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Low temperature deposition of SnO_2 thin films as transparent electrodes by spray pyrolysis of tetra-*n*-butyltin(IV)

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Abstract

Low temperature deposition of SnO_2 thin films from tetra-*n*-butyltin(IV) was investigated by a spray pyrolysis deposition (SPD) technique. The substrate temperature was successfully reduced as low as 340°C by adding H_2O_2 to the source solution. The role of H_2O_2 is to promote SnO_2 formation not only by inducing an oxygen atmosphere during the pyrolysis of tetra-*n*-butyltin(IV) but also by producing tin peroxide complexes in the source solution. The average transmittance of the film exceeded 80% in the visible light region, and the electrical resistivity was lowered to 1.5×10^{-3} Ω cm, which is attributed to the high crystallinity. These findings lead to the possibility that a new substrate with lower melting point would be applicable to this SPD technique.

Keywords: Electrical properties; Electron microscopy; Films; Grain growth

1. Introduction

Tin(IV) oxide (SnO_2) is an oxygen defect *n*-type semiconducting material, which exhibits high infrared reflectance as well as high visible light transmittance due to a wide band gap.[1] Its electrical and optical properties are then easily handled by a carrier doping. This material is so hard and chemically stable that SnO_2 thin film has been utilized as a transparent resistor, heater and coating for an optical absorbent, abrasion resistance and antistat. Recent interest has focused on the application of a SnO_2 transparent electrode to electronic devices such as electrochromic, electroluminescent, photovoltaic and gas sensing.[2,3] In order to spread these devices into a practical use, an industrial and a low cost thin film processing system should be developed. Among many processing techniques, a spray pyrolysis deposition (SPD) technique is the most promising one, since the film formation is carried out in air by a simple apparatus. The complicated vacuum system such as CVD and sputtering is no longer necessary in the SPD system.

We have reported SnO_2 thin film syntheses from organotin compounds by a SPD technique.[4–6] The films prepared from di-*n*-butyltin(IV) diacetate showed three characteristic features, that is, high transmittance in the visible light region, high electrical conductivity and high crystalline orientation along the [200] direction.[4] On the other hand, the oriented growth along the [101] direction was observed for films deposited from tetra-*n*-butyltin(IV).[5] The mechanism of the crystallization was explained by the atomic configuration of the grown surfaces originated from molecular structures of organotin compounds.[6]

In this paper, we report a low temperature synthesis of SnO_2 thin films from tetra-*n*-butyltin(IV) by a SPD technique. The substrate temperature was successfully reduced as low as 340°C by adding H_2O_2 to the source solution without losing the three excellent features mentioned above. This finding suggests that novel substrates with lower melting point would be employed in the SPD technique and that various electric devices would be spread widely in our life at reasonable cost.

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2. Experimental

Tetra-*n*-butyltin(IV) (0.1 mol/l) (95% purity, Wako Pure Chemical Industries, Ltd.), abbreviated as TBT hereafter, ethanol solutions with additives of H_2O_2 (30% purity, Wako Pure Chemical Industries, Ltd.) and NH_4F (97% purity, Wako Pure Chemical Industries, Ltd.) with molar ratios of $[H_2O_2]/[TBT] = 0–2.5$ and $[NH_4F]/[TBT] = 0–3.2$, respectively, were prepared.

The SPD apparatus used in this study is described elsewhere.[4–6] A spray gun (Lumina STA-6R-1mmϕ, Fuso Seiki Co., Ltd.) was fixed at approximately 30 cm above the substrate holder, and then a glass substrate (25 mm×25 mm×1 mm in size, Corning 7059) was put on the holder. After heating up the substrate between 300 and 480°C, the source solution was sprayed onto the glass substrate with 2.0 kg/cm^2 of compressed air. The mist was pyrolized on the substrate to form a film. Since the mist cooled down the substrate temperature, the spraying was not carried out continuously but intermittently. The spray rate of the solution and the period for each spraying was kept 1.25 ml/s and 0.4 s, respectively. This process was repeated 50–200 times to prepare the film with the thickness of 120 nm.

The crystal structure of the film was determined by XRD using CuK_α radiation (RIGAKU RINT-1100). The texture coefficient of the (hkl) plane, *TC*(hkl), was calculated from the following equation;[6]

$$TC(\mathrm{hkl}) = \frac{I(\mathrm{hkl})/I_0(\mathrm{hkl})}{I/N[\Sigma_n I(\mathrm{hkl})/I_0(\mathrm{hkl})]} \quad (1)$$

where I is the normalized peak intensity, I_0 the corresponding standard intensity of SnO_2 rutile, and N the total reflection number of 31.[7] The transmittance in the visible light region was measured by a spectrophotometer (Jasco V-570). The surface morphology was observed by FE–SEM (JSM-6320F, JEOL). Hall effect measurement was done by the Hall System (Bio-Rad Microscience HL5500) using the van der Pauw method.

