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ANNEALING TREATMENT OF ZnO THIN FILMS PREPARED BY NON-REACTIVE E-BEAM EVAPORATION TECHNIQUE

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In this research, Zinc Oxide (ZnO) thin films were deposited on glass substrates by the electron beam evaporation technique at various substrate temperatures. As-deposited films show high crystallinity at 250˚C. X-ray diffraction, Hall-Effect measurement and optical spectroscopy on annealed films reveal that ZnO films exhibit stable physical properties up to an annealing temperature of 200˚C with a little improvement in crystallinity. By increasing the annealing temperature, crystallinity deteriorates and electrical resistivity enhances. The same result has been observed for two-stage annealing, although both X-ray intensity and Hall mobility enhance. As-deposited films demonstrate high visible transparency that preserves after post-deposition heat-treatment.

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1. Introduction

ZnO is a unique material with exceptional characteristics which have made it a highlight among new functional materials. Although, research focusing on ZnO goes back many decades, the renewed interest is originated by its large exciton binding energy of 60 meV which potentially paving the way for efficient room-temperature exciton-based emitters [1]. Because of a direct band gap of 3.37 eV at room temperature and high carrier concentration, ZnO would have transparency and conductivity simultaneously. While stoichiometric ZnO films are highly resistive, the acceptable conductivity of ZnO films is mainly caused by native defects (e.g.: oxygen vacancy, zinc interstitial atoms)[2] and hydrogen atoms which can be incorporated in the structure by the adsorption of humidity [3,4]. The interesting properties of ZnO thin films bring along so many applications in ferromagnetic semiconductors [5], solar energy materials [6] and also devices in optoelectronics [7] which are totally dependent on the deposition technique [8-11]. Due to few reports on the preparation of ZnO thin films by the non-reactive e-beam evaporation technique [12-15] and their annealing procedure, this research gives a discussion on the effect of post-deposition heat-treatment of ZnO thin films which have been prepared by the non-reactive e-beam evaporation technique.

2. Material and methods

In this research, ZnO thin films were prepared from a pure cold pressed zinc oxide powder (99.9%). Thin films of ZnO were grown onto chemically cleaned glass substrates using the electron beam evaporation technique. In order to extend the diffusion process and consequently improve the homogeneity of the material, the tablets of target were sintered up to 800 °C for 8 hours. Electron beam that has been generated by a high power supply was guided to the target material, which triggers the evaporation process. Prior to the deposition on substrate, the shutter was closed for 10 min in order to obtain pure and clean evaporation. The glass substrates have

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been immersed inside a highly dilute (HNO_3) acid solution for more than 2 hours, washed well by distilled water, sunk into acetone and dried by a nitrogen gas flasher. The deposition unit is a Hindhivac Model 15F6 with an ultimate vacuum of 10^{-6} Torr and by a 10kW electron beam gun. The substrate temperature during the deposition can be raised to nearly 300˚C. The film thickness and the deposition rate were controlled by means of a digital film thickness monitor. Structural properties of the samples were carried out by means of an X-ray diffractometer with Cu-Kα (Phillips pw-1840). The optical properties (transmittance and reflectance spectra) were obtained utilizing two UV-visible spectrophotometers (Models: Carry 100 varian; UV-2100 shimadzu).The electrical studies have been performed by the RH 2010 Hall effect measurement system of PhysTech. A horizontal cylindrical-type electric furnace has been designed for annealing the thin films.

The following research has focused on post-deposition heat treatment of ZnO thin films. For this experiment we prepared two series of ZnO thin films using electron beam evaporation under two different growth temperatures, first at 180˚C and second at 250˚C. Other deposition parameters were tried to be preserved. For convenience we called as-deposited sample at 180˚C by S.1 and as-deposited sample at 250˚C by S.2. ZnO thin films deposited at low temperature range show nearly the same crystallinity with S.1 and by increasing the substrate temperature, the crystallinity is improved. Films thicknesses also have been checked by a Dektak 3 profilometer that was 795 nm for S.1 and 439 nm for S.2.

3. Results and discussion

Fig.1a shows the X-ray diffraction pattern of S.1. According to ASTM data, in addition to ZnO polycrystalline lattice, (203) crystal orientation which belongs to zinc metal is also detected. S.1 has no optical transparency in UV-visible spectra region (dark black in appearance) and shows nearly unity reflectance in visible spectra, which confirms their metallic nature. In order to understand better the darkness of the films, the S.1 was immersed in dilute hydrochloric acid and observed that the zinc metal is peeled out and dissolved in acid. Another evidence for confirming the metallic behavior of S.1 has been observed by its acceptable electrical sheet resistance which is 400 Ω/□.

