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Nano-structural Characterization of Post-annealed ZnO Thin Films by X-ray Diffraction and Field Emission Scanning Electron Microscopy

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ABSTRACT

ZnO thin films were deposited on Si(400) substrates by e-beam evaporation technique, and then post-annealed at different annealing temperatures (200-800°C). Dependence of the crystallographic structure, nano-strain, chemical composition and surface physical Morphology of these layers on annealing temperature were studied. The crystallographic structure of films was studied using X-Ray Diffraction (XRD) method, while the chemical composition and surface morphology of layers were investigated by Field Emission Scanning Electron Microscopy (FESEM). The XRD results showed that ZnO (002) crystallographic orientation was a preferred orientation for growth of ZnO thin films. Increasing of annealing temperature caused increasing of intensity and decreasing of FWHM for ZnO (002) peak and decreasing of dislocation density in the films. The nano-structural investigations also showed that mentioned peak position and nano-strain were varied with increasing of annealing temperature. Chemical composition analysis showed that the ratio of oxygen to Zinc increased with increasing of annealing temperature. SEM images showed a mixed structure of nanowires and nanosheets for annealed films at 350 and 500°C, and a granular structure for annealed samples at 200 and 800°C. However, the annealed films at the highest temperature (800°C) had a dense structure and larger grains than the annealed film at 200°C temperature.

Keyword: ZnO; Thin films; Crystallographic structure; Nano-strain; Dislocation density; Morphology.

1. INTRODUCTION

There has been a great deal of interest in zinc oxide (ZnO) semiconductor materials lately, as seen from a surge of a relevant number of publications. The interest in ZnO is fueled and fanned by its prospects in optoelectronics applications owing to its direct wide band gap (Eg 3.3 eV) at 300 K. Some

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optoelectronic applications of ZnO overlap with that of GaN, another wide-gap semiconductor (Eg 3.4 eV) at 300 K, which is widely used for production of green, blue-ultraviolet, and white light-emitting devices. However, ZnO has some advantages over GaN among which are the availability of fairly high-quality ZnO bulk single crystals and a large exciton binding energy (60 meV) [1]. A variety of nanostructured ZnO materials such as nanodots, nanorods, nanobelts, nanotubes, etc. have been fabricated, but ZnO thin film is still the ZnO material, which is studied most widely and most deeply at present. That is because the preparation technology of one- and three-dimensional nanostructured ZnO materials is usually complicated and consequently these ZnO nanostructured materials are difficult to be massively produced under present conditions. Compared with ZnO nanostructured materials, ZnO thin film has some advantages like the relatively simple preparation technology, good crystalline quality, being able to be massively produced, etc., which are very important for commercial application of ZnO materials [2]. Many researchers have been reported on obtaining of ZnO thin films(or nanowire) by several techniques such as Chemical Vapor Deposition (CVD), molecular beam epitaxy, sputtering, pulsed laser deposition, sol-gel and thermal annealing [3-9], and investigation of different properties of these layers including structural, optical, electrical, mechanical, luminescence and gas sensing properties [9-18]. In all these methods, the crystal quality and different properties of ZnO thin films strongly depend on the preparation technique, growth conditions and selected substrate. For this reason, the study of different growth methods with several conditions can be interesting. The goal of this paper is preparation of ZnO thin films by deposition of Zn films on Si substrate with e-beam evaporation method, and then post-annealing of these films at presence of oxygen flow. We also investigated the annealing temperature effect on nanostructure, dislocation density, nano-strain, chemical composition and surface morphology of produced thin films by this method.

2. EXPRRIMENTAL DETAIL

Silicon (400) n-type with dimension of 20 × 20 mm^2 was used as substrate. Prior to deposition, the substrates were ultrasonically cleaned in acetone then ethanol. Zn thin films with 90 nm thickness were deposited on Si substrate, using an electron beam evaporation technique at room temperature. The purity of zinc was 99.998%. An Edwards (Edwards E19 A3) coating plant with a base pressure of 2×10^{-7} mbar was used. Film thickness and deposition rate were measured using a quartz crystal deposition rate controller (Sigma Instruments, SQM- 160, USA) positioned close to the substrate. The deposition rate and deposition angle were 0.3 Å/s and 10°, respectively.

Post-annealing of the Zn/Si films was performed by a tube furnace at five different temperatures (200 to 800°C in steps of 150°C) with oxygen flow (purity of 99.98%) with at a flow rate of 200 SCCM (Standard Cubic Centimeter per Minute). The samples reached the selected annealing temperature with a thermal gradient of 7 degree/min and were kept at the annealing temperature for 60 min, then gradually cooled down to room temperature.

