Influence of Thickness and Annealing on Some Physical Properties of Zinc Oxide Films

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Abstract

Zinc oxide transparent conductive films were deposited on glass substrates at 400 °C using chemical spray pyrolysis method. The effect of annealing of ZnO samples with the increase in thickness has been studied. The X-ray diffraction results indicate that the polycrystalline films exhibited a distinguished orientation along (002) direction with a hexagonal wurtzite phase type. It is found that good crystallinity is obtained in the samples annealed at 500 °C. All films showed an average transmittance of about 85% measured by UV/VIS/NIR spectrophotometer. The grain size and lattice parameters of films were computed. The grain size increases as thickness increases. Hence the values of the optical gap energy (Eg) are found to be in the range of 3.238 to 3.273 eV without annealing and in the range of 3.252 to 3.280 eV with annealing when the thickness varies from 355 to 445 nm.

Keywords: Zinc Oxide Film, Strain, Spray pyrolysis, XRD

تأثير السمك والتلدين على بعض الخصائص الفيزيائية لاغشية اوكسيد الزنك

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الخلاصة

حضرت اغشية اوكسيد الزنك شبه الموصلة باستخدام تقنية التحلل الكيميائي الحراري على ركائز الزجاج في محلول مائي على قواعد من الزجاج بدرجة حرارية 400 درجة سيليزية. وقد تم دراسة تأثير التلدين وسمك الاغشية على الخصائص التركيبية والبصرية. بينت نتائج حيود الاشعة السينية أن الاغشية المحضرة متعددة التبلور وتمتلك تر كيبا من النوع السداسي المتراص (Heaxagonal Wurtzite). وجد أن الحصول على تبلور جيد للاغشية المحضرة يكون عند تلدين العينات في 500 درجة سيليزية. أظهرت جميع الاغشية معدل نفاذية حوالي 85٪ حيث تم قياسها بجهاز مقياس طيف الأشعة فوق البنفسجية- المرئية – تحت الحمراء القريبة. تم حساب الحجم الحبيبي وثوابت الشبيكة للاغشية. حيث وجد ان الحجم الحبيبي يزداد مع زيادة السمك. ومن ثم وجد ان قيم فجوة الطاقة البصرية بين 3.238 إلى 3.273 الكترون فولت بدون التلدين ومن 3.252 إلى 3.280 الكترون فولت مع التلدين ولسماكات مختلفة بين 355 إلى 445 نانومتر.

الكلمات المفتاحية: أغشية اوكسيد الزنك، التحلل الكيميائي الحراري، الاجهاد، حيود الاشعة السينية.

Introduction

Zinc oxide has been a widespread topic in semiconductor research for more than 70 years, with references to publications dating back to 1945 [1]. Naturally ZnO is an n-type due to the existence defects originates of substantial donor centers in the ZnO lattice. These carriers are likely producing defect levels that lead to n-type doping lie nearly 0.05 eV below the conduction band [2]. ZnO has a wide band gap (3.37 eV) group II–VI semiconductor with a hexagonal wurtzite structure (a=0.3259 nm, c=0.52079 nm). In particular, ZnO has entice much attention because of its high transparency in the visible range low electrical resistivity and large exciton binding energy (60 meV) as the next generation transparent conductive material [3, 4]. This semiconductor is of interest for UV and visible region optical devices, like laser diodes and light emitting diodes [5], window materials in solar cells [6], flat panel display and gas sensors [7-9]. ZnO is also well-known as a piezoelectric material that has been used in acoustic wave [10] and various optoelectronic devices. ZnO thin films with high electrical conductivity and high optical transmission, nontoxicity, chemical and mechanical stability and low cost because of the high abundance [11]. Various fabrication methods have been vastly used to prepare ZnO thin films. The most intensively studied methods include, the chemical vapor deposition [12], pulsed laser deposition (PLD) [13-15], chemical bath deposition [16], sol-gel method [17-19], metal oxide chemical vapor deposition (MOCVD) [20], and spray pyrolysis technique (CPS) [21, 22]. Among these methods, chemical spray pyrolysis (CSP) is one of the most vastly used techniques because it has several advantages such as, easily controlled over wide range by changing the spray parameters, cheaper and large area fabrication for applications compared with other ways which need complex equipment and accessories with very expensive parts. In present work, effect of annealing temperature at 500 °C and thickness on crystalline structure and optical properties of ZnO thin film fabricated by spray method was investigated.

