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Preparation of tin oxide monolith by the sol–gel method from inorganic salt

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Tin oxide monolith was prepared by a sol–gel process using inorganic salt as a starting material. The tin oxide prepared had no aggregations visible to the naked eye and was very transparent in the visible wavelength even after heating in air at 600 °C. It was confirmed from X-ray diffraction results that the crystal structure of the tin oxide was of the rutile type. The crystal size changed from 1.4 nm to 23.5 nm as the heating temperature increased from room temperature to 700 °C, indicating a possibility to control the crystal size.

1. Introduction

The sol–gel process is often used to fabricate metal oxide films or powders from metal alkoxide without any large-scale apparatus. Many researchers have prepared silica monoliths, such as plates or rods. Tin oxide film is transparent in the visible range and is electroconductive. Therefore, it has been used as transparent electrodes, heat insulators and infrared reflectors. Usually, tin oxide film is prepared by techniques such as chemical vapour deposition [1, 2], splaying [3–9] and sputtering [10–12]. However, it is difficult to prepare large, strong and homogeneous tin oxide monoliths by these methods, which moreover, are neither simple nor easy. Therefore, it seems attractive to prepare tin oxide monoliths by the sol–gel process. The preparation of tin oxide by this process using tin alkoxide as a raw material has already been reported [13, 14]. However, the transparency and electrical conductivity of the resultant oxide film were unsatisfactory, because some alcohol derived from hydrolysis of the alkoxide remains in the oxide. If tin inorganic salt, which is readily available and inexpensive, is used as a starting material, the formation of pure tin oxide can be expected. Kodaira *et al.* [15] and Furusaki *et al.* [16] reported studies on the preparation of tin oxide by the sol–gel process using tin inorganic salt as starting material. However, the purity of the resultant tin oxide film was not high enough, because polyvinyl alcohol was added to the tin oxide sol solution in order to avoid crack formation. Orel *et al.* [17] also prepared tin oxide from tin salt [17]. However, tin oxide cracked or was pulverized as the water content of the oxide decreased. In this study, attempts were made to prepare stronger tin oxide monolith by the sol–gel process using only $SnCl_4 \cdot xH_2O$.

2. Experimental procedure

Aqueous NH_3 solution (6 M) was added to 0.2 M aqueous $SnCl_4$ solution until the pH of the mixture reached 7, where white tin hydroxide precipitate was produced. The precipitated hydroxide was aged for 12 h, filtered, and washed with distilled water. Aqueous NH_3 solution (6 M) was added to the precipitate until the pH of the mixture reached 10. Over a period of 12 h, this mixture became clear. This clear sol was put into a polystyrene petri dish and converted to a transparent gel monolith by slow dehydration under an ambient atmosphere. Attempts were made to prepare a monolith with a size of about 10 mm × 10 mm × 1 mm. The monolith thickness could be controlled by the amount of sol put into the petri dish. For the ultraviolet–visible (UV–VIS) absorption measurements, the sol was coated on a silica plate by the dipping process. UV–VIS absorption spectra were recorded on a Hitachi U-3500 photometer. X-ray diffraction (XRD) patterns were measured using a Shimadzu XD-D1 instrument with CuK_α radiation and a nickel filter (30 kV, 20 mA). Infrared (IR) absorption spectra were recorded on a Shimadzu FT-IR-8100-M Fourier transform–infrared spectrophotometer for samples diluted with KBr powder. Thermogravimetric (TG) analysis was performed with Rigaku-2000 in an air atmosphere at a heating rate of 10 °C min^{-1}. Pulverized gel was used for XRD, IR and TG measurements.

3. Results and discussion

The resultant monolith was mechanically strong. Fig. 1 shows a photograph of tin oxide gel monolith without a substrate. The film is transparent. The clear sol was coated on a silica plate for UV–VIS absorption measurements. Furusaki *et al.* [16] reported that

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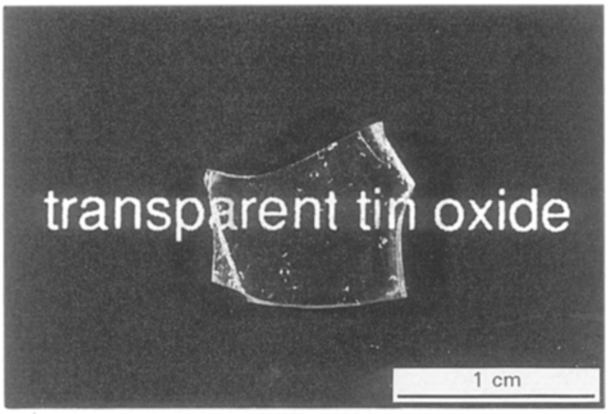

Figure 1 Photograph of tin oxide gel monolith.

