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Crystal growth and optical properties with preheating temperature of sol-gel derived ZnO thin films

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Abstract We try to use isopropanol which has low boiling point to prepare ZnO thin films at low temperature. ZnO thin films were prepared by sol-gel spin-coating method using zinc acetate dehydrate-isopropanol-monoethanolamine (MEA) solution. The c-axis preferred orientation and optical properties of ZnO films with preheating temperature have been investigated. ZnO thin films were preheated at 200 to 300°C with an interval of 25°C and post-heated at 650°C. The ZnO film preheated at 275°C and post-heated at 650°C was highly oriented along c-axis (002) plane, and the surface with homogeneous and dense microstructures was formed having nano-sized grains. The optical transmittance was above 90 % in the visible range and exhibited absorption edges at 368 nm wavelength.

Key words Zinc oxide, Sol-gel process, Thin films, Preheating temperature

1. Introduction

ZnO is II-VI group compound semiconductor with a wide band gap of 3.3 eV. Basically, ZnO crystallizes in the hexagonal wurtzite structure (c = 5.21 Å, a=3.25 Å), oxygen ion located in hexagonal site and zinc ion in tetrahedral site [1]. In particular, ZnO films with preferential orientation along the c-axis have been demonstrated to work as surface acoustic wave (SAW) devices because of the large piezoelectric constant [2, 3], and owing to their better stability in hydrogen plasma than that of ITO, ZnO thin films can be used in the fabrication of hydrogenated amorphous silicon solar cells [4]. Besides, ZnO thin films are full of promise for applications in semiconductor gas sensors, varistor, and LED [5].

ZnO thin films have been prepared by various methods of film deposition, such as sputtering [6], pulsed laser deposition [7], chemical vapor deposition [8], spray pyrolysis [9, 10], and sol-gel process [11, 12]. Although physical deposition methods have been extensively used, sol-gel process has distinct advantages over the other techniques due to excellent compositional control, homogeneity on the molecular level.

The preferential orientation and photoluminescence of the ZnO thin films prepared by the sol-gel process have been reported. A solvent of high boiling point like 2-methoxyethalol is likely to help preferred orientation of ZnO films on silica glass substrate. In the meanwhile, the preferred crystal growth does not exhibit by using isopropanol as a solvent which has a low boiling temperature, because of defects such as pores, decomposed organic residues or precipitates in ZnO films [13].

In this study, a solvent of low boiling temperature, isopropanol, is used to promote optical properties and a crystal orientation along (002) plane. ZnO thin films from zinc acetate dihydrate-isopropanol-monoethanolamine (MEA) solution were deposited on glass substrates by the spin-coating method. After that, the ZnO films were carried out heat treatment. Tendency of c-axis growth in the ZnO thin films is investigated as function of preheating temperature. The structural and optical properties are performed by XRD, SEM, XPS, and UV-visible spectrometer.

2. Experimental Procedure

Zinc acetate dehydrate ($Zn(CH_3COO)_2$-$2H_2O$) was first dissolved in a isopropanol ($(CH_3)_2CHOH$)-monoethano-

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lamine (MEA : $H_2NCH_2CH_2OH$) solution at room temperature. The molar ratio of MEA to zinc acetate was kept at 1.0 and concentration of zinc acetate was 0.7 mol/*l*. The resultant solution was stirred at 50°C for 1 h to yield a clear and homogeneous solution, which served as the coating solution after cooling to room temperature. The solution was dropped into glass (Corning Inc. 7059) substrates, which were rotated at 3000 rpm for 20s. After deposited by spin coating, the films were preheated at 200 to 300°C with an interval of 25°C for 10 min over a furnace the solvent and remove organic residuals. The procedures from coating to preheating were repeated five times, giving the final film thickness of 250 nm. The films were then post-heated in furnace in air at 650°C for 1 h. The thermal decomposition behavior of a ZnO sol solution was examined by thermogravimetry-differential thermal analyer (TG-DTA: Seiko Exter 6000). The c-axis orientation in the ZnO thin films was analysized by X-ray diffractometer (Rigaku Rotaflex D/max system). The surface and cross-sectional morphologies of the films were investigated by scanning electron microscopy (SEM : XL30 ESEM-FEG, FEI Company). Surface and chemical bonding states of zinc and oxygen in ZnO thin films were investigated by X-ray photoelectron spectroscopy (XPS) in a VG Microtech (ESCA 2000) with Mg Ka radiation. Optical transmittances were observed using a UV-visible spectrometer (Hitach U3000) and calculated the optical band gap energy.

