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Effect of Annealing Temperature on Structural, Optical and Electrical Properties of ZnO Thin Films Prepared by Sol-Gel Method

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A transparent semiconductor ZnO thin film was prepared on glass substrates using spin coating sol-gel method. The coated ZnO films were annealed in air for 2 hours at different temperatures of 0, 450, 500, 550 and 600 °C. The films were obtained at a concentration of sol-gel solution is 0.5 M. In present paper, the structural, optical and electrical properties of the ZnO thin films were studied as a function of the annealing temperature. The DRX analyses indicated that the coated ZnO films exhibit an hexagonal structure wurtzite and (002) oriented with the maximum value of crystallite size $G = 69.32$ nm is measured of ZnO film annealed at 600 °C. The crystallinity of the thin films improved at high annealing temperature which was depends too few defects. Spectrophotometer (UV-vis) of a ZnO films deposited at different annealing temperatures shows an average transmittance of about 88 %. The band gap energy decreased after annealing temperature from $E_g = 3.359$ to 3.117 eV for without annealing and annealed films at 450 °C, respectively, than increased at 600 °C to reaching the maximum value 3.251 eV. The minimum value of the sheet resistance R_{sh} of the films is 107635 Ω was obtained for ZnO thin film annealed at 600 °C. The best estimated structure, optical and electrical results are achieved in annealed ZnO film at 600 °C.

Keywords: ZnO, Thin films, Transparent conducting films, Annealing temperature, Spin-coating method.

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1. INTRODUCTION

The transparent conductive oxide (TCO) films have been attracted significant attention in optoelectronic devices. Among these materials, 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, have attracted a large interest because of their high electrical conductivity and good optical transparency due to their interesting applications such as transparent conductive, ferromagnetism, semiconductors, piezoelectric and solar cells, and are widely exploited in various technological applications [1-3]. ZnO has been intensively studied as a promising material for gas sensors because of its wide band gap of 3.37 eV at room temperature, a large exciton binding energy (~ 60 meV) [4].

Nanocrystalline ZnO thin films can be produced by several techniques such as reactive evaporation, molecular beam epitaxy (MBE), magnetron sputtering technique, pulsed laser deposition (PLD), spray pyrolysis, sol-gel process, chemical vapor deposition, and electrochemical deposition [5-7]. Although these, we will focus more particularly in this work on the sol-gel process that is a low method suitable for producing thin, transparent, multi-component oxide layers of many compositions on various substrates, including glass, it has several advantages in producing nanocrystalline thin films, such as, relatively homogeneous composition, a simple and deposition on glass substrate, easy control of film thickness and fine and porous microstructure. There are still many factors affecting the physical properties of ZnO thin films. These factors include ZnO sol concentration, preheating temperature, post annealing temperature, annealing atmosphere, dopant, and film thickness [5-10]. Among these factors, the influence of annealing temperature on structural and optical properties of ZnO thin films (especially undoped ZnO thin films) derived from sol-gel method was less studied. The choice of temperature in range between 450 and 600 °C is important study with deposition the thin films on glass substrate. We observe that the glass substrate was brittle at a temperature higher than 600 °C.

This paper is to present new results of the effect of the annealing temperature on the crystalline structure, optical and electrical properties of ZnO films, ZnO thin films on glass substrate by spin-coating method using homogeneous and stable zinc acetate dihydrate with a concentration of 0.5 M.

2. EXPERIMENTAL DETAILS

2.1 Preparation of Precursor Sol

ZnO solution were prepared by dissolving (0.5 M) zinc acetate dehydrate $Zn(CH_3COO)_2$, H_2O in the solvent containing equal volumes absolute ethanol solution (99.995 %) purity, then have added a drops of monoethanolamine solution as a stabilized, the mixture solution was stirred an heated at 50-70 °C for 4 h to yield a clear and transparency solution. which served as the coating solution after cooling to room temperature. The coating was made one day after the precursor was prepared.

2.2 Deposition of Thin Films

The first sample was prepared by dropping the coating solution onto glass substrate, which was rotated at

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4000 rpm for 40 s by using spin coater. The coating process was repeated for eight times to obtain a thin film. The preheat-treatment temperature of 200 °C is required for the complete evaporation of organics and the initiation of formation and crystallization of the ZnO film. After the deposition of the five layers, the resulting thin films were annealed at 0 °C, 450 °C, 500 °C, 550 °C and 600 °C in air for 2 h.