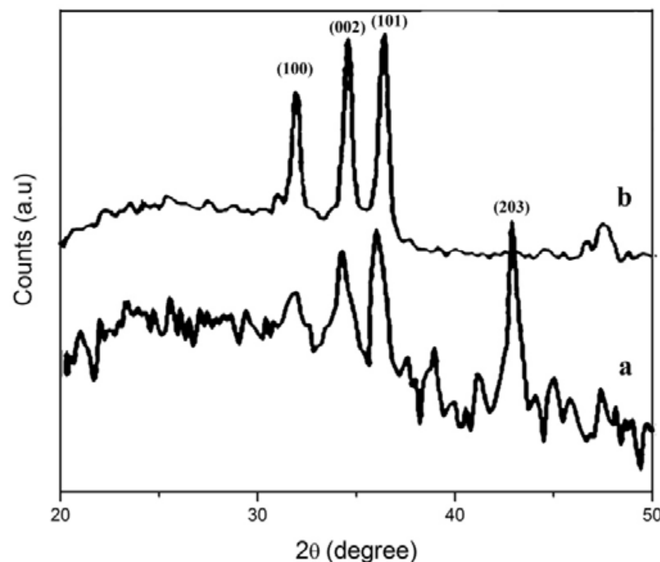

Fig. 1) X-ray diffraction pattern of a) as-deposited at 180˚C and b) annealed at 500˚C.

Fig.1b demonstrates the X-ray diffraction pattern of S.1 that has been annealed at 500˚C. X-ray diffraction pattern of annealed film exhibits a better crystallinity in three main growth directions of ZnO that are (100), (002) and (101) phases. Another significant result is that the obtained metallic films were oxidized following the post deposition heat treatment and become transparent.

According to the Scherer's formula [16] for (002) orientation, the mean grain size of S.1 and S.2 are 10nm and 20 nm respectively, indicating crystallinity improvement of S.2 in comparisons with S.1. By virtue of the final aim which is preparing a high quality ZnO thin film with superior physical properties, S.2 is a better choice for heat-treatment analysis in comparison with S.1 due to its better in-situ crystallinity.

The effect of annealing at different temperatures in nitrogen ambience reveals that the X-ray intensity increases by annealing process up to 200˚C and thereafter a diminution is observed up to 500˚C (Fig. 2c). It seems that annealing brings about this capability for as-deposited films to desorb and adsorb oxygen simultaneously and the rate of these two phenomena varies in different temperatures for ZnO structure.

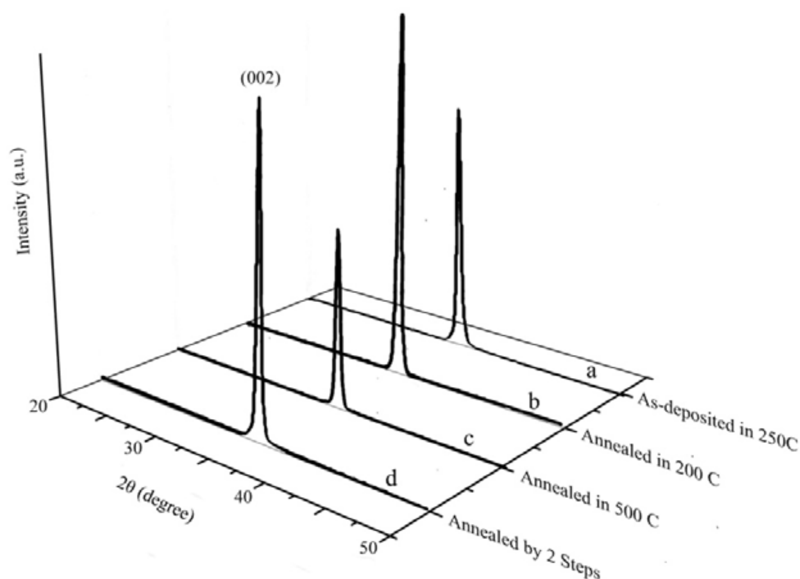

Fig. 2) X-ray diffraction pattern of a) as-deposited ZnO thin films at 250˚C and b,c,d) annealed at 200˚C, 500˚C and by two-step.

As the annealing temperature for films heat treated at 100˚C and 200˚C is less than the deposition temperature ($T_s = 250$˚C), thermal energy is not enough to totally break the Zn-O binding and just makes it weak to some extent, which is not an appropriate situation for accepting oxygen and other atoms from the annealing atmosphere; but ZnO structure is well-prepared to disrobe oxygen from grain boundaries that make a reduction in the defect density and improve crystallinity [17]. A little enhancement in crystallinity, grain size and as a result, in Hall-mobility has been observed (Fig.2b and Table.1) which is very likely due to oxygen desorption from grain boundaries. Our claim can be expressed more reasonably when it becomes clear that one of the demonstrative factors in oxygen desorption from grain boundaries is the lack of electron concentration [18].

Although the basis of crystal does not have enough energy to accept a new atom from ambience, lattice will continue to grow and whenever temperature coincides with deposition temperature, this procedure will be more complete, thereby crystallinity, grain size and as a result, mobility enhance.

Table 1. The electrical properties of as-deposited and annealed ZnO thin films.