Experimental

CSP is an efficient technique for the preparation of thin films of metallic oxides, as is the case for the ZnO material. In this preparation method, a starting solution, containing Zn precursors, was sprayed by means of a nozzle, assisted by a carrier gas, over a hot substrate. When the fine droplets arrive at the substrate, the solid compounds react to become a new chemical compound. ZnO thin film was prepared on glass substrate preheated at 400°C using the CSP. A concentration of solution of 0.1 M zinc acetate hydrate (Zn $(CH_3COO)_2$, $2H_2O$) is prepared by analyzing in mixture of distilled water. The nozzle was kept at a space of 29±1 cm from the substrate during prepared films. The solution flow rate was kept constant at 2.5 ml per minute. Air was used as the transporter gas, at the pressure of 1.56 bar. When spray aerosol droplets were near the substrates, a pyrolysis process occurs and highly adhesive ZnO samples were fabricated. Thickness was measured using gravimetric method. The transmittance of the films was measured in the domain of 300-1100 nm at room temperature by using an UV/VIS/NIR analyzer (Shimadzu 1800 double beam spectrophotometer). The structural properties of the thin films were estimated by X ray diffraction system (Lab XRD-6000/Shimadzu) CuKα radiation (λ =1.5406 A°). in the scanning domain of (2θ) was between

10° and 80°. The average crystallites were calculated by the Scherrer's formula from the expanding of the diffraction peaks.

Results and discussion

Structural characterization

Figure. 1 shows the X-ray diffraction patterns of the ZnO films annealing and various film thicknesses. Strongest peaks observed at phases corresponded to (100), (002), (101), (102), (110), (103) and (112) diffraction planes for hexagonal structure of ZnO. Comparable observations have been found by other investigators [23, 24]. In addition, figure. 1 shows the effect of annealing at 500 ◦C on crystal structure, the annealed films have stronger and small width reflection peak showing an enhancement in (100); (002) and (101) peak intensity compared to without annealing. XRD results exhibit that all the samples are multiphase polycrystalline and random growth orientations, this result is due to the difference in the precursor chemistry and annealing temperatures [25]. However, there are several reported oriented along the c-axis ZnO thin films prepared on glass [26, 27]. The lattice constants shown in Table 1 are computed using the following equation [28]:

$$\frac{1}{d^2} = \frac{4(h^2+hk+k^2)}{3a^2} + \frac{l^2}{c^2} \qquad (1)$$

Where c and a are the lattice constants and d_{hkl} is the interplanar spacing.

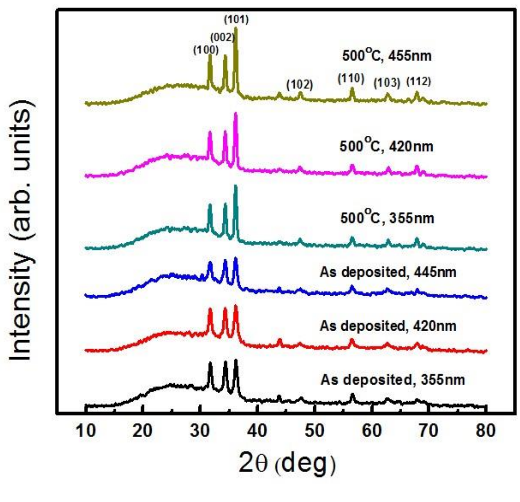

Figure 1: X-ray diffraction patterns of as-deposited and annealed ZnO thin films with different thicknesses