Table 1 – Bragg angle, the full width at half-maximum FWHM, the grain size, lattice parameter and the strain for (002) plane of ZnO thin films were measured as a function of annealing temperature

Annealing temperature °C	2θ (deg)	β (deg)	G (nm)	c (nm)	ε (%)
450	34.45	–	–	–	–
500	34.46	–	–	–	–
550	34.46	0.13	63.98	0.5201	– 0.493
600	34.52	0.12	69.32	0.5192	– 1.369

2.3 Characterization of Thin Films

The crystal phase and crystalline orientation of the thin films were determined by X-ray diffraction (XRD, Bruker D8 advanced X-ray diffractometer) with Cu Kα radiation ($\lambda = 1.541$ Å), the analysis the samples were scanned from 25° to 55°. A scanning electron microscopy (SEM, JSM-6700F) equipped with EDX was used to examine both morphology and elemental analysis of the samples. The optical transmission spectra of the films were measured in the range of 300-800 nm using a double-beam Lambda 35 UV/visible spectrophotometer. And the electrical conductivity of the films was measured in a coplanar structure obtained with evaporation of four golden stripes on film surface. All spectra were measured at room temperature (RT).

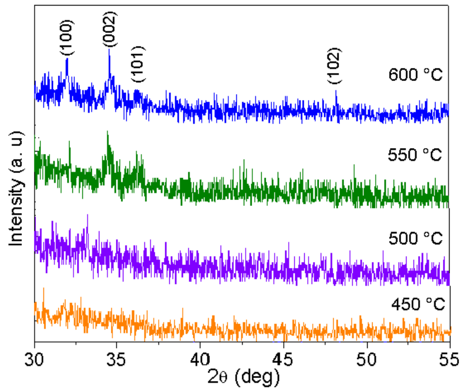

Fig. 3 – The XRD patterns for ZnO thin films as a function of annealing temperature

3. RESULTS AND DISCUSSION

3.1 The Crystalline Structure of ZnO Thin Films

The XRD patterns for ZnO thin films as a function of annealing temperature are shown in Figure 1. The obtained XRD spectra matched well with the space group P63mc (186) (No. 36-1451). There are four peaks that could be observed for the thin films annealed at 550 and 600 °C, it are (100), (002) (101) and (102) planes. Among them the peak at position 34.4° corresponding to the (002) plans is very sharp for 550 and 600 °C. But, can not found any peaks detected for others films. XRD spectra indicate that the films exhibit polycrystalline structure that belongs to the hexagonal wurtzite type of ZnO [11]. The film annealed at 600 °C has higher diffraction peaks indicating an improvement in (002) peak intensity compared to other films, revealing that the films are nanocrystalline and a preferred orientation with the c-axis perpendicular to substrate.

To further investigate the effect of annealing temperature on the ZnO films, the average uniform strain for the lattice along the c-axis in the randomly oriented ZnO films deposited on glass substrate has been estimated from the lattice parameters using the equal below [12]:

$$\varepsilon = \frac{c - c_0}{c_0} \times 100\% , \quad (1)$$

where ε is the mean stress of ZnO thin films, c the lattice constant of ZnO thin films and c_0 the lattice constant of bulk (standard $c_0 = 0, 5206$ nm).

According to the hexagonal symmetry, the lattice constant can be calculated by the following formula [9]:

$$d_{hkl} = \left(\frac{4}{3} \frac{h^2 + hk + k^2}{a^2} + \frac{l^2}{c^2} \right)^{-1/2} , \quad (2)$$

where a, c are the lattice parameters, (h,k,l) are the Miller indices of the planes and d_{hkl} is the interplanar spacing.

In order to attain the detailed structure information, the grains sizes G of (002) planes were calculated according to the Scherer equation [9]:

$$G = \frac{0.9\lambda}{\beta \cos\theta} \quad (3)$$

where G is the crystallite size, λ is the X-ray wavelength ($\lambda = 1.5406$ A), β is the full width at half-maximum (FWHM), and θ is Bragg angle of the diffraction peaks, the variations are shown in Table 1.

The variation of mean strain of (002) peak for the ZnO thin films is presented in Table 1. As can be seen, the measurements values were obtained for annealed ZnO thin films at 550 and 600 °C. The means strain decreases at 600 °C can be explain by the oxygen vacancy in formation of ZnO molecular. The structural properties can be improved at higher temperature than those used which is larger than 600 °C.

The variation of crystallite size of ZnO thin films at annealing temperature of 550 and 600 ° is 63.98 and 39.32 nm (see Table 1). As annealing temperature increases, the crystallite size of ZnO was increased at 600 °C. This result can be explained by coalescence of the crystallite of the thin films to improvement with oxygen diffusion [13].