3. Results and Discussion

Figure 1 shows TG-DTA curves of ZnO sol. Three weight losses were observed at 30~60°C, 100~200°C and 210~250°C. The first weight loss is due to the evaporation of isopropanol, the second and third weight losses were caused by the evaporation of water and the combustion of residual organics and MEA. From these results, the preheating temperature for the gelation of ZnO thin films was decided from 200 to 300°C at an interval of 25°C, and the post-heating temperature for grain growth was set up to 650°C, which considered with softening temperature of glass substrate and the previous reports of heat treatment [9].

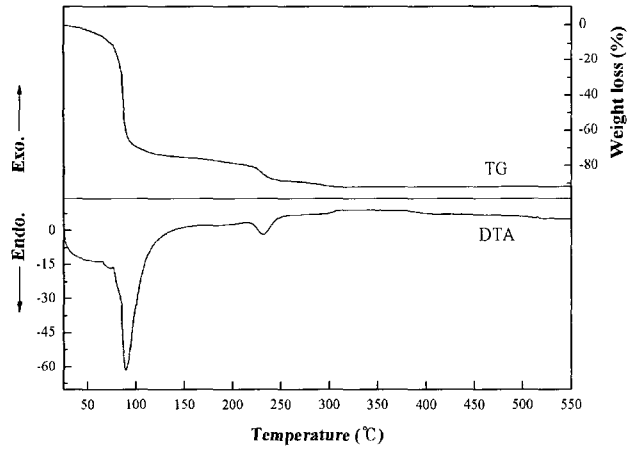

Fig. 1. TG-DTA curves of the 0.7 mol/*l* ZnO sol.

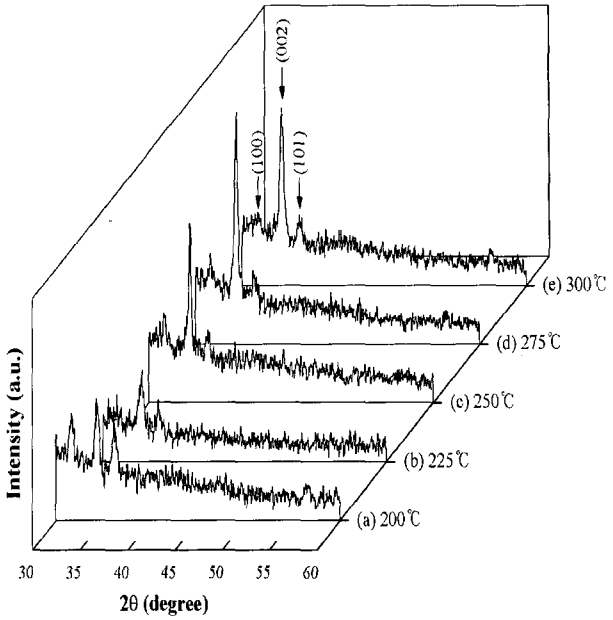

Fig. 2. The XRD patterns of ZnO films preheated at (a) 200°C (b) 225°C (c) 250°C (d) 275°C (e) 300°C and post-heated at 650°C.

XRD patterns of ZnO thin films preheated at different temperatures and post-heated at 650°C for 1h are shown in Fig. 2. In cases of the films preheated at 200 and 225°C, the (100), (002) and (101) diffraction peaks appeared. The (100) and (101) diffraction peaks reduced with increasing preheating temperature above 250°C, while the (002) peak increased strongly. It indicates that the grains preferably grow along the (002) plane. The ZnO thin film preheated at 275°C has a highly preferred orientation along the (002) plane. The film preheated at 275°C was appeared a maximum (002) peak and the (100) and (101) peaks nearly disappeared.

