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Highly *c*-axis oriented ZnO film on silica glass using zinc naphthenate precursor

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High transmittance and good electrical conductivity thin conducting oxides (TCOs) have potential use in a variety of technological applications including plasma display panels (PDPs), electroluminescent devices, flat cathode ray tube (CRTs) and solar cells [1–4].

Recently, zinc oxide (ZnO) thin films have emerged as one of the most promising oxide materials owing to their optical and electrical properties, together with their high chemical and mechanical stability. ZnO is a wide band gap (3.3 eV) semiconducting, piezoelectric, and photoconducting material.

In particular ZnO films with preferential orientation along the *c*-axis have been shown to work as SAW devices because of large piezoelectric constant. Ohyama *et al.* [5] prepared ZnO films on silica glass substrates from zinc acetate sol containing 2-methoxyethanol and monoethanolamine (MEA) with extremely preferred orientation along (002) plane. Ohya *et al.* [6] reported transparent, electrically conductive ZnO thin films with polycrystalline structure from zinc acetate and alkoxide. Recently Wessler *et al.* [7] reported textured ZnO thin films on (0001) sapphire by spin-coating a sol of acetate and ethanolamine.

In this letter, the preparing of highly *c*-axis oriented ZnO thin film on amorphous silica substrates from a zinc naphthenate precursor is reported. Crystallinity, surface morphology, surface roughness, and optical behavior were studied.

A coating solution was prepared using zinc naphthenate (Nihon Kagaku Sangyo Co., Ltd., Japan) and by diluting the solution with toluene (concentration: 4 wt% metal/100 mL sol). Metal naphthenates are more advantageous than metal alkoxides as starting materials, in terms of cost, stability in air, and ease of handling. Preparation of the coating solution using zinc naphthenate was easily performed by the addition of toluene, while complicated procedures were needed for the preparation of sol from zinc alkoxide [6].

The starting solution was spin-coated onto the cleaned substrate at 1500 rpm for 10 s in air. The as-deposited film was prefired at 500 °C for 10 min in air. The coating process was repeated five times to prepare a thick coating of ZnO. Then the final annealing was performed in air at 1000 °C for 30 min.

The thickness of the heat-treated ZnO thin film was approximately 0.65–0.7 μm, as determined by observations of fracture-cross-sections using a field emission-scanning electron microscope (FE-SEM, S-4700, Hitachi, Japan). Crystallinity and orientation of the thin films were investigated by X-ray diffraction (XRD, D-Max-1200, Rigaku, Japan) analysis in θ-2θ geometry. A Cu K_α ($\lambda = 1.54056$ Å) source was used. The surface morphology and surface roughness of the thin films were evaluated using the FE-SEM and a scanning probe microscope (SPM, PSIA, USA). All the SPM measurements were performed in air using the tapping mode. The absorption coefficient was obtained from the transmittance curve measured by a UV-visible-NIR spectrophotometer (CARY 500 Scan, VARIAN Co., Australia).

Fig. 1 shows the XRD curve and FE-SEM image of the ZnO film. Only the ZnO (002) peak at $2\theta \sim 34^\circ$ was observed. This indicates that the ZnO thin film from zinc naphthenate shows a high *c*-axis orientation. From Ohyama's work [8], for ZnO films prepared by chemical solution deposition (CSD) using zinc acetate-2 methoxyethanol-MEA solution, structural relaxation of the precursor gel before crystallization, by employing solvents of relatively high boiling points of about 200 °C, is necessitated for obtaining strongly preferred oriented thin film. In this letter, boiling point of toluene used as solvent is lower, 110.6 °C, than those of 2-methoxyethanol (125 °C) and MEA (170 °C) used in Ohyama's work. More research is under current investigation to identify the relationship between the film's orientation and the property of naphthenic acid diluted with toluene.

The value of the full width at half maximum (FWHM) of the diffraction peak, 0.194° was comparable to those of highly-textured ZnO thin films prepared by the physical coating method [1]. On the basis of XRD data, the lattice *c* parameter has been estimated to be 5.2039 Å, which is similar to the ASTM value of 5.2066 Å for bulk ZnO [9].