The crystallographic structure of these films was obtained using a Philips XRD X'pert MPD Diffractometer (Cu kα radiation) with a step size of 0.02° and step time of 1 s. A Field Emission Scanning Electron Microscope FESEM (model: CamScan MV2300, Czech & England) was also employed for investigation of surface physical morphology and chemical composition.

3. RESULTS AND DISCUSSION

3.1. Crystallographic structure

X-ray diffraction patterns of annealed Zn/Si thin films are shown in Figure 1. As can be seen, XRD pattern of annealed sample at 200°C shows three peaks that can be attributed to ZnO (100), ZnO (002), ZnO (101) crystallographic orientations (with reference to JCPDS Card No.: 36-1451, symmetry: Hexagonal P and space group: P63mc). In the XRD pattern of annealed sample at 350°C, the intensity of ZnO (100) and ZnO (101) diffraction lines decreased, but ZnO (002) peak intensity increased. By increasing of annealing temperature to higher temperature (namely 500, 650 and 800°C) this process was repeated, so that the ZnO (002) diffraction line could be introduced as a preferred orientation. A similar kind of this behavior with annealing temperature for produced films by rf. Magnetron sputtering on SiO_2 substrates has been reported earlier by Kim and et al. [19]. Figure 2 depicts the plot of ZnO (002) peak intensity and FWHM as a function of annealing temperature. The figure shows that increasing of annealing temperature causes an increase of intensity and a decrease of Full Width at Half Maximum (FWHM) of ZnO (002) peak. Increasing of peak intensity indicates the improvement of structural quality of ZnO thin films, while decreasing of FWHM denotes the increasing of crystalline size (according to Scherrer formula ($D= k\lambda/B\cos\theta$). This behavior may be due to high annealing temperature that provides energy of film atoms to enhance mobility. Increasing of mobility also can increase the coalescence and decrease the defects and cause the improvement of pores and quality of ZnO films.

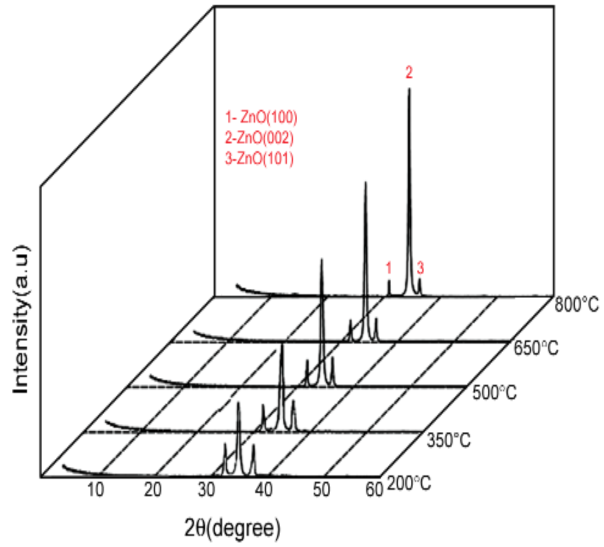


***Figure 1:** XRD pattern of annealed Zn/Si thin films at different temperatures (substrate diffraction line (namely Si (400)) is at 69.15° with reference to JCPDS Card No.: 75-0589).*

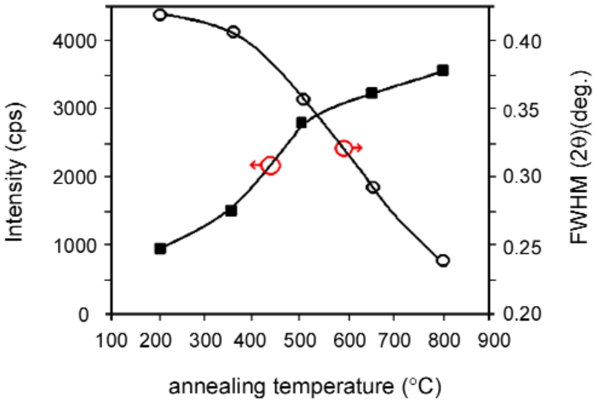


***Figure 2:** Variation of Peak intensity and FWHM of ZnO (002) diffraction line as a function of annealing temperature.*

To confirm this phenomenon, we have calculated the dislocation density in the films. The dislocation density, which represents the amount of defects in the film, is determined from the formula $\delta= 1/D^2$ [20]. Where D is crystalline size and is calculated using Scherrer's formula. These values are shown in Figure 3. The result shows that increasing of annealing temperature causes the better crystalli-zation, and improves the amount of pores in the films.

