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Article in *Journal of Crystal Growth* · February 2005

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Zinc oxide films prepared by sol–gel method

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Available online 8 December 2004

Abstract

ZnO films with preferred orientation along the (002) plane were fabricated by the sol–gel method using a spin-coating technique. The effects of annealing process on the microstructure, transparent properties, and morphology of ZnO films were studied. The films which were dried at 300 °C and then postheated at 600 °C showed the preferred (002) orientation of ZnO and high transmittance above 80% in the visible range. Also, SEM images of the films showed microstructure consisting of many round shaped particles for the films heated at 400 °C and 500 °C and hexagonal particles as the temperature increased to 600 °C.

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PACS: 78.20.Ci; 68.55.Jk; 61.16.Bg

Keywords: A1. Atomic force microscopy; A3. Sol–gel method; B1. Oxides

1. Introduction

Metal oxide semiconductor films have been widely studied and have received considerable attention in recent years due to their optical and electrical properties. Some of them are good candidates for transparent conductive oxide films. Among them, ZnO is one of the metal oxide semiconductors suitable for use in optoelectric devices. It is an alternative material to tin oxide and indium oxide, which have been most used to

date [1]. ZnO is extensively studied because of its potential applications in various fields, such as gas sensor, solar cells [2], photo-detectors, light emitting diodes (LEDs) and laser systems [3], etc. ZnO films are grown by many different methods such as pulsed laser deposition (PLD) [4,5], magnetron sputtering [6], MOCVD [7,8], spray pyrolysis [9] and sol–gel process [10,11]. The properties of ZnO thin films are much influenced by not only the growth methods but also the heat treatment parameters, especially the thermal annealing [12]. Therefore, it is essential to investigate the effect of annealing process on the microstructure, transparent properties, and morphology of ZnO films.

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2. Experimental detail

Fig. 1 shows the flow chart of the preparation of the ZnO coating films. In this work, ZnO thin films were prepared by sol–gel method. Zinc acetate dihydrate, 2-methoxyethanol and monoethanolamine (MEA) (Analytic grade, Shanghai Chemical Reagent Co.) were used as a starting material, solvent and stabilizer, respectively. Zinc acetate dihydrate was first dissolved in a mixture of 2-methoxyethanol and MEA solution at room temperature. The molar ratio of MEA to zinc acetate was maintained at 1.0 and the concentration of zinc acetate was 0.75 M. The solution was stirred at 60 °C for 2 h to yield a clear and homogeneous solution, which served as the precursor solution.

The precursor solution was filtered through a 0.2 µm TF WHATMAN syringe filters and dropped onto silica glass substrates, which were rotated at 3000 rpm for 30 s. After being deposited by spin coating, the films were dried at 300 °C for 10 min to evaporate the solvent and remove organic residuals. The procedures from coating

to drying were repeated seven times. The films were then heated at 400–600 °C as the second heat treatment.

We used a Rigaku D/MAX-γ A X-ray Diffractometer to investigate crystal quality and crystal structure. The thickness of ZnO film was measured by a XP-2 step meter made in Ambios Technology Company of USA. The transmittance spectra were performed by a Hitachi U-3500 spectrophotometer. The surface morphology of the films was observed using scanning electron microscopy (SEM) (type S-520 Hitachi, Japan) with an accelerating voltage of 20 kV.

3. Results and discussion

3.1. X-ray diffraction analysis

The thickness of the film is about 300 nm after repeating seven times measured by Ambios XP-2 step meter. Fig. 2 shows the X-ray diffraction (XRD) spectra of the ZnO thin films on silica glass substrates postheated at temperatures of 400, 500 and 600 °C, respectively. All the peaks of the samples annealed at different temperatures are corresponding to the peaks of standard ZnO (JCPDS #751526). For the sample prepared at temperature of 400 °C, (100), (101) and (002) diffraction peaks are very strong in the XRD pattern (Fig. 2a), showing that the ZnO grains in the film grow along different directions, and weak preferential growth was observed. When the annealing temperature increases to 500 °C, compared with the XRD pattern of the sample annealed at 400 °C, the peaks of (100) and (101) are lower than (002) peak apparently (Fig. 2b). It indicates that the thin film annealed at 500 °C is preferential grown along (002). From Fig. 2c, we can see that (002) peak is much higher than the other two peaks, which indicates that the film annealed at 600 °C is strongly c-axis oriented. From the XRD measurement results on the film annealed at different temperatures, we can conclude that the degree of crystal orientation increases with increasing postheating temperature.