The strain Ɛ values in samples were evaluated using the relation [29]:

$$\varepsilon = \frac{C-Co}{Co} * 100\% \qquad (2)$$

where Ɛ is the mean strain in ZnO thin films (Table 1), *c* is the lattice parameter of ZnO films and C_0 the lattice parameter of bulk (standard C_0 = 0.5206 nm). In thin films, strains are produced fundamentally due to mismatch between the film and the substrate and difference in coefficients of thermal expansion of the film and the substrate. The crystallite size (D) can be presented by the following equation [30]:

$$D = \frac{k\lambda}{\beta\cos\theta} \qquad (3)$$

Where k is about 0.9 and β is the Full Width at Half Maximum (FWHM). Table 1 gives the lattice parameter, particle size and strain (ε) % of the as-deposited and annealed at 500°C ZnO thin films. The resulted 'c' and 'a' are in agreement with the standard values according to the ICDD card no. 75-0576. The average uniform strain (Ɛ), along the c-axis in the film, increases as the thickness increases. The crystalline quality of the film gets better as the film grows thicker. Figure. 2 shows the change of strain at different thicknesses for as prepared and annealed films. In larger thickness the crystallinity becomes better. Figure. 3 shows the increasing the thickness and the heat treatment decrease the FWHM value, showing a better crystallinity of the films. The particle size increases with heat treatment, but decreases with lower thickness, like previous work [31].

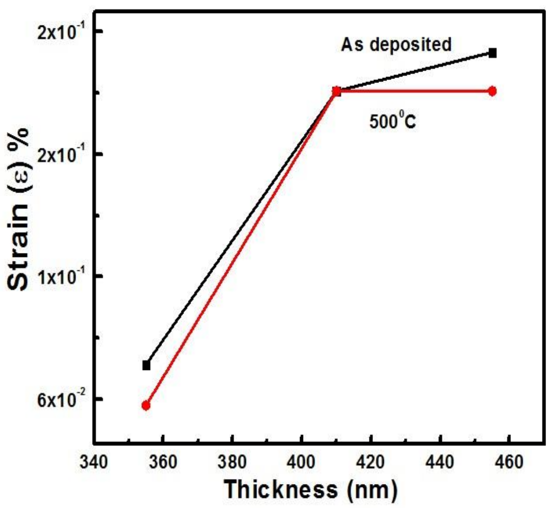

Figure 2: The variation of strain at different thicknesses for as deposited and annealed films.

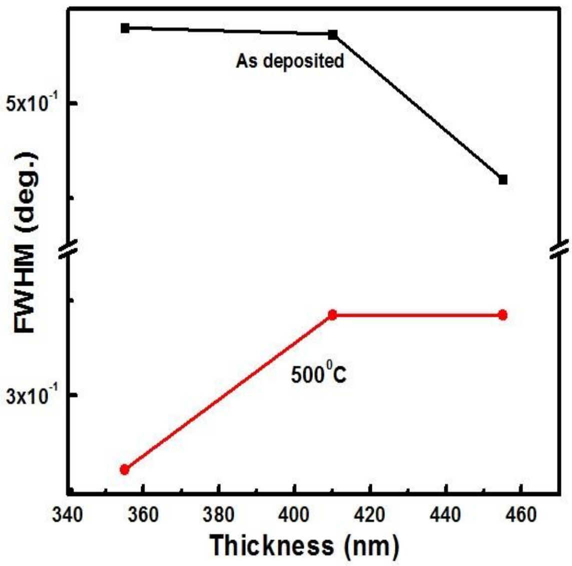

Figure 3: FWHM at different thicknesses for as deposited and annealed samples.

Table1: Lattice parameters, crystallite size and strain (ε) % of ZnO thin films before and after annealing at 500 ºC.