In the study related with c-axis growth from zinc acetate solution [14], the crystallization of ZnO thin films is affected by solvent type, preheating temperature, and post-heating temperature. Since the boiling points of the solvents, isopropanol and MEA are 82.4°C and 170°C, respectively, the preheating temperature as high as 200°C must be required for these solvents to vaporize com-

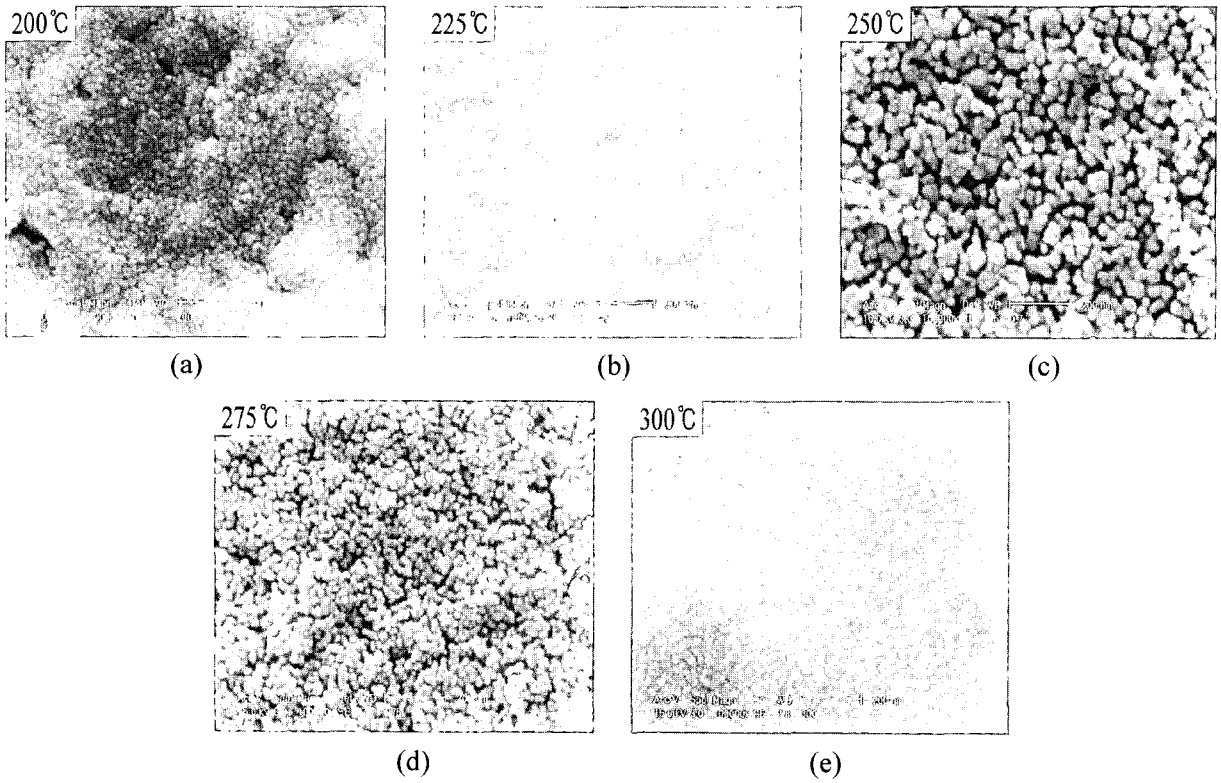

Fig. 3. SEM photographs for the surfaces of the ZnO films preheated at (a) 200°C, (b) 225°C, (c) 250°C, (d) 275°C and (e) 300°C. All the films were post-heated at 650°C for 1 h.

pletely out of the gel film. The thermal decomposition temperature of the zinc acetate is 240°C [15] and the crystallization of the ZnO film prepared from zinc acetate-isopropanol-MEA solutions begins at about 250°C. When the preheating temperature is too high above 300°C, the vaporization of the solvents and the thermal decomposition of zinc acetate will occur abruptly and simultaneously with the crystallization, disturbing the preferred crystal growth. When the preheating temperature is too low below 200°C, on the other hand, the complete vaporization and the thermal decomposition of zinc acetate do not occur at the preheating step. Thus, the preheating temperature is an important factor for preparing ZnO films with a preferred orientation along c-axis, affecting the solvent vaporization, zinc acetate decomposition and ZnO crystal growth [10, 15].

