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Nanocrystalline ZnO films on amorphous substrates from zinc naphthenate

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Nanocrystalline zinc oxide thin films were prepared on silica glass and soda-lime-silica substrates from a zinc naphthenate precursor. Films pyrolyzed at 500 °C for 10 minutes were annealed for 30 minutes in air at 600 °C. A field emission scanning electron microscope and an atomic force microscope were used for characterizing the surface morphology and the surface roughness of the ZnO film. A sharp absorption edge of the ZnO film on the silica glass substrate was observed, while it was difficult to obtain an exact result from the ZnO on soda-lime-silica glass.

Key words: ZnO film, zinc naphthenate, absorption edge.

Introduction

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, which is transparent in the visible wavelength range and therefore used in a wide variety of applications, ranging from a transparent electrode material to gas sensors and surface acoustic wave (SAW) guides [1, 2].

Fukushima *et al*. [3] previously reported on the preparation and properties of polycrystalline ZnO films on a glass or fused silica substrates by thermal decomposition of zinc naphthenate. Metal naphthenate was a better material than metal alkoxide as a starting material, in terms of cost, stability in air and ease of handling [4-6]. However, in the previous work [3], little information was given on the surface morphology, roughness and optical band gap of ZnO films formed from metal naphthenate [3]. To investigate the effect of substrates on the surface and optical properties, we prepared ZnO films on soda-lime-silica slide glass (SLSG) and silica glass (SG) from zinc naphthenate.

Experimental

A precursor solution (Concentration: 4 wt% Zn/100 ml sol) was prepared by mixing zinc naphthenate (Nihon Kagaku Sangyo Co., Ltd., Japan) and toluene. Substrates were cleaned in distilled water, immersed in H_2O_2 and rinsed in toluene. The starting solution was spin coated onto the cleaned substrates at 1500 rpm for 10 s. The as-deposited film was pyrolyzed at 500 °C for 10 minutes in air. The coating process was repeated five times to prepare a thicker coating. A final annealing was performed at 600 °C for 30 minutes in air by directly inserting the samples into a preheated tube-type furnace, followed by fast cooling. Transmittance in the visible wavelength range was observed by using a UV-Visible-NIR spectrophotometer (Cary 500 Scan, Varian Co., Australia). The surface morphology of the film was observed with a field emission scanning electron microscope (FE-SEM, S-4700, Hitachi, Japan). The surface roughness of the film was studied with an atomic force microscope (AFM, Nanoscope Multimodel™, AFM-Digital Instruments, U.S.A.). All the AFM measurements were performed in air using the tapping mode with silicon probes having a ~260 kHz resonant frequency.

Results and Discussion

FE-SEM photographs of the free surface for the ZnO films on SG (a) and SLSG (b) annealed at 600 °C are shown in Fig. 1. A fine nano-structure became evident and the surface of the film on SG was homogeneous. However, some cracks probably due to vaporization of organics or diffusion of alkali ions, such as Na or Ca, from substrate during annealing [6] were visible on the surface of the film on SLSG, while the surface of the ZnO film on SG exhibited no defects.

Figure 2(a) and (b) shows the AFM images of the ZnO/SG and ZnO/SLSG, respectively. The surface of

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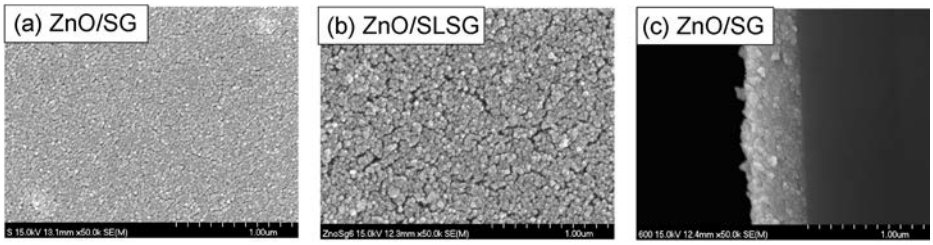

Fig. 1. FE-SEM images of the ZnO thin films on SG (a) and SLSG (b), and fractured-cross section of the ZnO/SG (c).

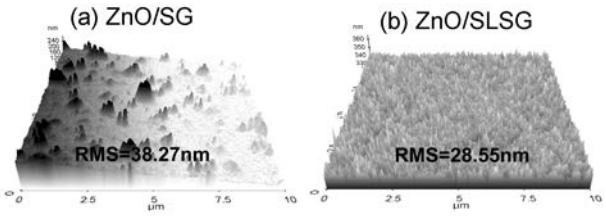

Fig. 2. AFM images and surface roughnesses of the ZnO thin films on SG (a) and on SLSG (b).

