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Effects of annealing temperature on the structural and optical properties of ZnO hexagonal pyramids

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ABSTRACT

ZnO thin films were deposited on quartz substrate at 550 °C by using spray pyrolysis method and subsequently annealed between 600–900 °C with a step of 100 °C. The characterizations of the structural and optical properties of the films have been carried out by means of X-ray diffraction, scanning electron microscopy (SEM) and optical transmittance measurements. XRD ans SEM images indicated that annealing temperature did not play a great role on the microstructure of ZnO films. ZnO thin films are all in hexagonal crystallographic phase and have (0 0 2) preferred orientation, regardless of the annealing temperature. However, SEM studies showed that there exist a high density of micro-rods in the shape of hexagonal pyramid with the width in the order of about 1 μm and height in range of 1–3 μm and the adjacent hexagonal crystals to start fusing with each other along their boundaries at high temperatures. As a result of the optical measurements, it was observed that the films show the low transmittance and optical band gap decreases from 3.15 to 3.10 eV with the increasing of the annealing temperatures up to 800 °C and followed by an increase to 3.20 eV upon further annealing at 900 °C.

1. Introduction

Considering the ever-decreasing dimensions of electronic devices, producing self-assembled micro- and nano-structured materials systems is becoming increasingly important for commercial applications. There is also significant academic interest in nano-systems, as their properties can be remarkably different from those of the bulk materials due to quantum-size effects. Much attention has been paid recently to the nano-structured materials such as ZnO and GaN due to their ability to exhibit near-ultraviolet (UV) emission. ZnO is especially interesting due to its direct band gap of about 3.37 eV, its high mechanical and thermal stability, and its large exciton binding energy (60 meV). ZnO is a low cost material with various industrial applications in manufacturing gas sensors, varistors, Schottky diodes, solar cells, piezoelectric devices, etc. [1–3]. ZnO films are required to have high crystalline quality for most applications. Thermal annealing is widely used to improve crystal quality, which affects electrical and structural properties by reducing study defects in materials. During the annealing process, dislocations and other structural defects may smear out in the material and adsorption/decomposition, especially at the surface regions may change the structural, stoichiometric and electrical properties of the material. Therefore, understanding the effects of annealing processes on ZnO surfaces and films is of interest for various technologies employing this material.

ZnO thin films may be prepared by different techniques including metal–organic chemical vapor deposition, magnetron sputtering and spray pyrolysis [4–8]. Among these methods, spray pyrolysis is an attractive method to obtain thin films of ZnO, since it is a simple and inexpensive method that can be scaled up easily. The morphology of the grown layers is usually a function of the method used. In our previous work [9] we demonstrated that spray pyrolysis method yields the micro-rod type growth on glass substrates under specific growth conditions. The deposited layers containing a high density of micro-rods have a large surface to bulk ratio naturally and thus, they are good candidates to study annealing effects in ZnO layers, especially to investigate effects due to the free surface of the material. In this work, ZnO layers were grown by spray pyrolysis on quartz substrates at 550 °C under specific conditions to form micro-rod structures and then annealed at elevated temperatures. Effects of the growth and post-depositional annealing processes on film properties were studied.

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2. Experimental details

ZnO thin films were grown by spray pyrolysis technique in air. Details of the experimental set up were described elsewhere [9]. The spray solution was prepared from a mixture 0.1 M zinc chloride ($ZnCl_2$) and distilled water. Film growth was carried out with a spray rate of about 5 ml/min, which resulted in a growth rate of ~50 nm/min on glass substrates. The substrates were previously cleaned in ethanol and then dried in vacuum. Substrate temperature was kept at 550 °C and the process was carried out at atmospheric pressure. During growth, substrates were rotated at 10 rpm in order to produce uniform and homogenous films. The grown films had good adhesion to the substrate surfaces and displayed a high density of micro-rods with the width in the order of 1 μm and height in the range of 1–3 μm.

The average thickness of the films measured from scanning electron microscopy (SEM) cross-sections was found to be about 5 μm. The X-ray diffraction (XRD) data taken using a Rigaku D/Max-IIIC diffractometer with Cu Kα radiation over the range 2θ = 3–70° at room temperature. The surface morphology was studied by using JEOL JST-6400 scanning electron microscopy. Optical transmission measurements were performed with a Shimadzu UV-1201 UV-VIS-NIR spectrophotometer over the wavelength range of 300–1100 nm.