Figure 3 shows SEM photographs for the surface of ZnO thin films prepared by spin-coating at 3000 rpm, preheating at 200 to 300°C for 10 min and post-heating at 650°C for 1 h. The particle size increases from 9 to 25 nm with increasing preheating temperature at 200 to 250°C, and then gradually decreases from 25 to 16 nm up to 300°C. According to the result of Ohyama *et al.* [15], the grain size depends on the post-heating temperature and the grain size increases with increasing post-heating temperature. In this study, we could confirm the grain size increases with increasing preheating temperature. When ZnO gel films are preheated at near 250°C, macro pores are distributed in the surface of the films. This is attributed to the easy evaporation of the solvents and residual organics in gel films. On the contrary, when the gel films are preheated at 275°C, such pores disappear, and the ZnO thin films become denser. The crystallinity of the ZnO film is enhanced as shown in Fig. 2(d), because the decomposition of Zn precursor may occur almost simultaneous nucleation and crystal growth in the films. Thus, the particle size and the crystallinity of the ZnO film slightly decreased with increasing preheating temperature up to 300°C as shown in Fig. 3(e) and Fig. 2(e), respectively. It indicates that the c-axis orientation of the ZnO films is closely related with the decomposition reaction of the precursor, and the successive nucleation and crystal growth in films [13, 15-16].

XPS analysis of ZnO thin films was performed to determine the film stoichiometry and chemical bonding state of the constituent elements. Figure 4 shows the chemical bonding states of zinc and oxygen analyzed by Auger signal in XPS spectrum in the ZnO thin films with preheating at 200 to 300°C for 10 min and post-

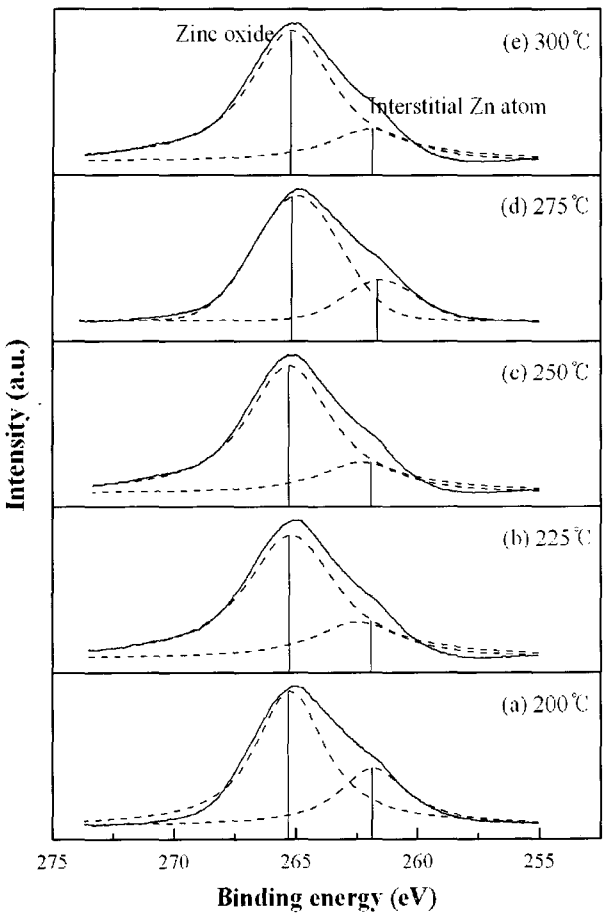

Fig. 4. XPS spectra of narrow range scan of Zn in ZnO films preheated at (a) 200°C, (b) 225°C, (c) 250°C, (d) 275°C and (e) 300°C. All films were post-heated at 650°C for 1 h.

heated at 650°C for 1 h. We did not observe any significant variation in the constituents of the ZnO and interstitial Zn atom with preheating temperatures. However, major peaks were observed at 264.9 eV and shoulder peak at 261.5 eV. The shoulder peak is due to Zn ($L_3M_{45}M_{45}$) of metallic zinc as interstitial zinc atom in the lattice of ZnO crystallites in the film [16-17]. The existence of interstitial metallic zinc indicates the reduction of the free energy for the formation of oxygen vacancies, thus n-type defect structures [18-19].

Figure 5 shows optical transmittance spectra in the wavelength range of 350~850 nm in the ZnO thin films with preheating at 200 to 300°C for 10 min and all films are post-heated at 650°C for 1 h. The optical transmittance in the visible range was about 80~90 % and sharp ultraviolet absorption edges at wavelength of about 368 nm, which corresponds to the intrinsic band gap energy, 3.2 eV of ZnO [15, 19, 21]. In particular, the optical transmittance of the ZnO thin film preheated at 275°C was above 90 % in the wavelength range of 400~500