Thickness (nm)	FWHM (deg.)	c (nm)	a (nm)	c/a	Strain (ε) %	Grain size (nm)
355 (As-deposited)	0.5200	0.5210	0.3252	1.6020	0.077	15.99
410 (As-deposited)	0.0.5183	0.5217	0.3254	1.6032	0.211	16.05
455 (As-deposited)	0.4800	0.5218	0.3255	1.6030	0.23	17.32
355 (500ºC)	0.2804	0.5209	0.3251	1.6022	0.057	29.66
410 (500ºC)	0.3213	0.5217	0.3256	1.6022	0.211	25.88
455 (500ºC)	0.3213	0.5217	0.3250	1.6052	0.211	25.88

Optical properties

In order to determine the influence of thickness and annealing on the optical band gap of ZnO, the optical transmission spectra of all films were recorded and shown in figures. 4 (a) and 4 (b). It is clearly seen that all the films exhibit a high transmittance, around 85%, in the visible. The transmittance decreases sharply near the UV range due to the band gap absorption. When the thickness increases, the transparency decreases. This outcome was expected; since when the thickness is increased a larger number of photons are adsorbed in a film. In addition, a shift of the absorption edge proportional to the thickness values, towards larger energies is apparent from the spectra. The optical absorption at the absorption edge is in agreement with the transition from valence band to the conduction band (λ<390nm). The optical gap energy of ZnO (direct interband transition) is given by the following formula [32]:

$$\alpha h\nu = B\,(h\nu - Eg)^{1/2} \qquad (4)$$

Where B is a constant and α is the absorption coefficient. The optical gap energy (Eg) can be obtained from the intercept of $(\alpha h\nu)^2$ versus $h\nu$. Figures. 5 (a) and 5 (b) show the curves of $(\alpha h\nu)^2$ versus $h\nu$ for all samples.

