

Effect of pyrolysis temperature on ZnO films prepared by chemical solution deposition

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ZnO thin films were prepared on soda-lime-silica glass substrates by a chemical solution deposition process using zinc naphthenate. To investigate the effect of pyrolysis temperature, the precursor films were pyrolyzed at 200 °C for 60 minutes or at 500 °C for 10 minutes, followed by a final heat treatment at 600 °C. Films highly transparent in the visible range were obtained. The relation between residual organic components and the properties of the films are discussed.

Key words: ZnO thin film, Chemical solution deposition, Residual organic components.

Introduction

Because of its semiconducting, optoelectric, pyroelectric and transparent properties, ZnO is used as a varistor, a transducer, a sensor, in infrared reflection films and as transparent electrodes etc. [1-5] and in particular films of ZnO with a preferential orientation along the *c*-axis have been demonstrated to work as surface acoustic wave (SAW) devices [6].

In recent years, a number of methods, including *rf* sputtering [7], chemical vapor deposition [8] and chemical solution deposition (CSD) [9-11] have been employed to fabricate ZnO coatings. CSD is a promising technique because of its low processing cost, ease of thickness control and ability to make complicated surface coatings.

Previously, to examine whether the property of PZT films is affected by the mode of elimination of organic components, the pyrolysis temperature was varied from 200 °C to 500 °C. The effect of residual carbon in the precursor on the properties of the films was investigated in previous work [12].

In this work, we report on the effect of organics in precursor ZnO coatings prepared by a CSD process using a metal naphthenate on the properties of the films. The surface roughness and transmittance were investigated.

Experimental

A homogeneous coating solution was prepared by mixing zinc naphthenate and toluene. To adjust the concentration and viscosity to deposit smooth films, more toluene was added (concentration: 8 wt% Zn/100 ml sol). Soda-lime-silica glass substrates were cleaned in distilled water, immersed in H₂O₂ and finally rinsed with toluene. The starting solution was spin-coated onto the substrates at 1500 rpm for 10 s in air. The coated films were pyrolyzed at 200 °C for 60 minutes or at 500 °C for 10 minutes in air, in order to examine whether the property of ZnO films is affected by the mode of elimination of organic components.

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

Thermogravimetric analysis (TGA, TGA 2950, TA Instruments, U.S.A.) of the starting sol was performed for each of the pyrolysis conditions. The thickness of ZnO films was about 0.4 μm, confirmed by observation of the fractured cross sections of the films with a field emission scanning electron microscope (FE-SEM, S-4700, Hitachi Co., Japan). A scanning probe microscope (SPM, XE-200, PSIA, Korea) was adopted to analyze the surface morphology of the films. Transmittance in the visible spectral region was analyzed by UV spectrophotometer (Cary 500 Scan, Varian Co., Australia).

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Results and Discussion

Figure 1 shows TGA curve of the starting solution (heating rate: 3 K·minute⁻¹). Weight loss corresponding to vaporization of the solvent and pyrolysis of the zinc naphthenate began at below 100 °C and was completed at above 460 °C. Therefore, pyrolysis of the starting sol is concluded to complete at about 500 °C. As seen in Fig. 1, a temperature of 200 °C corresponds to the initial stage of the pyrolysis. The weight decrease at 200 °C was determined to be about 50.4 wt%. This value is very much smaller than 96.9 wt% achieved by gradual heating to 500 °C. So a larger amount of hydrocarbon is expected to still remain in the precursor film after pyrolysis at 200 °C.

The precursor films, pyrolyzed through the above two annealing paths, were found to have smooth surfaces without cracks or voids by FE-SEM observation and a significant difference was not recognized between these films. There were differences, however, about the content of residual carbon or carbon hydr-

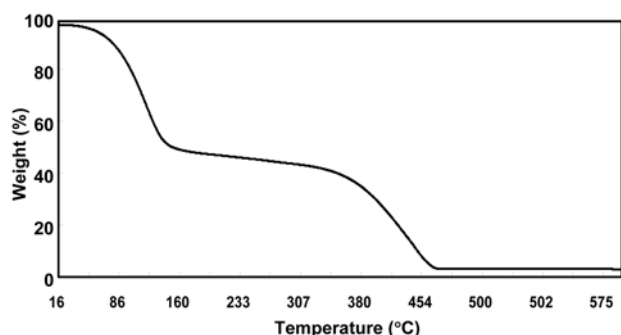


Fig. 1. TGA curve of the starting sol.