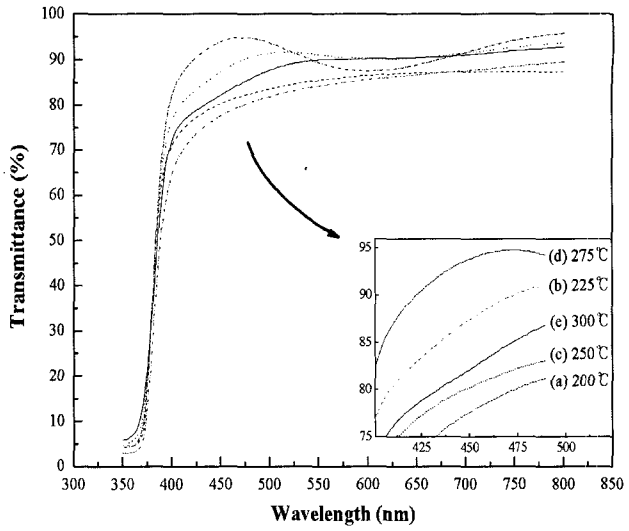

Fig. 5. The optical transmittance spectra of the ZnO films preheated at (a) 200°C, (b) 225°C, (c) 250°C, (d) 275°C, (e) 300°C and post-heated at 650°C.

nm as shown inset. The transmittance increases with increasing preheating temperature from 200 to 275°C and then decreases at 300°C. The high transmittance at the preheating of 275°C corresponds with the XRD results, being highly preferred oriented to c-axis, the transmittance increased. When light is irradiated to polycrystalline structure, which grows along (100), (002) and (101) planes, the transmittance decreases because much light is dispersed in the grain boundary. Consequently, the ZnO thin films highly oriented along to c-axis have high transmittance by decreasing dispersion of light.

In direct transition semiconductor, the absorption edge is given by $\alpha = C(h\nu - Eg)^{1/2}$, where α is the optical absorption coefficient and C is a constant for a direct

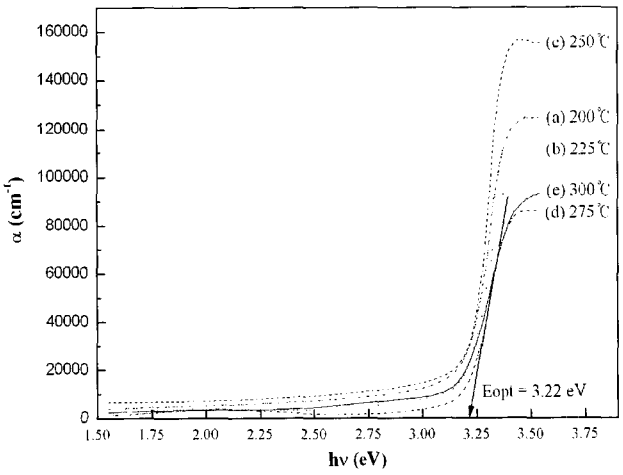

Fig. 6. Absorption coefficient a versus hn plot from the results related to transmittance spectra. Preheated at (a) 200°C (b) 225°C (c) 250°C (d) 275°C (e) 300°C.

transition. The optical absorption coefficient is defined as $I = I_0 \exp(-\alpha t)$ where I is the intensity of the transmitted light, I_0 is the incident light and t is the thickness of the film [22]. Figure 6 shows the α versus $h\nu$ curves of the ZnO films with preheating temperatures, where α presents the absorption coefficient of the ZnO film and $h\nu$ (eV) means the photon energy. Absorption coefficient was calculated from Fig. 5 and the optical energy band gap Eg of ZnO films was obtained by extrapolating downwards the corresponding straight lines till the intersection with the energy axis as shown in Fig. 6. The optical band gap for the films with preheating temperatures showed 3.22~3.24 eV. Absorption edges at wavelength of about 370 nm represent about 3.2 eV. The optical band gap energy is in a good agreement with the value, 3.2 eV for ZnO polycrystalline thin films [19, 21].

4. Conclusions

ZnO thin films were fabricated on glass substrate by the sol-gel spin-coating method and their structural and optical properties with preheating temperatures were investigated. The ZnO thin film preheated at 275°C was highly oriented along to c-axis (002) plane and the film surface with homogeneous and dense microstructures was formed having nano-sized grains. Even though the solvent of low boiling point like isopropanol was used, the thin films with preferred orientation along c-axis were produced by controlling the preheating temperature. As the c-axis crystallinity of ZnO thin films increased, the optical transmittance in the visible range enhanced higher than 90 % and exhibited absorption edges at about 368 nm.

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