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Influence of organics on ZnO coatings prepared by chemical solution deposition

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Abstract

Highly *c*-axis-oriented ZnO thin films were prepared on soda–lime–silica glass substrates by chemical solution deposition process using a zinc-naphthenate precursor as a starting material. In order to investigate the effect of pyrolysis temperature on properties of the films such as crystallinity, surface morphology and transmittance in visible spectra region, the precursor films were pyrolyzed at 300 °C or 500 °C, followed by final heat treatment at 600 °C. Highly transparent films in visible spectra region were obtained. The relationship between residual organics and properties of the annealed films was discussed.

Keywords: ZnO thin film; Chemical solution deposition; Residual organics

1. Introduction

ZnO is II–IV group compound semiconductor, having the wurtzite structure and cheap, abundant and stable materials. Because of its semiconducting, optoelectric, pyroelectric and transparent properties, it is used as varistor, transducer, sensor, infrared reflection films and transparent electrode, etc. [1–5] and in particular those with preferential orientation along the *c*-axis have been demonstrated to work as surface acoustic wave (SAW) devices [6].

In recent years, a number of physical and chemical methods, which including rf sputtering [7], chemical vapor deposition [8] and chemical solution deposition (CSD) [9–15] have been employed to fabricate highly-oriented ZnO films. CSD is a promising technique because of its low processing cost, ease of thickness control and large and complicated surface application. However, films prepared by CSD process frequently exhibited cracks and pores caused by burning of residual organics during pyrolysis and final annealing.

Previously, in order to examine whether the crystallinity of PZT films was affected by the elimination mode of organics, pyrolysis temperature was varied from 200 °C to 500 °C. Effects of residual carbon in the precursor on properties of the annealed films were investigated in previous work [16].

In this work, we report on the effect of organics in precursor ZnO layers prepared by CSD process using a metal naphthenate. Since ZnO has a wide energy band gap and relatively low cost, fabrication of *c*-axis-oriented ZnO films is attractive. Surface roughness and transmittance were also investigated.

2. Experimental

A homogeneous coating solution was prepared by mixing zinc-naphthenate and toluene. To adjust the concentration and viscosity for depositing smooth films, an additional toluene was annexed (concentration: 8 wt.% Zn/100 mL sol). Soda–lime–silica glasses were cleaned in distilled water, immersed in H_2O_2 and finally rinsed by toluene. The starting solution was

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spin-coated onto the substrates at 1500 rpm for 10 s in air. The as-deposited films were pyrolyzed at 300 °C for 30 min or at 500 °C for 10 min in air, in order to examine whether the property of ZnO films is affected by the elimination mode of organic components.

The spin coating and pyrolysis were repeated five times to adjust the thickness of the precursor films. These pyrolyzed films were finally heat treated at 600 °C for 30 min in air.

Thermogravimetric analysis (TGA, TGA2950, TA Instruments, U. S. A.) of the starting solution was also performed for each of the prefiring conditions. The thickness of ZnO films was about 0.65–0.70 μm, confirmed by observation of the fractured-cross section of the films with a field emission-scanning electron microscope (FE-SEM, S-4700, Hitachi Co., Japan). Crystallinity of the films was examined by high resolution X-ray diffraction (HRXRD, X'pert PRO, Philips, Netherlands). A scanning probe microscope (SPM, XE-200, PSIA, Korea) was used to analyze the surface morphology of the films. Chemical composition was observed by FE-SEM with energy dispersive X-ray spectroscope (EDS). Transmittance in the visible spectra region was analyzed by UV spectrophotometer (Cary 500 Scan, Varian Co., Australia).