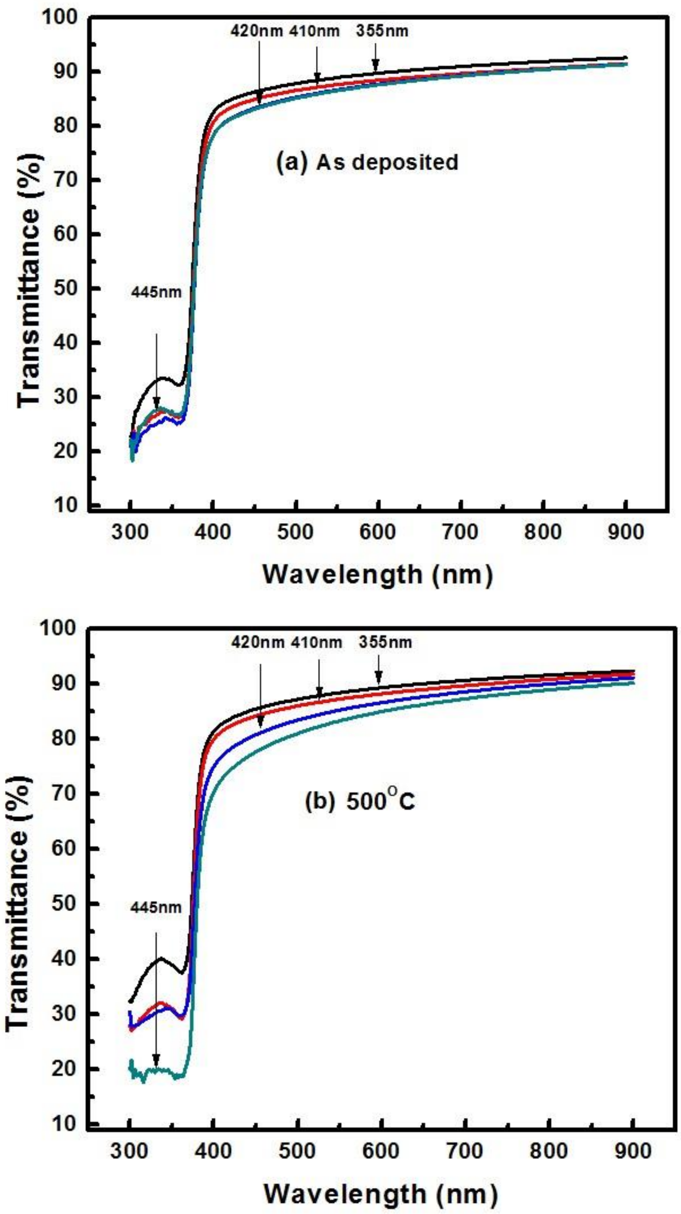

Figure 4: The UV-visible transmission spectra of ZnO films, (a) without and (b) with annealing for different thicknesses.

Hence the values of the optical band gap are found to be between 3.238 to 3.273 eV without annealing and from 3.252 to 3.280 eV with annealing when the thickness changes from 355 to 445 nm. We can explain the rise in optical gap energy by the oxygen diffusion with heat treatment [33]. The increase in optical band gap with the thickness increase is also proportionate with increasing trend in the strain. Previous research reported that strain variation of the interatomic distance in semiconductors influences the energy gap [33].

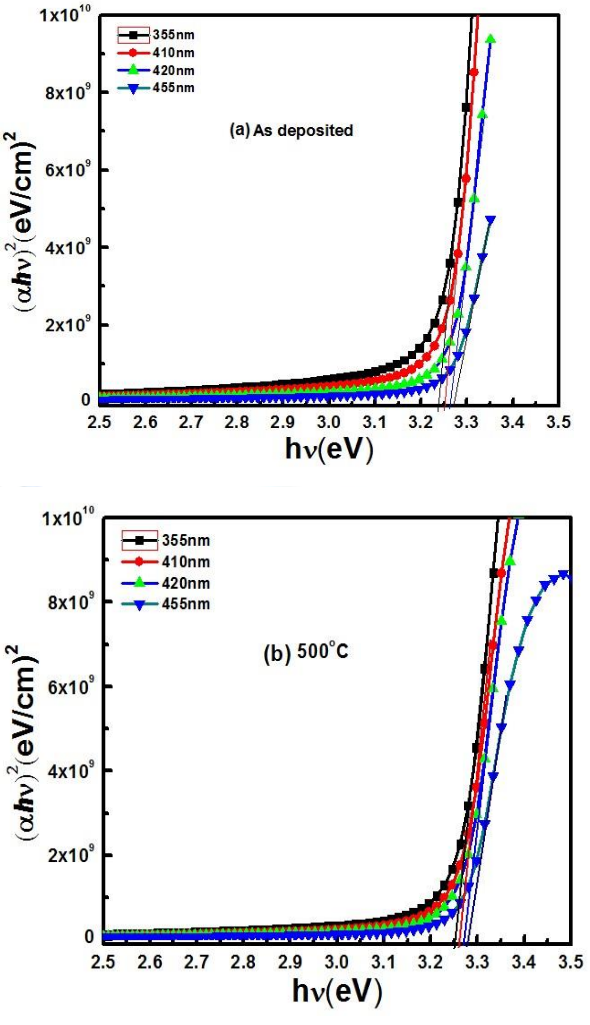

Figure 5: The typical variation of $(\alpha h\nu)^2$ versus photon energy of ZnO thin films, (a) without and (b) with annealing.

Conclusions

CSP technique used in this work gave highly transmittance conductive ZnO thin films deposited on glass. The structural and optical properties of the ZnO films have been found to be affected by the thickness of the film. The annealing treatment was found to enhance some physical properties of ZnO thin films. The crystalline quality, crystallite size and strain of the films get better as the thickness increases.

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