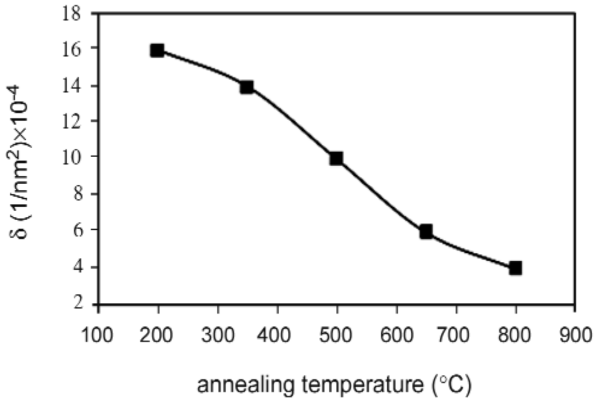


***Figure 3:** Dislocation density values of the ZnO films as a function of annealing temperature.*

Figure 4 illustrate the variation of X-ray diffraction angle (2θ) of mentioned peak as a function of annealing temperature, when the dashed line is the peak position of ZnO powder. The result shows that the annealing at the presence of oxygen flow at different temperatures causes the variation of peak position. The deviation of the position of the diffraction peak from its powder value (34.4220) is mainly due to a uniform state of strain (or stress) with tensile components parallel to C axis. Meanwhile, we have calculated the nano-strain in the films for Zn (002) diffraction line. The Nano-strain cab is calculated from the following formula [21]:

$$\varepsilon = (d-d_0)/d_0$$

Where ε is lattice strain, d is plane spacing of sample and d_0 is plane spacing of standard powder. Variations of nano-strain (for Zn (002) diffraction line) are shown in Figure 5. This result agrees with the angular peak position analysis (Figure 3), so that films nano-strain decreased by increasing of annealing temperature up to 350°C and then increased. This behavior can be attributed to higher thermal expansion coefficient of ZnO to Si, and this difference increases at higher annealing temperatures.

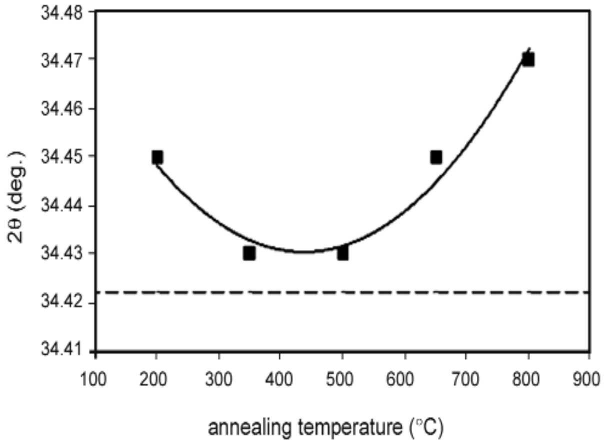


Figure 4: *Variation of X-ray diffraction angle (2θ) of (002) diffraction line as a function of annealing temperature. (The dashed line is the peak position of ZnO powder).*

3.2. Chemical composition

The chemical composition of all sample prepared in this work was studied by EDAX analysis. The obtained results from this analysis are given in Table 1, while a typical graph of this analysis for selected sample is shown in Figure 6. The results showed that the ratio of Zn/O decreased (or the amount of oxygen increased) by increasing of annealing temperature. In fact, increasing of annealing temperature caused increasing of influence of oxygen and improved the oxidization process that is consistent with the XRD results.