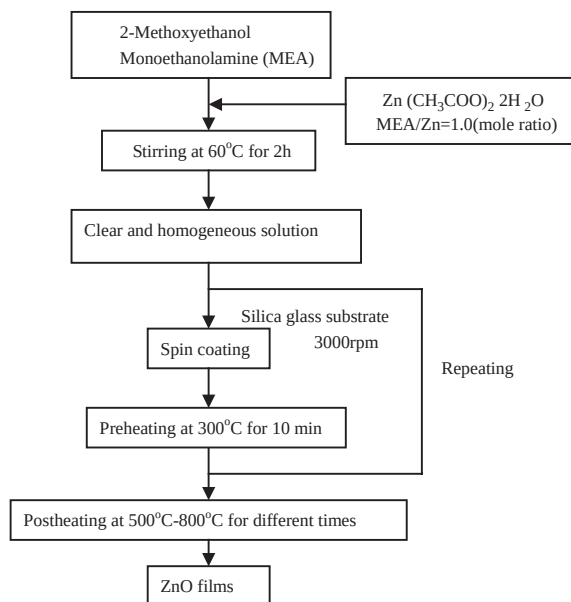


Fig. 1. The flow chart showing the procedure for preparing ZnO films.

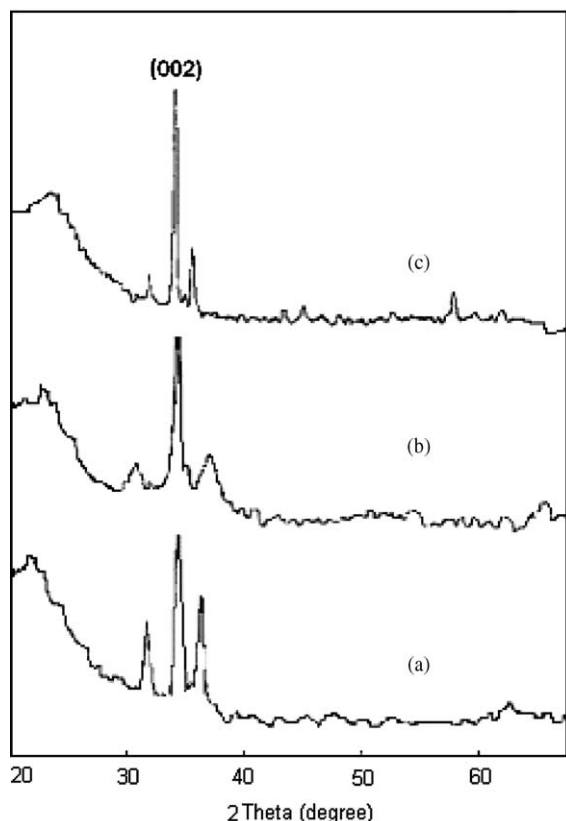


Fig. 2. XRD patterns of ZnO films dried at 300 °C and then heated at various temperatures (a) 400 °C for 1 h, (b) 500 °C for 1 h, and (c) 600 °C for 1 h.

3.2. Optical transmittance results

Fig. 3 shows the optical transmittance of ZnO films annealed at different temperatures on silica glass substrate. The weak fluctuation in the transmission spectrum is due to the interferences in the thin film owing to the reflection at the air–ZnO and ZnO–silica glass interfaces. The films were found to be transparent in the visible range with a sharp absorption edge at wavelengths of about 370 nm, which is very close to the intrinsic band-gap of ZnO (3.3 eV). The average transmittance of the film (a), (b) and (c) in the visible range was about 60%, 70% and 80%, respectively. As shown in Fig. 3, the increase in transmittance with higher annealing temperatures may be due to

