (100) oriented, thus is favor to the diffusion of atoms absorbed on the substrate. The value of crystallite size G = 28 nm is attained in ZnO film grown at 350 °C. All the films having high transparency in the visible region, the band gap energy decreased from 3.44 to 3.29 eV with increasing in the substrate temperatures from 300 to 400 °C, respectively according to the Burstein-Moss effect (blue shift of E_g). The the Urbach energy decreased reaching to minimum at 350 °C; indicating to decrease of the defects. The electrical resistivity of the films for 350 °C is 50 Ω.cm. A systematic study on the influence of the substrate temperatures on optical, electrical and structural properties of ZnO thin films deposited by ultrasonic spray has been reported.

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