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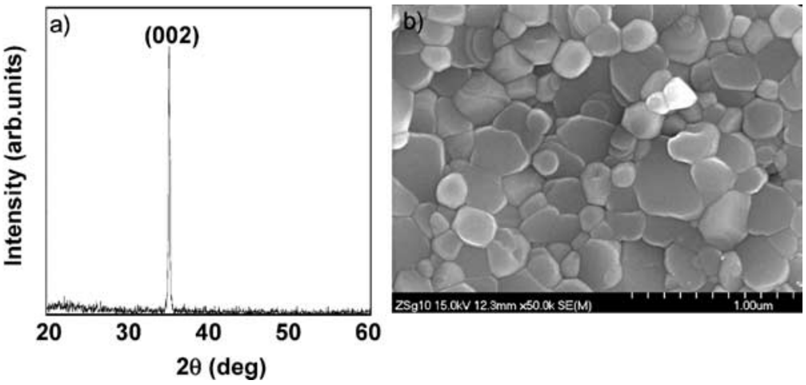

Figure 1 XRD spectra (a) and FE-SEM image (b) of ZnO film on silica glass substrate after annealing.

In the CSD method, pores and cracks are easily recognized in the product films. On the contrary, surface of the film produced in this work had closely packed, well-defined crystals, as shown in Fig. 1b.

To evaluate the surface roughness and morphology of the film, SPM analysis was performed. Fig. 2 shows the SPM top-view images (5 × 5 μm^2) and surface roughness of the silica substrate and ZnO film. The surface of polished silica glass substrate is composed of relatively low-surface roughness with some impurities. After heating at 1000 °C, surface roughnesses of the ZnO film increased by larger grain growth, resulting in higher RMS roughness as shown in Fig. 2b.

The optical absorption coefficient, α, is defined as,

$$I = I_0 e^{-\alpha \mathrm{t}} \qquad (1)$$

where I is the intensity of transmitted light, I_0 is the intensity of incident light, and t is the thickness of ZnO film. As the transmittance is defined as I/I_0, we obtained α from Equation 1. In the direct transition semiconductor, α and optical energy band gap (E_g) are related by [9, 10],

$$\alpha = (hv - E_g)^{1/2} \qquad (2)$$

where, h is Plank's constant, and v is the frequency of the incident photon. Fig. 3 shows the transmittance of ZnO film and the plot of α^2 vs. $\cdot hv$. It was observed that ZnO film exhibits transmittance ranges 60–80% in visible range. The linear dependence of α^2 to hv indicates that ZnO film is the direct transition-type semiconductor. The photon energy at the point where α^2 is zero is E_g. E_g is determined by the extrapolation method [10]. Optical band gap, E_g, is determined to be 3.288 eV. The estimated value of the band gap for the film is within the range reported for films prepared by CSD [11].