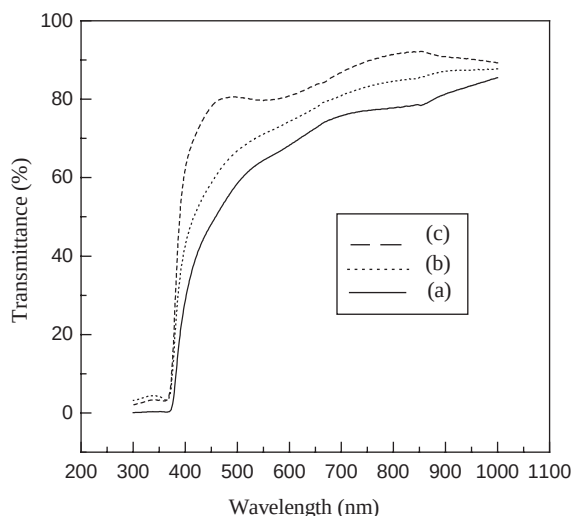


Fig. 3. Optical transmittance spectra of ZnO films fired at (a) 400 °C for 1 h, (b) 500 °C for 1 h, and (c) 600 °C for 1 h.

decreasing optical scattering caused by the densification of grains followed by grain growth and the reduction of grain boundary density.

3.3. The morphology of the ZnO films

Fig. 4 shows the SEM photographs of the surface of ZnO films prepared by postheating at 400, 500 and 600 °C for 1 h, respectively. It is seen in Fig. 4 that the particle size increases with increasing postheating temperature, which is consistent with the XRD results. Compared with the film annealed at 400 °C (Fig. 4a), the packing density of the film increased when annealed at 500 °C (Fig. 4b), which may be due to disappearing gaps between particles. However, the packing density decreased as annealed at 600 °C (Fig. 4c), which may be caused by the evaporation of ZnO. The size of the grains are regular and the microstructure consists of many round shaped particles for the films heated at 400 and 500 °C, as the temperature increases to 600 °C, the grains become larger with hexagonal shape, which is consistent with the ZnO hexagonal wurtzite type. At higher temperature, the atoms have enough activation energy to occupy the correct sites in the crystal lattice and grains with lower surface energy

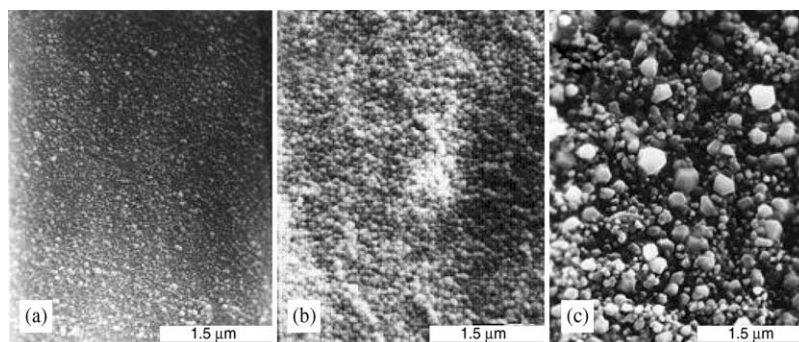


Fig. 4. The SEM photograph of the surface of the ZnO films preheated at 300 °C seven times and postheated at (a) 400 °C for 1 h, (b) 500 °C for 1 h, and (c) 600 °C for 1 h.

become larger, then growth orientation becomes strong and leads to an improvement in the crystallinity of ZnO.

4. Conclusion

The effect of annealing process on the microstructure, transparent properties, and morphology of ZnO films was studied. The peak intensity of the (002) plane increases with increasing postheating temperatures from 400 to 600 °C, at the same time, the average transmittance of the films also increases from 60% to 80% with increasing annealing temperature. The size of the grains is regular and the microstructure consists of many round shaped particles for the films heated at 400 and 500 °C, as the temperature increases to 600 °C, the grains become larger with the shape of hexagonal, which is consistent with the ZnO hexagonal wurtzite type.

Acknowledgements

This work was supported by the significant research project of ministry of education with contract No.03104.

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