Effects of annealing temperatures on structural properties of ZnO thin films

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Abstract:

Zinc oxide (ZnO) thin films were grown on glass substrates at 300 °C using DC magnetron sputtering method. The effects of annealing under various temperatures (350,400) C ° for 2 h on the structural properties of ZnO thin films were investigated by X-ray diffractometer. X-ray diffraction analysis revealed that all films have a polycrystalline hexagonal wurtzite crystal structure with the preferentially c-axis oriented normal to the substrate surface. The crystal structure of annealed films did not change considerably, but the peak position(002) and surface grain size increased slightly. The crystallinity levels of the films and other structural parameters were investigated and analyzed.

Keywords: ZnO thin films , effects of annealing, XRD, DC magnetron sputtering.

1. Introduction

Zinc oxide (ZnO) has attracted much attention recently for potential applications because of its wide band gap of 3.37 eV and large exciton binding energy of 60 meV at room temperature [1, 2]. ZnO is one of the typical II–VI semiconductor materials having various optoelectronic device applications such as blue light-emitting diodes, electroluminescent devices, electro optic modulators and window layers in photovoltaic cells and gas sensors[3–5].Several techniques were used to prepare ZnO thin films namely: spray pyrolysis [6], thermal evaporation [7], RF/DC magnetron sputtering [8], chemical vapor deposition (CVD) methods [9], Molecular beam epitaxy [10], pulsed-laser deposition (PLD) [11] and chemical bath deposition technique [12]. The structural, physical, and electrical properties of ZnO films were governed by deposition parameter [13], post treatment [14], and doped material [15]. In this research, the effects of annealing process on the structural properties of ZnO thin films prepared by DC magnetron sputtering method were investigated.

2.Experimental

The ZnO thin films were prepared by using DC-magnetron sputtering source Edwards 306 pumping system. The sputtering conditions are: Target – anode distance (30mm), substrate type (glass), substrate temperature 300 °C magnetic field 760G, DC power 50W, gas pressure $7x10^{-2}$Torr and at atmosphere of argon 100%.

ZnO thin films were sputtered from targets on the glass at 300 °C for 3 h. The target materials are in the form of plates with 60mm diameter and 2mm thickness made from ZnO powder (99.98% purity).After deposition process, films were annealed in air ambient at different temperatures of 350 °C and 400°C for 2 h in order to study the effect of annealing on their structural properties. The structure and lattice parameters of ZnO films were analyzed by X-ray diffractometer (XRD) with Cu (Kα) radiation with λ = 1.5406 Å (40 kV, 30 mA).

Film thickness was measured by scanning Electron microscope (SEM). the film thickness was measured to be about(400±10 nm) using the cross-section scanning electron microscopy (SEM) image as shown in Fig(1).

3.Results and discussions

Fig (2) shows the X-ray diffraction patterns of the as-prepared and annealed ZnO films at different temperatures. It is clear from the figure that all films have a polycrystalline structure of hexagonal form, with a sharp (002) preferred orientations, which suggests that the film is aligned with the c-axis oriented perpendicularly to the substrate surface. It can be seen that the intensity as well as full width- half-maximum (FWHM) of (002) peak is dependent on annealing temperatures and the film remains highly oriented with the c-axis normal to the substrate. Intensity reaches the maximum value after annealing at 400 °C for 2 h comparing with as-grown sample or thermally treated one at 350 °C for 2 h. The position of

the (002) peaks (see Table 1) is shifted to a higher 2Θ values from initial 34.324° (as-grown) to 34.328 ° and 34.425 ° after annealing at 350 °C and 400 °C, respectively. This could be due to the release of intrinsic strain through annealing [16]. The full-width-half maximum (FWHM) values of (002) peak of ZnO films are 0.62 °, 0.543 ° and 0.395 ° Table 1 for the as-deposited and after annealing at 350°C and 400°C, respectively. These reasonably narrow FWHM widths demonstrate the high crystal quality of ZnO films obtained by annealing proccess. The values of lattice constants *a* and *c* for the as prepared and annealed films at various temperature are calculated using equation (1) and the calculated values are given in Table

1. Comparing with the lattice constants for hexagonal ZnO crystal given in JCPDS standard data file a = 3.2498 Å and c= 5.2066 Å [17], it is seen that the calculated values are in good agreement with the standard values for ZnO wurtzite structure [18]

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

Where'd' is the inter planar spacing and h, k, and l are the Miller indices.

Strain and stress on ZnO films are calculated using the following equations [19]:

$$strain = \left|\frac{c-c_o}{c_o}\right| \% \qquad 2$$

$$stress = -232.75\frac{c-c_o}{c_o} \quad GPa \qquad 3$$

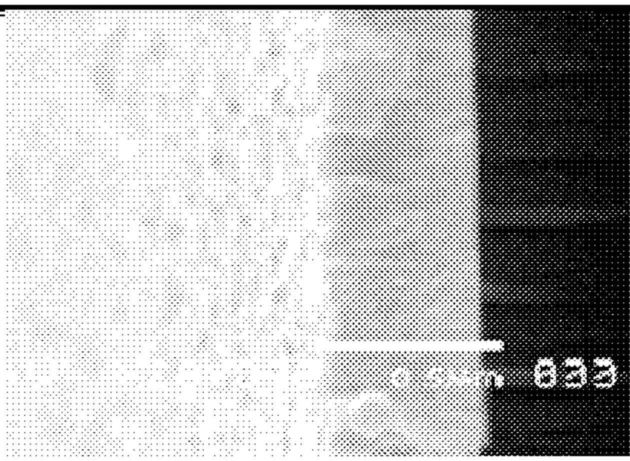
Where c is the lattice parameter of the strained ZnO films calculated from X-ray diffraction data and c_o (5.206 Å), At the same time, the stress can be positive (compressive) or negative (tensile). As can be seen from Table 1, the heat-treated thin films give negative sign and smaller value of stress, which means that the tensile stress is relaxed/relieved due to the rearrangement of atoms in ZnO.