3. Results and discussion

Fig. 1 shows TGA curve of the starting solution (heating rate: 3 °C/min). Weight loss corresponding to vaporization of the solvent and pyrolysis of the zinc-naphthenate began at below 100 °C and completed at above 460 °C. Therefore, pyrolysis of the starting zinc-naphthenate solution is concluded to complete at about 500 °C. As seen in Fig. 1, the temperature of 300 °C corresponds to the intermediate stage of the pyrolysis. The weight decrease at 300 °C was found and weight loss about 55.3 wt.% was obtained. This value is smaller than that 96.9 wt.% by gradual heating to 500 °C. So larger amount of hydrocarbon is supposed to still remain in the precursor film after pyrolysis at 300 °C. All the precursor films, pyrolyzed through two ways, were found smooth surfaces without cracks or voids by FE-SEM observation and significant difference was not recognized among these films. There were differences, however, about the content of residual carbon or carbon hydroxides in the precursor films.

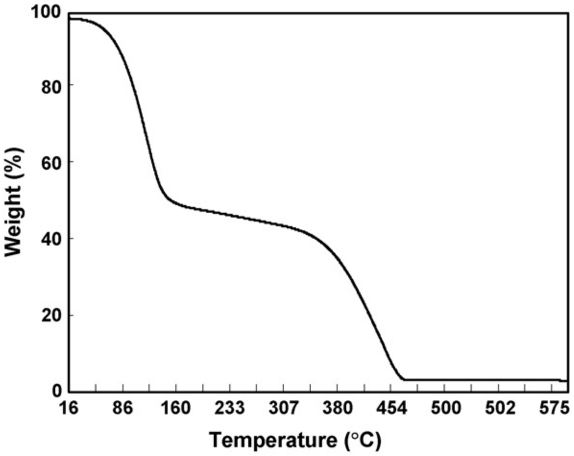

Fig. 1. TGA curve of the coating sol.

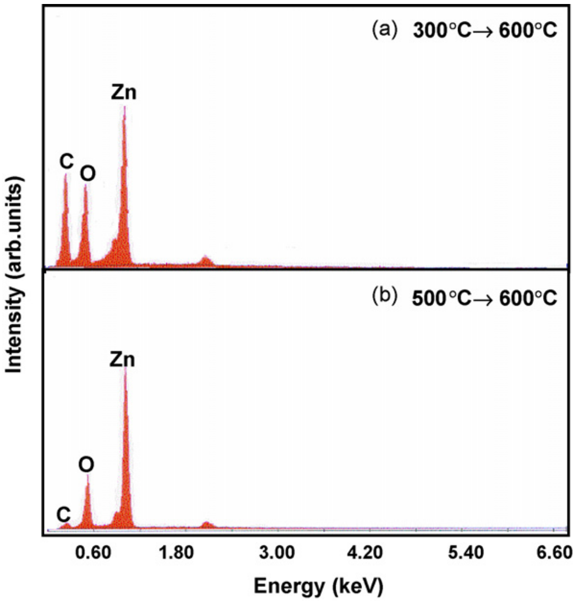

Fig. 2. EDS spectra of precursor films pyrolyzed at 300 °C for 30 min (a) or at 500 °C for 10 min (b), respectively.

Residual carbon in the films was investigated by EDS. Fig. 2(a and b) shows EDS spectra of the precursor films pyrolyzed at 300 °C for 30 min and at 500 °C for 10 min, respectively. Comparing these two spectra, an apparent large peak of C Kα was recognized in Fig. 2(a). It is difficult to obtain quantitative data of carbon content by FE-SEM-EDS with a UTW detector if the sample is not bulk but thin film and carbon signal is also generated from carbon contamination during irradiation of electron beam. It is apparent, however, that precursor films pyrolyzed at 300 °C for 30 min contained a larger amount of carbon than those pyrolyzed at 500 °C for 10 min from the results of Fig. 2(a and b). It should be noted that most of residual carbon in precursor films pyrolyzed at 300 °C for 30 min had been eliminated at final heat treatment. EDS spectrum of the ZnO films pyrolyzed at 300 °C for 30 min or at 500 °C for 10 min, followed by final heat treatment at 600 °C for 30 min gave similar spectra, not shown here. There