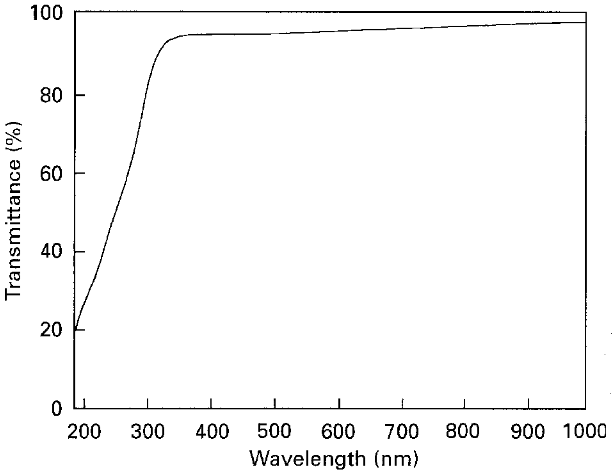

Figure 2 UV–VIS absorption spectrum of tin oxide film coated on a silica plate. The thickness is about 10 μm.

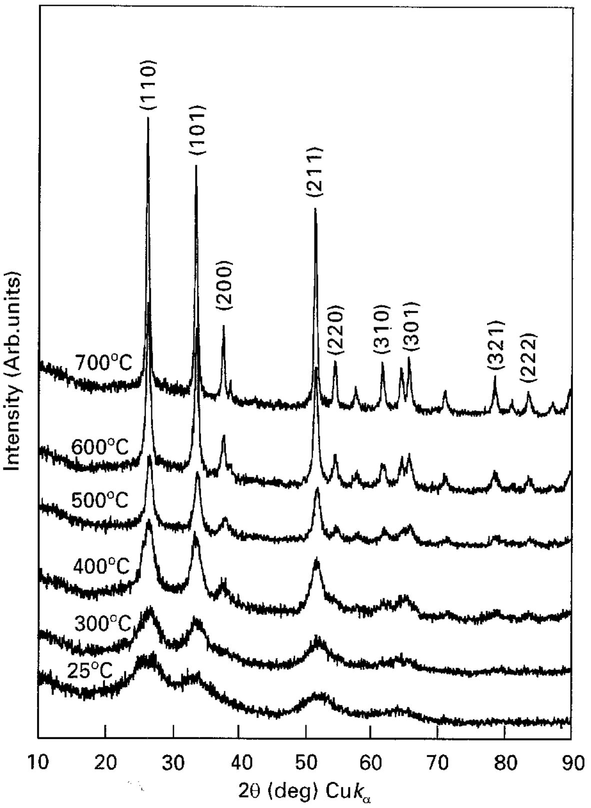

Figure 3 XRD patterns of tin oxide heated in air for 2 h. The heating temperatures are shown.

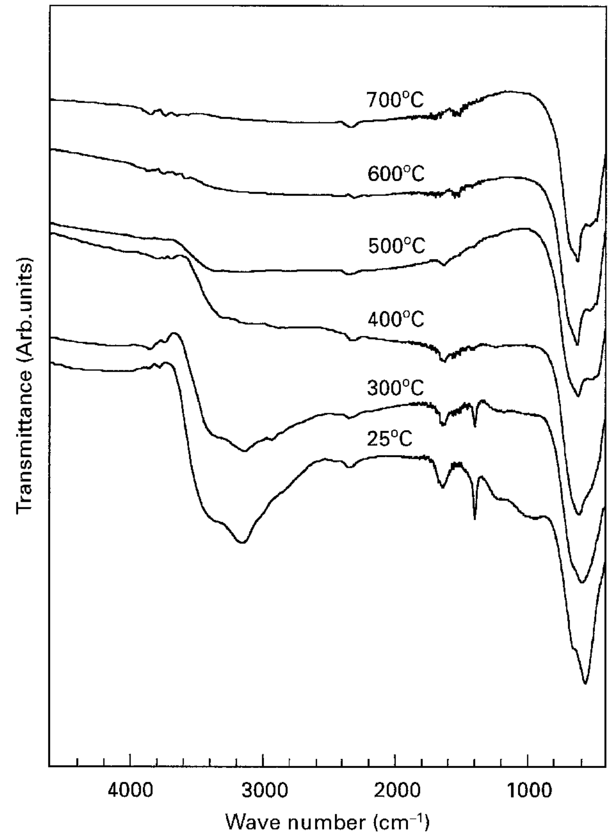

Figure 4 IR spectra of tin oxide heated in air for 2 h. The heating temperatures are shown.