3.2 The Optical Properties of ZnO Thin Films

The optical transmission of the ZnO thin films were measured as a function of the wavelength is present in Figure 2, it shows the optical transmission spectra of the ZnO thin films deposited at different annealing temperatures. As can be seen, for the longer wavelengths ($\lambda > 400$ nm) all the films become transparent, it is found that all the films show a high optical transmission, around 90 %, in the visible region. The optical absorption at the absorption edge corresponds to the transition from valence band to the conduction band ($\lambda < 400$ nm), while the absorption in the visible region was related to some local energy levels caused by intrinsic defects, As clearly seen in this region found that the transmission decreased because of the onset fundamental absorption in the region between 350-390 nm.

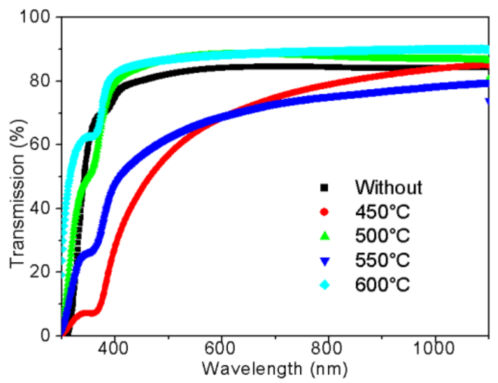

Fig. 2 – Variation of transmittance spectra (T) with wavelength (λ) of ZnO thin film annealed at different temperatures

The optical band gap energy (Table 2) of the ZnO thin films obtained by the following expression [14]

$$A = \alpha d = -\ln T \quad (4)$$

$$(Ah\upsilon)^2 = C(h\upsilon - E_g), \quad (5)$$

where A is the absorbance, d is the film thickness; T is the transmission spectra of thin films; α is the absorption coefficient values; C is a constant, $h\upsilon$ is the photon energy and E_g the band gap energy of the semiconductor. On the other hand, we have used the Urbach energy (E_u), which is related to the disorder in the film network, as it is expressed follow [15]:

$$A = A_0 \exp\left(\frac{h\upsilon}{E_u}\right) \quad (6)$$

where A_0 is a constant $h\upsilon$ is the photon energy and E_u is the Urbach energy, is presented in Table 2.

The graph of $(Ah\upsilon)^2$ versus $h\upsilon$ plots of ZnO films annealed at different annealing temperatures is shown in Figure 3. It can be seen that the extrapolation of linear portion of the graph to the energy axis at $A = 0$ [16] gives band gap energy E_g is shown in Table 2. Besides, Figure 3 shows the graph of LnA versus $h\upsilon$ plots for which used to deduce the Urbach energy [15].

Table 2 – The variation of optical band gap E_g and Urbach energy E_u of ZnO thin films with annealing temperature.

Annealing temperature °C	E_g (eV)	E_u (meV)
Without	3.359	576.52
450	3.117	338.88
500	3.245	263.44
550	3.098	419.63
600	3.251	195.55

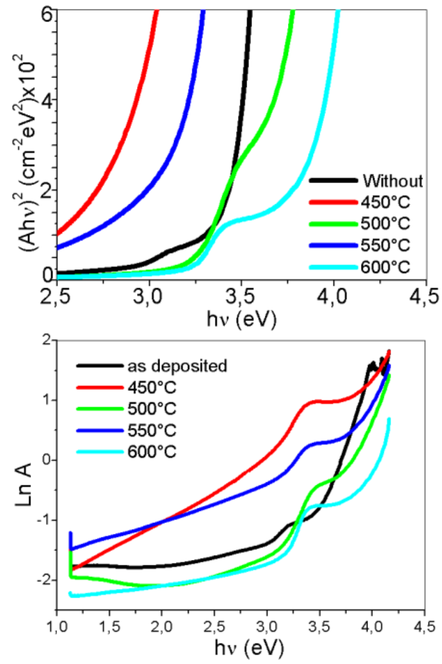

Fig. 3 – Typical variation of $(Ah\upsilon)^2$ and LnA drawn as a function of photon energy $h\upsilon$ used respectively for extrapolation of the band gap energy and Urbach energy determination, respectively