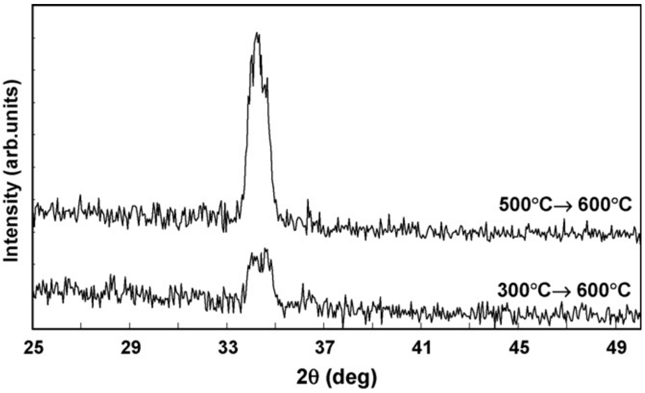

Fig. 3. XRD θ–2θ scans of the ZnO films pyrolyzed at 300 °C or 500 °C, followed by final heat treatment at 600 °C.

are no significant peaks of residual carbon in finally heat-treated ZnO.

Fig. 3 shows XRD θ–2θ scans of the product films pyrolyzed at 300 °C for 30 min and at 500 °C for 10 min, followed by final heat treatment at 600 °C for 30 min. The (0 0 2) oriented ZnO thin films were obtained by final heat treatment at 600 °C, and no significant evidence of misoriented peaks such as (1 0 0) or (1 0 1) phases was observed. Films after pyrolysis at 300 °C and 500 °C were found to be amorphous, not shown here. In previous work [17], highly-oriented ZnO films prepared by CSD with a zinc acetate–2-methoxyethanol–monoethanolamine solution could be explained by structural relaxation of the films as a function of vaporization rate of the solvent, resulting in dense precursor films and preferred crystal orientation. However, in our previous work [9], structural relaxation of the precursor gel before crystallization, by employing solvents having a high boiling point (about 200 °C), is unessential for obtaining highly-oriented ZnO films when using a zinc-naphthenate precursor. The boiling point of the toluene used in our work was much lower, 110.6 °C, than those of solvents used in the work by Ohyama et al. [17].

It should be noted that the peak intensity of the films was affected by pyrolysis temperature although the final heat-treatment temperature was the same. The lower peak intensity of the annealed film pyrolyzed at 300 °C for 30 min (see Fig. 3) may be attributed to the presence of residual organics. EDS results for the pyrolyzed films indicated that the ZnO film pyrolyzed at 300 °C for 30 min was assumed to contain some residual carbon or carbon hydroxides. In this case, crystallization of the films and decomposition of organics concurrently proceeded during final heat treatment. Crystal growth may be suppressed by residual carbon during the final heat treatment, resulting in the low peak intensity of ZnO film.

Fig. 4 shows the SPM images (5 μm × 5 μm) of ZnO films pyrolyzed at 300 °C for 30 min (a) and at 500 °C for 10 min (b), followed by final heat treatment at 600 °C for 30 min. The surface of the film pyrolyzed at lower temperature has relatively low surface roughness. At 500 °C, the surface roughness of the film increased due to larger grain growth, resulting in higher root mean square (RMS) roughness. Surface morphology of the films was found to depend chiefly on their crystallinity. Optimum surface morphology, i.e., a smooth and homogeneous texture, was obtained at lower crystallinity. This may be attributed to an effect of residual carbon in the film pyrolyzed at 300 °C for 30 min, e.g., by giving rising to a suppression of excessive grain growth and a reducing atmosphere in the final heat treatment.

Fig. 5 shows transmission spectra of the ZnO films pyrolyzed at 300 °C (a) and 500 °C (b), followed by final heat treatment at 600 °C. All ZnO films exhibited a higher transmittance (>85%) in the visible spectra region. The visible transmittance was further higher than those of previous works performed by physical dry method [18,19]. A sharp absorption edge at wavelengths about 390–380 nm was very close to the intrinsic band gap of ZnO (3.2 eV). The film pyrolyzed at lower temperature, 300 °C, showed a shift towards the UV range in the absorption threshold. Generally, a film consisting of fine crystallites showed a 'blue shift' [20]. A comparison of absorption threshold between the films pyrolyzed at 300 °C and at 500 °C showed a blue shift in the film pyrolyzed at lower temperature. The blue shift is considered to be due to fine grain growth.