Sample	Resistivity (Ω-Cm)	Carrier Concentration (Cm^{-3})	Hall Mobility ($Cm^2/V.s$)
As-deposited at 250 ˚C	1.26×10^{-2}	2.69×10^{19}	18.4
Annealed at 200˚C	1.27×10^{-2}	2.53×10^{19}	19.4
Annealed at 500˚C	4.36×10^{2}	1.22×10^{15}	11.1
Annealed by 2 Step	4.39×10^{2}	4.44×10^{14}	14.0

At higher temperatures the growth procedure continues, but the rate of adsorption overtakes the rate of desorption, which is due to the significant weakness of the Zn-O binding. This permits the nitrogen, oxygen and some defect-like atoms (e.g.: Carbon) to incorporate inside the ZnO films and these are responsible for the diminution of X-ray intensity, deterioration in crystallinity (Fig.2c) and finally decrease in the Hall-mobility (Table.1). Diminution in crystallinity may also be admitted by the mean grain size calculation through Scherer's formula that shows S.2 grain size has decreased from 20nm to 15nm after annealing at 500˚C. Zhaoyuan and Huoquan [19] also reported the annealing temperature as a key factor in controlling the balance between the adsorption and desorption of oxygen atoms in ZnO films.

As has been shown in Fig.2d, the intensity of diffracted X-ray for two-stage annealed ZnO thin films demonstrates high intensity values which convince that two-stage annealing has improved the crystallinity. In two-stage annealing procedure, first, films have been exposed to nitrogen at the annealing temperature of 250˚C for 30 minutes and then it took one hour to increase the temperature to 500˚C and finally films have been annealed in the same atmosphere at 500˚C for 30 minutes. The same process has been done by Shao for zinc thin films under the oxygen ambience and drastic changes have been reported [20]. In the first stage, the temperature is sufficient to simulate a situation like the deposition condition and the deposition will be completed in 30 minutes and ZnO films will find their stoichiometric form. When the first stage of annealing is completed, temperature increases slowly to 500˚C and remains the same for 30 minutes in nitrogen ambience and during this long time period, microstructures of the film will find the chance to continue their growth procedure (Fig.2d). Deterioration in resistivity reported in Table 1 is due to the compensation role of oxygen during the long period of annealing which makes a drastic decrease in electron concentration. The same electrical behavior is observed for annealed films through routine procedure of heat-treatment at 500˚C.

Transmission spectra in UV-visible region for S.1 annealed at 500˚C, S.2 annealed at temperatures from 100˚C to 500˚C and S.2 annealed by two-stage method, have been illustrated in Fig. 3. S.1, as mentioned in the previous discussions, does not show any transparency in visible region and is totally reflective, which is due to its metallic structure. In accordance with our expectations after oxidizing, the result will be a stoichiometric compound with fewer defects which improves the transparency of annealed films being evident in S.1 annealed spectrum. The variation of visible transmission for S.2 before and after annealing is not much significant and changes on its structure caused by annealing could not be detected by spectrophotometer.

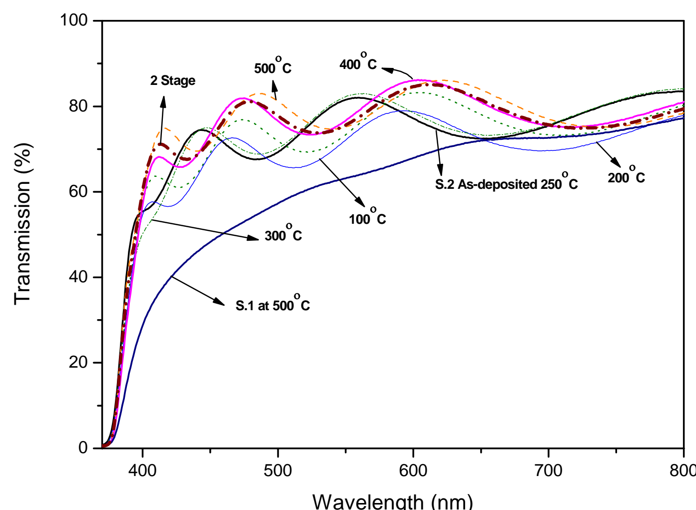

Fig 3. Transmission in visible spectra of as-deposited and annealed ZnO thin films (S.1: As-deposited in 180˚C and post-annealed in 500˚C).

4. Conclusions

In this research we have focused on the effect of annealing in ZnO thin films prepared by the non-reactive e-beam evaporation technique. We fabricated two series of ZnO thin films under two different growth temperatures, first at 180˚C and second at 250˚C. The latter shows a better crystallinity with high transparency in visible spectra and has been selected for annealing experiments. X-ray intensity of films increases by annealing process up to the annealing temperature of 200˚C and thereafter a diminution was observed up to 500˚C and a good agreement has been shown in electrical findings obtained by Hall-effect. The intensity of X-ray for two-stage annealed ZnO thin films demonstrates a high intensity value which testifies that two-stage annealing has improved the crystallinity and predicts a higher mobility which has been detected, although generally the electrical properties deteriorate. Optical studies demonstrate a stable transparency in different methods of annealing.

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