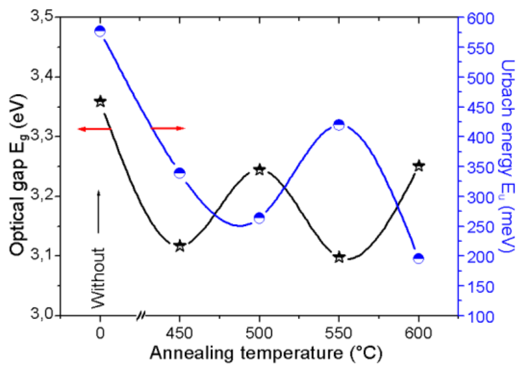

Fig. 4 – The variation of optical band gap E_g and Urbach energy E_u of ZnO thin films with annealing temperature

Figure 4 shows the variation of the band gap energy E_g and the Urbach energy E_u as a function of the annealing temperatures. The optical gap and disorder vary inversely, it is observed that the band gap energy and Urbach energy of ZnO thin films decreased after annealed, this result can be explained by oxygen vacancy, can be found in the evaporated with annealing temperature, which located at 450 and 550 °C. Some extra electrons may be present in the Fermi level which reduces the transparency of the films (see Figure 2). The increases optical gap at 500 and 600 °C can be indicated by oxygen diffusion with annealed. As can be seen in Figure 4, that a minimum Urbach energy were reached with ZnO thin film at 600 °C, which means that this temperature of was adequate for less disorder as it was expressed in the literatures [11, 12, 16]. This can be explained by increasing of the crystallite size.

3.3 The Electrical Conductivity of ZnO Thin Films

The four-point probe is preferred for measurement of sheet resistance (R_{sh}); in the linear four-point probe technique, the current (I) is applied between the outer two leads and the potential difference (V) is measured across the inner two probes [17]. Since negligible contact and spreading resistance are associated with the voltage probes, one can obtain a fairly accurate estimation of R_{sh} using the following relation:

$$R_{sh} = \frac{\pi}{\ln(2)} \frac{V}{I}, \qquad (7)$$

where I is the applied currant and V is the measurement voltage. In the above said configuration, a correction factor of 4.532 was applied for the sample 2 cm × 1 cm with equally spaced (2 cm) probes. Table 3 and Figure 5 give the sheet resistance R_{sh}. The result shows the conductivity of the ZnO thin film decrease as the annealing temperatures. This is due to the decreasing of the strain (less defects) in the films hence the potential barriers decreased and decreases defects (see Figure 4), which resulted in an increased carrier density [12, 18]. The conductivity can be improved by increased in donors, improved crystallinity and decrease the grain boundary scattering [19].

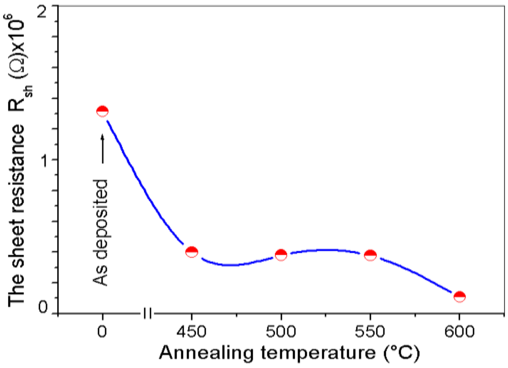

Fig. 5 – Variations the sheet resistance R_{sh} of ZnO thin films annealed at different temperatures

Table 3 – Variations the sheet resistance R_{sh} of ZnO thin films annealed at different temperatures

Annealing temperatures (°C)	R_{sh} (Ω)
Without	1314280
450	399269
500	379101
550	377289
600	107635

4. CONCLUSION

In summary, high-quality transparent ZnO thin films were grown on glass substrates at room temperature by spin coating sol-gel method with 0.5 M; the influence of annealing temperature on structural, optical and electrical properties was investigated. The coated ZnO films were annealed in air for 2 hours at different temperatures of 0, 450, 500, 550 and 600 °C. The whole obtained films have a nanocrystalline wurtzite structure and are mainly (002) oriented. We have observed an improvement in the films crystallinity with increasing annealing temperature up to 600 °C. Which found that the film annealed at 600 ° have a higher crystallite size of the films is 69.32 nm. All films have an average transmittance is about 88 %, in the visible region. The optical gap decreased after annealing temperature from 3.359 to 3.117 eV for without annealing and annealed films at 450 °C, respectively, than increased at 600 °C to reaching the maximum value 3.251 eV. The minimum value of the sheet resistance of the films is 107635 Ω was obtained for ZnO thin film annealed at 600 °C. The best estimated structure, optical and electrical results are achieved in annealed ZnO film at 600 °C.

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