The size of crystallites is calculated using the well-known Scherer's formula as given in equation (4) [20].

$$D = \frac{0.94\,\lambda}{\beta\cos(\theta)} \qquad 4$$

Where D is the size of crystallite, λ (=1.5406 Å) the wavelength of X-rays used, β the broadening of diffraction line measured at half its maximum intensity in radians and θ is the angle of diffraction. The grain size varies from 14 to 22 nm. The grain size values of all the films are given in Table 1. The grain size of the as-prepared ZnO thin film is small compared to the annealed films. The grain size increases as the annealing temperature increases this is due to that as the film annealed the atoms gained sufficient kinetic energy and surface mobility to occupy stable positions inside the crystals that helped in enhancement of crystalline property of thin films, which is good agreement with [21].

Additionally, the dislocation density (δ), listed in Table 1 and defined as the length of dislocation lines per unit volume of the crystal, was calculated from the $\delta=1/D^2$ formula [19], Larger D and smaller δ values Indicate better crystallization of the material. This means that thermal annealing process decrease the defects in the as-grown ZnO films.



Fig(1) SEM picture of cross sections as deposited ZnO film

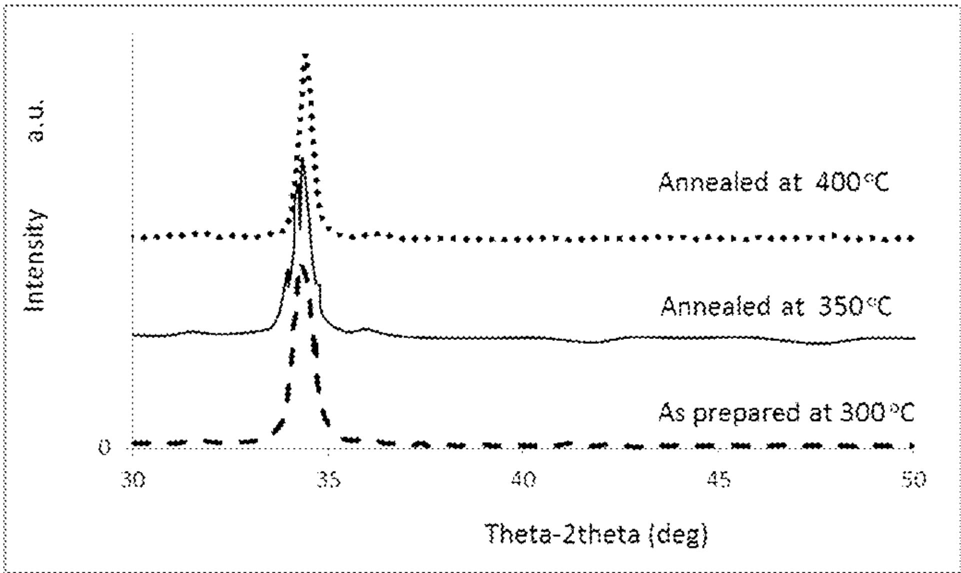


Fig (2) XRD patterns of as-prepared and annealed at different temperatures ZnO thin film.

Table 1

Effect of annealing temperatures on structural properties of ZnO thin films.

Annealing temperature °C	XRD(002) Peak position(2Θ)	d(002) Å	a Å	c Å	D nm	strain	stress GPa	δ x10^{15} m^{-2}	FWHM deg.
As prepared at 300°C	34.324	2.611	3.255	5.222	14	0.296	-0.689	5.10	0.620
Annealed at 350°C	34.328	2.610	3.252	5.220	16	0.270	-o.626	3.91	0.543
Annealed at 400°C	34.425	2.603	3.245	5.206	22	0.022	-0.051	2.07	0.395

4.Conclusions

ZnO Nano crystalline thin films have been prepared successfully by DC magnetron sputtering method. These thin films were annealed in air ambient at different temperatures of 350 ^{o}C and 400^{o}C for two hours . XRD pattern of ZnO thin films showed polycrystalline wurtzite with a preferential (002) orientation. XRD studies indicate that the crystallanity is enhanced on annealing and the average crystalline grain size also increases with annealing.

5.References

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الخلاصة

تم تحضير اغشية اوكسيد الزنك (ZnO) باستخدام طريقة الترذيذ المغناطيسي(DC sputtering) على قواعد زجاجية مسخنة الى درجة ($300^{\circ}C$). تم دراسة تأثير التلدين للأغشية المحضرة وبدرجات حرارة مختلفة C° (350,400) لمده ساعتين على الخصائص التركيبية باستخدام حيود الاشعة السينية. اظهرت نتائج حيود الاشعة السينية بان جميع الاغشية متعددة التبلور وذات تركيب سداسي وان المحور (c-axis) عمودي على سطح القاعدة والتلدين لم يغير من التركيب البلوري للغشاء ولكنه سبب في زيادة طفيفة في موقع المستوي (002) و الحجم الحبيبي. وكذلك تم دراسة وتحليل مستوى بلورية الاغشية والمتغيرات التركيبية الاخرى.