a coated film cracked and peeled off the plate without the addition of PVA. In contrast, our film remained unbroken, even after heating to 700 °C. It seems that aqueous ammonia, which was added to the white tin hydroxide precipitate, enhanced the strength of the coated film. Fig. 2 shows the UV–VIS absorption spectrum of tin oxide film coated on the silica plate. The film exhibited high transmittance for light ranging from the ultraviolet to the near infrared.

Fig. 3 shows XRD patterns of tin oxide gel film heated in air. Many peaks appeared over a wide range from 10°–90°. These are attributed to rutile-type crystals of tin oxide. The intensity of the peaks increased and the line width decreased with heating temperature. Crystallite sizes calculated from the (1 1 0) peak by Scherrer's equation are 1.4 (25 °C), 2.1 (300 °C), 4.0 (400 °C), 6.6 (500 °C), 13.3 (600 °C) and 23.5 nm (700 °C), respectively. Fig. 4 shows IR spectra of tin oxide films heated at 25–700 °C. Peaks at 3700–3000, 3150, 1640 and 1400 cm^{-1} are assigned to –OH stretching, –NH stretching of ammonia, –OH deformation of physically adsorbed water and –NH deformation of ammonia, respectively [18]. These peaks were reduced as heating temperature increased. Above 400 °C, the peaks due to ammonia and physically adsorbed water disappeared. The broad peak at 3700–3000 cm^{-1} was almost extinguished above 600 °C. The OH group chemically bound to tin was eliminated above 600 °C. Peaks at about 620 and 540 cm^{-1} are attributed to Sn–O stretching modes of Sn–O–Sn and Sn–O–H, respectively [19]. As the

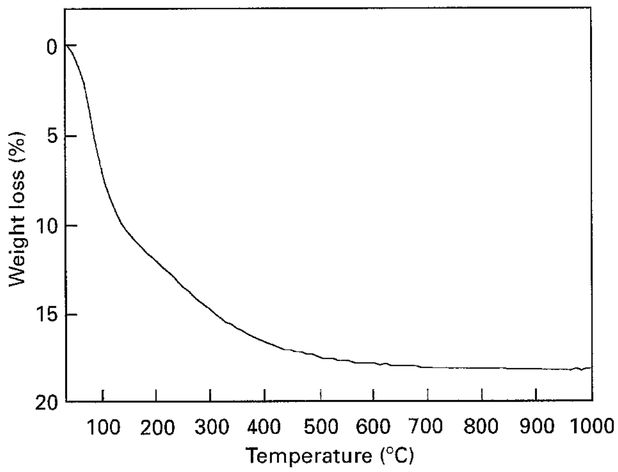

Figure 5 TG curve of tin oxide heated in an air atmosphere at 10 °C min^{-1}.

heating temperature increased, the peaks at about 620 and 540 cm^{-1} became strong and weak, respectively, indicating that the following reaction occurred on heating

$$\text{Sn–O–H} + \text{H–O–Sn} \rightarrow \text{Sn–O–Sn} + H_2O \qquad (1)$$

Fig. 5 shows the TG curve of tin oxide gel powder. The TG curve shows a marked weight loss with heating temperature. Above 700 °C, the weight did not change. The weight loss was due to elimination of ammonia, physically adsorbed water and water from Sn–O–H. This result agreed with the IR results. Specific resistivity of the coated film as used in Fig. 2 was measured by a conventional four-point method. The value reached about 50 Ωcm. Although this is larger than those (10^{-2}–10^{-4} Ωcm) of indium tin oxide glass or antimony-doped tin oxide film, it is expected that the specific resistivity of the present tin oxide film will approach those values if doped with indium or antimony.

4. Conclusion

Electrically conductive, transparent tin oxide monoliths were easily prepared by a sol–gel process using inorganic salt as a starting material. The crystal structure of the tin oxide was of the rutile type. The crystallite size, 1.4–23.5 nm, was dependent on the heating temperature.

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