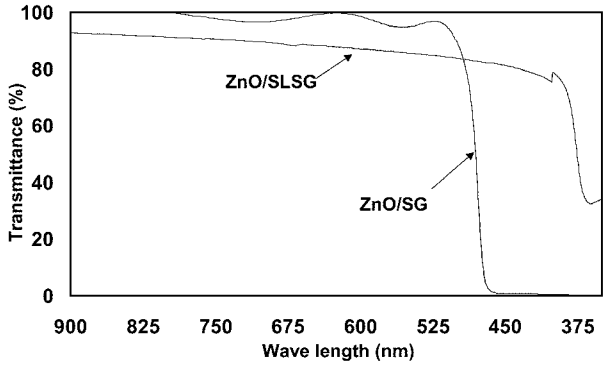

Fig. 3. Transmittance of the ZnO films after annealing at 600 °C.

the ZnO on SG has a relatively high surface roughness with some grain out growth, while the ZnO film on SLSG shows a lower root mean square (RMS) roughness.

Figure 3 shows the visible spectra of ZnO/SG and ZnO/SLSG after annealing at 600 °C. A clear absorption edge of the ZnO film on the SG substrate was observed, while it is difficult to obtain a distinct peak edge from the ZnO film on SLSG. It is noted that a high optical transmittance, above 90%, was obtained for the annealed film on the SG substrate. The high transmittance of the ZnO film in this study is attributed to the small particle size which eliminates light scattering [6]. This fact was supported by the FE-SEM and AFM images (See Figs. 1 and 2). In the case of the ZnO film on SLSG, however, a low transmittance was obtained, although a lower RMS roughness than that of the ZnO on SG was confirmed by AFM. Furthermore, a sharp fundamental absorption edge of the intrinsic band-gap of ZnO [7] had disappeared as shown in Fig. 3. From our previous report, the thermal effect of an SLSG substrate at 550 °C on the TiO_2 film was harmful

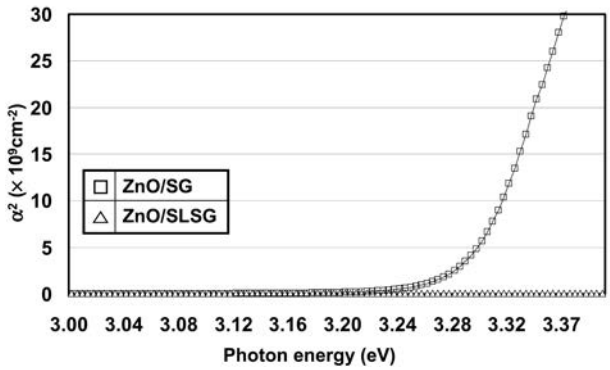

Fig. 4. Square of the absorption coefficient as a function of photon energy for the ZnO films.

to the optical property of the film. The formation of Na_xTiO_2 phases caused by sodium diffusion near the interface between the TiO_2 film and SLSG substrate appeared at 550 °C [6].

The optical absorption coefficient, α, is defined as,

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

where I is the intensity of the transmitted light, I_0 is the intensity of the incident light, and t is the thickness of the ZnO film. As the transmittance is defined as I/I_0, we obtain α from Eq. (1). In a direct transition semiconductor, the α and optical energy band gap (E_g) are related by [8],

$$\alpha = (h\nu - E_g)^{1/2} \quad (2)$$

where, h is Plank's constant, and ν is the frequency of the incident photon. Figure 4 shows the plot of α^2 *vs* $h\nu$. The linear dependence of α^2 on $h\nu$ indicates that a ZnO film on SG is a direct transition-type semiconductor. The photon energy at the point where α^2 is zero is E_g. Then E_g is determined by an extrapolation method [9]. The optical band gap, E_g, is 3.285 eV, as shown in Figure 4. The estimated value of the band gap for the film on SG is very close to the intrinsic band-gap of ZnO (3.2 eV). However, no observable energy band gap was exhibited in the ZnO film on SLSG annealed at 600 °C. We assume that alkali diffusion from the SLSG substrate to the ZnO film during annealing at 600 °C probably affected the optical property of the ZnO film, since the thermal instability of the SLSG substrate at 550 °C was confirmed from the chemical solution derived-TiO_2

films in our previous report [6].

More research will be done to identify chemical composition of ZnO films on SLSG substrates and how this depends on the annealing temperature.

Conclusions

Nanocrystalline zinc oxide thin films were prepared on silica and soda-lime-silica substrates from a zinc naphthenate precursor. Films pyrolyzed at 500 °C for 10 minutes were annealed for 30 minutes in air at 600 °C. The surface of the ZnO on SG had a relatively high surface roughness with some grain out growth, while the ZnO film on SLSG showed a lower RMS roughness. The estimated value of the band gap for the film on SG is very close to the intrinsic band-gap of ZnO (3.2 eV). However, no observable energy band gap was exhibited for the ZnO film on SLSG substrate annealed at 600 °C.

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