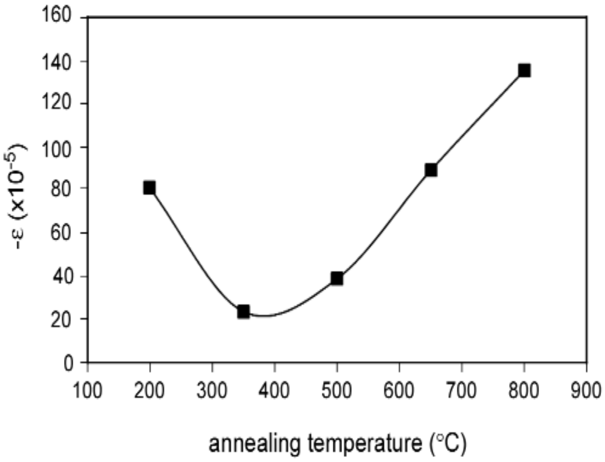


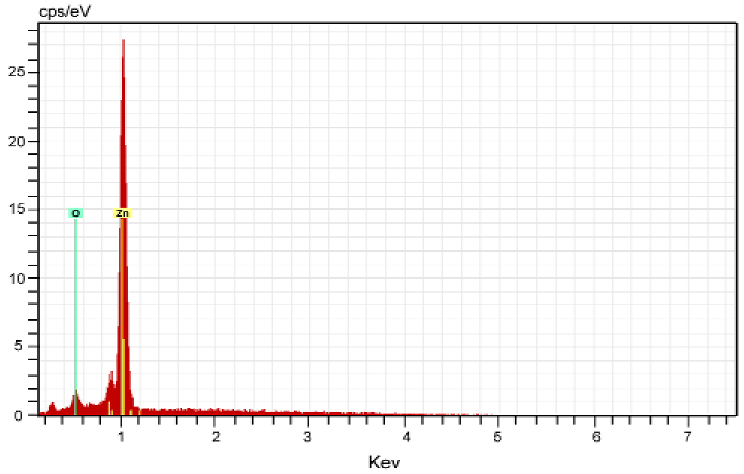
Figure 5: *Variation of nano-strain in ZnO thin films obtained from (002) diffraction line.*

Table 1: *The results of EDAX analysis.*

Code	Temp.	at (%)	
	(°C)	Zn	O
I	200	88.78	11.22
II	350	48.60	51.40
III	500	46.38	53.62
IV	650	46.17	53.83
V	800	45.81	54.19

3.3. Surface morphology

Figure 7 (a-e) depicts the SEM images of post-annealed Zn/Si thin films at different temperatures. As can be seen, surface of annealed sample at the lowest temperature (200°C) shows a granular structure with void space between the grains. But, by increasing of annealing temperature to middle temperatures (i.e. 350 and 500°C) surface morphology changes to a mixed structure of nanowires and nanosheets. Interestingly, the



Figue 6: *EDAX spectrum of selected ZnO/Si sample (annealed at 200°C).*

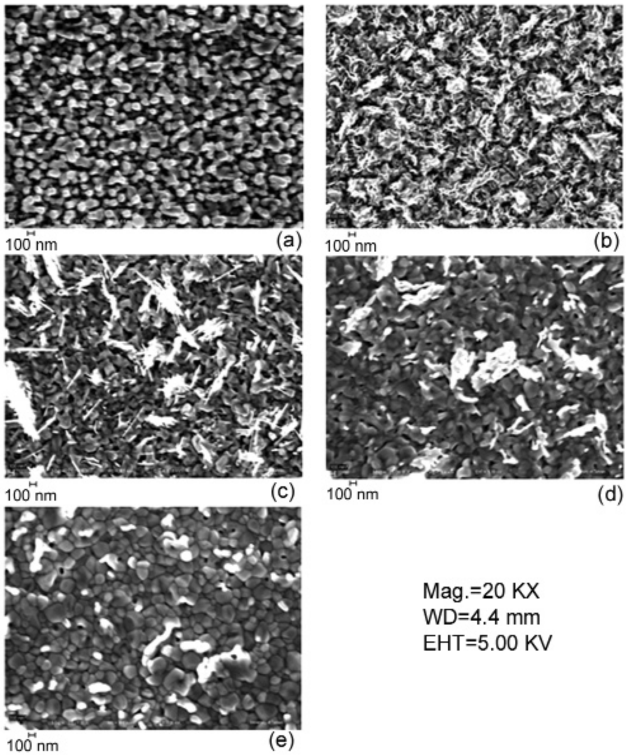


Figure 7: *SEM images of annealed Zn/Si thin films at different temperatures, a) 200°C, b) 350°C, c) 500°C, d) 650°C and e) 800°C.*

obtained nanowires are rooted in the outer surfaces of the nanosheets. This behavior can be related to the nature of ZnO growth [22].The surface morphology of films again changes by an increase in annealing temperature to higher temperatures (650 and 800°C) (Figure 7 d and e), so that the annealed sample at 800°C finds a granular structure. Both of annealed films at 200 and 800°C have granular structure, but the annealed sample at the highest temperature (800°C) has larger grains and denser structure in comparison with annealed sample at the lowest temperature (200°C). This behavior is due to increasing of surface diffusion (mobility) which causes the coalescence of the grains. A similar morphology for formed sample at high annealing temperatures has been reported earlier by different researchers [18, 19].

4. CONCLUSIONS

Zn thin films were deposited on Si substrates by e-beam evaporation method, and then post-annealed at different temperatures with flow rate of oxygen. Nano-structure, chemical composition and surface morphology of prepared films were studied by XRD and FESEM. The results showed the improvement of growth in the (002) crystallographic orientation with increasing of annealing temperature. Increasing of annealing temperature also caused increasing of nano-strain (at >350°C temperatures) and the ratio of O/Zn, and decreasing of FWHM and dislocation density in ZnO films. The surface morphological investigation showed a mixed structure of nanowires and nanosheets for annealed films at 350 and 500°C, and a granular structure for annealed samples at 200 and 800°C. However, the annealed films at the highest temperature (800°C) had a denser structure and larger grains than the annealed film at 200°C temperature.

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