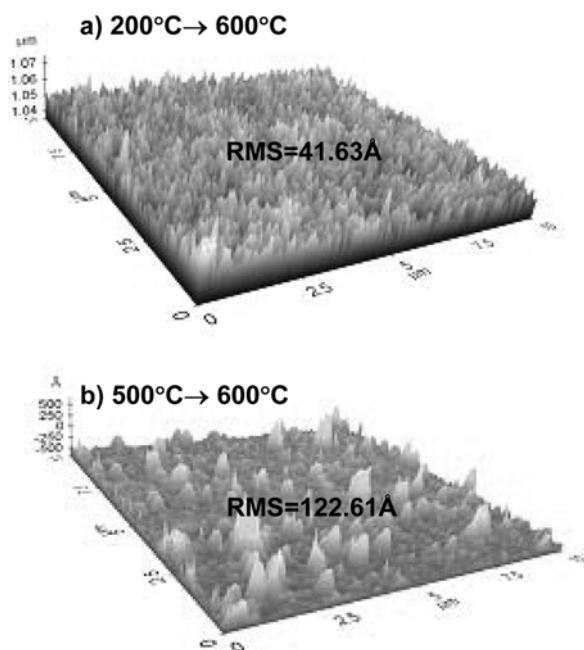


Fig. 2. SPM images of the ZnO films pyrolyzed at 200 °C (a) and 500 °C (b), followed by a final heat treatment at 600 °C.

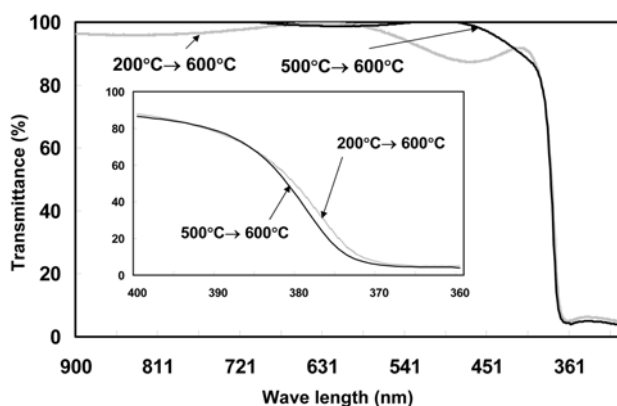


Fig. 3. Transmittance of ZnO films pyrolyzed at 200 °C and 500 °C, followed by a final heat treatment at 600 °C.

oxides in the precursor films, as shown in Fig. 1.

Figure 2 shows SPM images (10×10 μm²) of ZnO films pyrolyzed at 200 °C (a) and 500 °C (b), followed by a final heat treatment at 600 °C. The surface of the film pyrolyzed at the lower temperature had a relatively low surface roughness. At 500 °C, the surface roughness of the film had increased greatly due to a larger amount of grain growth, resulting in a higher root mean square (RMS) roughness. This may be attributed to the effect of the residual carbon in the film pyrolyzed at 200 °C, e.g., which suppresses excessive grain growth and creates a reducing atmosphere in the final heat treatment. Crystal growth may be suppressed by the residual carbon during the final annealing for the ZnO pyrolyzed at 200 °C [12].

Figure 3 shows transmission spectra of the ZnO thin films pyrolyzed at 200 °C and 500 °C, followed by a final heat treatment at 600 °C. It was observed that all ZnO films exhibit a transmittance higher than 90% in the visible region. The visible transmittance of our films is greater than those from previous work created by a dry physical method [13]. A sharp absorption edge at a wavelength of about 390–380 nm is very close to the intrinsic band-gap of ZnO (3.2 eV). The film pyrolyzed at the lower temperature, 200 °C, showed a shift towards the UV range in the absorption threshold. Generally, a film consisting of fine crystallites shows a ‘blue shift’ [14]. A comparison of the absorption thresholds between the films pyrolyzed at 200 °C and at 500 °C shows a blue shift in the film pyrolyzed at lower temperature. The blue shift is considered to be due to the fine-grain structure.

Conclusions

The effect of the pyrolysis temperature during the process on the surface roughness and transmittance in the visible region were discussed. Precursor films pyrolyzed at 200 °C for 60 minutes contained a larger amount of carbon than those pyrolyzed at 500 °C for 10 minutes. A comparison of absorption thresholds bet-

ween the films pyrolyzed at 200 °C and at 500 °C shows a blue shift in the film pyrolyzed at the lower temperature.

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