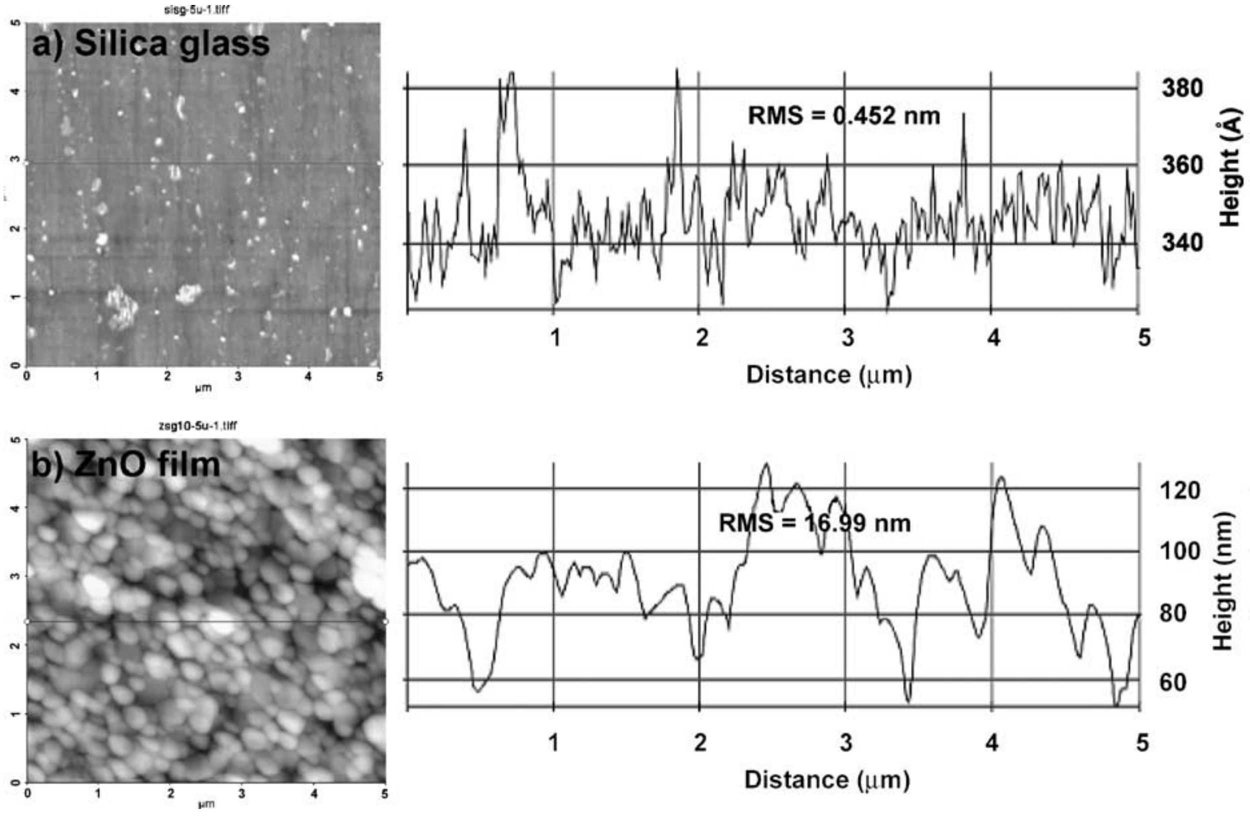

Figure 2 SPM top-view images and line profiles (5 × 5 μm^2) for the substrate (a) and the ZnO film.

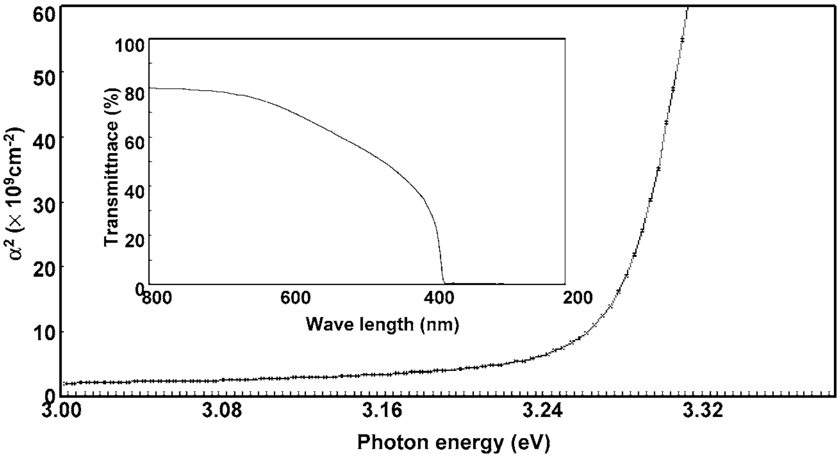

Figure 3 Square of the absorption coefficient as a function of photon energy for the ZnO film and optical transmittance spectra.

In summary, highly *c*-axis oriented ZnO thin film on silica glass substrate was prepared by spin coating—pyrolysis process with a zinc naphthenate precursor. As-deposited films were heat treated at 1000 °C for 30 min in air. Only (002) peak is observed for the sample after annealing at 1000 °C. No evidently aggregated particles are present. From SPM analyses, three-dimensional grain growth, which is thought to be due to *c*-axis oriented grain growth of the ZnO phase, was observed. The estimated energy band gap is within the range reported for films and single crystal.

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