In this work, the pyrolyzing temperature was varied from 300 °C to 500 °C, in order to examine whether the properties of finally annealed films are affected by the elimination mode of organics. The films pyrolyzed at higher temperature for a short time, i.e., at 500 °C for 10 min, exhibited higher crystallinity after the same final annealing at 600 °C. However, although low-temperature pyrolysis lowed the crystallinity of the annealed films if the final annealing temperature was the same, a smooth texture was obtained at lower pyrolysis temperature.

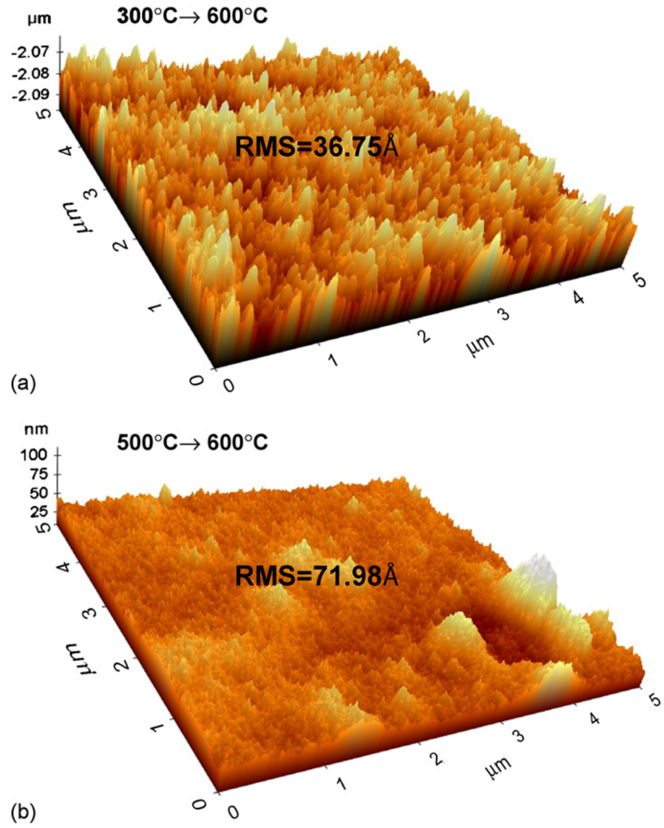

Fig. 4. SPM images of the ZnO films pyrolyzed at 300 °C (a) or 500 °C (b), followed by final heat treatment at 600 °C.

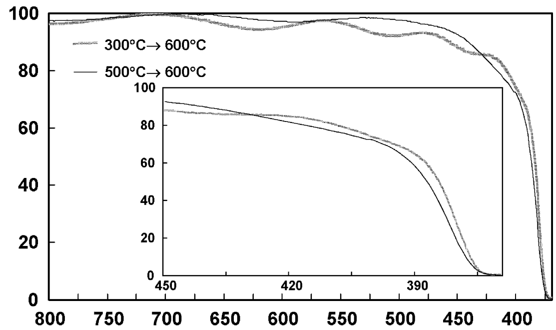

Fig. 5. Transmittance of ZnO films pyrolyzed at 300 °C or 500 °C, followed by final heat treatment at 600 °C.

4. Conclusions

Fabrication of ZnO thin films using a zinc-naphthenate precursor as a starting material was performed by CSD. Effect of the pyrolysis temperature on the crystallinity, surface roughness and transmittance in visible spectra region was discussed. Precursor film pyrolyzed at 300 °C for 30 min contained a larger amount of carbon than those of the film pyrolyzed at 500 °C for 10 min. The lower XRD peak intensity and smoother surface of the film pyrolyzed at 300 °C may be attributed to the presence of residual organics. A comparison of absorption threshold between the films pyrolyzed at 300 °C and at 500 °C showed a blue shift in the film pyrolyzed at lower temperature.

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