3. Results and discussion

Fig. 1 shows the X-ray diffractograms taken from a set of ZnO samples before and after annealing process. They reveal the formation of ZnO polycrystalline with a hexagonal structure. No diffraction peaks of other impurity phases are found in these data. Before annealing, the spectra show a strong diffraction peak of ZnO at (0 0 2) direction and weaker diffraction peaks belonging to (1 0 1) and (1 0 2) plane directions (Fig. 1(a)). After increasing the annealing temperature, it is obvious that the intensity of ZnO (0 0 2) diffraction peak increases as seen in Fig. 1(a)–(e). This suggests that annealing treatments improve the preferred orientation of the films. Generally, ZnO thin films deposited by spray pyrolysis with a hexagonal structure show a preferential orientation along (0 0 2) direction. It is worth noting that the (0 0 2) plane in ZnO is the most thermodynamically favorable since it offers the lowest surface energy [10]. The calculated value of the lattice constant along the *c*-axis was 0.520 nm for the as-grown ZnO film. This is in a good agreement with ASTM data for ZnO powder [11]. The calculated lattice parameters decreased from 0.520 to 0.518 nm after annealing at 900 °C. This corresponds to a shift in the 2θ from 34.51° to 34.56°. If the diffraction peaks shift to lower angles, such a shift may be attributed to a tensile stress in the film [12,13]. The origin of our compressive stress may be the difference in the linear thermal expansion coefficients of ZnO film ($\alpha = 7 \times 10^{-6}\,°C^{-1}$) and quartz ($\alpha = 0.5 \times 10^{-6}\,°C^{-1}$). The gradual decrease of the lattice parameter with increasing annealing temperature suggests that stress is partly relieved.

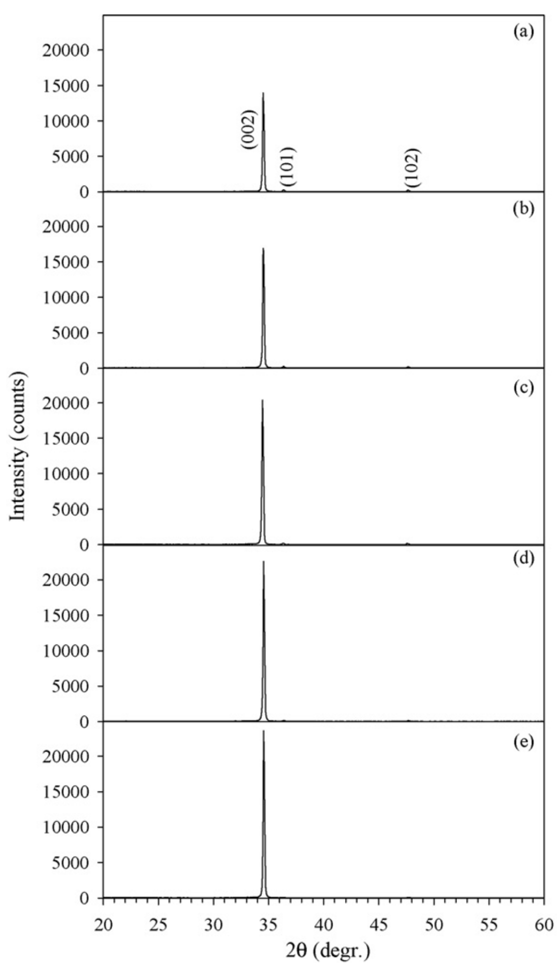

Fig. 1. X-ray diffraction patterns of ZnO thin films for as-deposited (a), annealed at 600 °C (b), 700 °C (c), 800 °C (d) and 900 °C (e).

To check whether the observed phenomena was related to defect or surface effects, a series of SEM micrographs were taken from as-deposited and annealed films at different temperatures. The scanning electron micrographs of as-grown and the annealed films at 600, 700, 800 and 900 °C are shown in Fig. 2(a)–(e). As can be seen from these figures, the high temperature annealing does not produce pronounced effect on the structure of these films. However, only at 900 °C there are some indications of adjacent hexagonal crystals to start fusing with each other along their boundaries.

Here it is worth to mention the results of our previous study on the structural and optical properties of Co doped ZnO thin films grown by spray pyrolysis method on the glass substrate [14]. The films with and without Co consisted of hexagonal-shaped rods having submicron diameters. However, as the ZnO films grown on the quartz substrate in the present study, the crystal shape of the ZnO films changed from the rod like to hexagonal pyramid like textured morphology. The individual ZnO rod had a diameter in the range of 100 nm to 4 μm and a length of more than 3 μm (Fig. 3). Consistent with the XRD pattern, the hexagonal pyramids were found to be regular and almost perpendicular to the substrate, indicating that ZnO rods preferentially grow along the (0 0 2) plane. Zhang and Kerr [15] have investigated the details of ZnO thin film growth mechanism with different Cd concentration. As the Cd content in ZnO thin films increases, the shape of ZnO crystals changes from slim-and-long rods to fat-and-short hexagonal pyramids. Valerini et al. [16] have studied the effect of substrate temperature on the formation of hexagonal pyramids in ZnO thin films obtained by pulsed laser deposition. As they increased the substrate temperature through 500–700 °C, the smooth surface obtained at low temperature gradually changed to some well-defined hexagonal-base pyramids. They attributed this change in the surface structure to the high temperature of the depositing species which have a high tendency to coalescence.

Fig. 4 shows the optical transmission spectra of ZnO films prepared on the quartz substrates at a temperature of 550 °C followed by annealing at various temperatures. The transmittance spectra reveal that all films have a low average transmittance about 25% regardless of annealing temperature because of the high absorption of the films. Since ZnO thin films were deposited with a thickness of about 5 μm at relatively high temperatures in this work, the decreases in the optical transmittance of the samples could be attributed to the large thickness of the films and scattering of light at the grain boundaries, which is also reported in the study of Krunks on the ZnO thin films [17]. In addition, the absorption edge in Fig. 4 shifted slightly to higher wavelengths as the annealing temperatures increases toward 900 °C.