3. Results and discussion

Fig. 1 shows XRD patterns of thin films with the thickness of 120 nm prepared from TBT solution without any additives at the substrate temperature between 300 and 480°C. Rutile SnO_2 single phase was observed for films synthesized at the substrate temperatures above 340°C, while amorphous at 300°C. The texture coefficient of the (110) plane reached the maximum for the film prepared at the substrate temperature of 340°C, indicating the highest crystallinity along the [110] direction among the films. The result suggests the possibility of the low temperature synthesis of SnO_2 thin films with

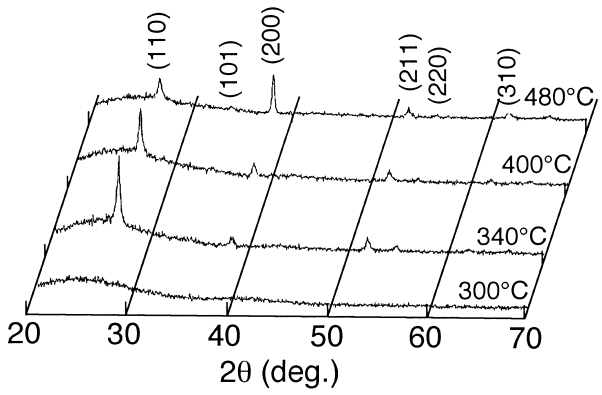

Fig. 1. XRD patterns of thin films with the thickness of 120 nm deposited at various substrate temperatures from the TBT solution.

excellent transmittance and conductivity at the substrate temperature below 340°C.

The deposition efficiency, *E*, was defined as below,

$$E = \frac{d}{M} \quad (2)$$

where d is the film thickness and M is a total molar number of the source solution consumed to deposit films. The efficiency was calculated as 3.3×10^3 nm/mol for the film prepared at the substrate temperature of 340°C. The efficiency is about 1/4 of that deposited from di-*n*-butyltin(IV) diacetate at the same substrate temperature.[5] In order to improve the deposition efficiency, aqueous H_2O_2 was added to the TBT source solution. Fig. 2 shows the deposition efficiency and the texture coefficient of the (110) plane, *TC*(110), for SnO_2 thin films as a function of $[H_2O_2]/[TBT]$ molar ratio.

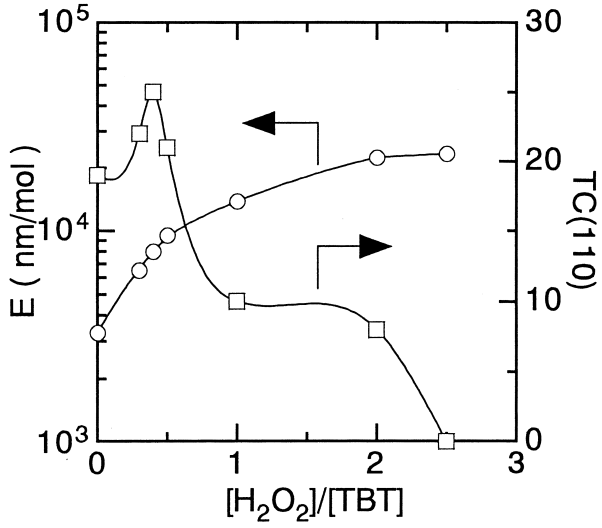

Fig. 2. Texture coefficient of the (110) plane, *TC*(110), and deposition efficiency, *E*, of SnO_2 thin films as a function of $[H_2O_2]/[TBT]$ molar ratio in the source solution. The film was deposited at the substrate temperature of 340°C.

The substrate temperature was kept at 340°C during the syntheses. The deposition efficiency was rapidly enhanced with increasing the $[H_2O_2]/[TBT]$ ratio, while saturated above $[H_2O_2]/[TBT]=1.0$. However, at $[H_2O_2]/[TBT]=1.0$, the efficiency reached as high as 1.4×10^5 nm/mol, exceeding the value of the film from di-*n*-butyltin(IV) diacetate.[4] On the other hand, *TC*(110) showed the maximum at $[H_2O_2]/[TBT]=0.4$, indicating the highest crystallinity at this ratio. Then we decided the $[H_2O_2]/[TBT]$ ratio to be 0.4 in the following study. We propose here two reasons for the enhanced deposition efficiency and the good crystallinity by adding H_2O_2 to the TBT source solution. One is that H_2O_2 decomposes easily on a substrate to produce an oxygen atmosphere, which is expected to promote the oxidation process of TBT and reduce residuals within the film. Another is that H_2O_2 and TBT form tin peroxide complexes which possess direct atomic bondings between tin and oxygen in the source solution.[8] The molecular structure is desirable to form SnO_2.

In order to produce SnO_2 thin film for a practical use, a high electric conductivity is required. In this study, NH_4F was employed as a doping agent for SnO_2 to meet this request. Fig. 3(a)–(c) shows the carrier concentration, mobility and electrical resistivity of SnO_2 thin films as a function of $[NH_4F]/[TBT]$ molar ratios. The substrate temperature was kept at 340°C during the syntheses. Both the carrier concentration and the mobility were increased with increasing $[NH_4F]/[TBT]$ ratio up to 1.6, indicating that electrons were effectively injected to the SnO_2 donor level. Fig. 4(a) and (b) shows the surface morphology of SnO_2 thin films prepared from the solution with H_2O_2, and both H_2O_2 and NH_4F, respectively. The grain size of the film deposited from the solution including NH_4F (b) is larger than that of (a), suggesting that NH_4F is effective to SnO_2 particle growth and that the carrier scattering is reduced along with increasing the SnO_2 grain size. This is the reason why the mobility became higher with increasing $[NH_4F]/[TBT]$ ratio as shown in Fig. 3(b). However, the mobility was lowered at $[NH_4F]/[TBT]=3.2$. This is supposed to be attributed to the residuals of NH_4F that remained within grain boundaries without dissolving in SnO_2, which is supported by the fact that the carrier concentration was saturated above $[NH_4F]/[TBT]=1.6$.

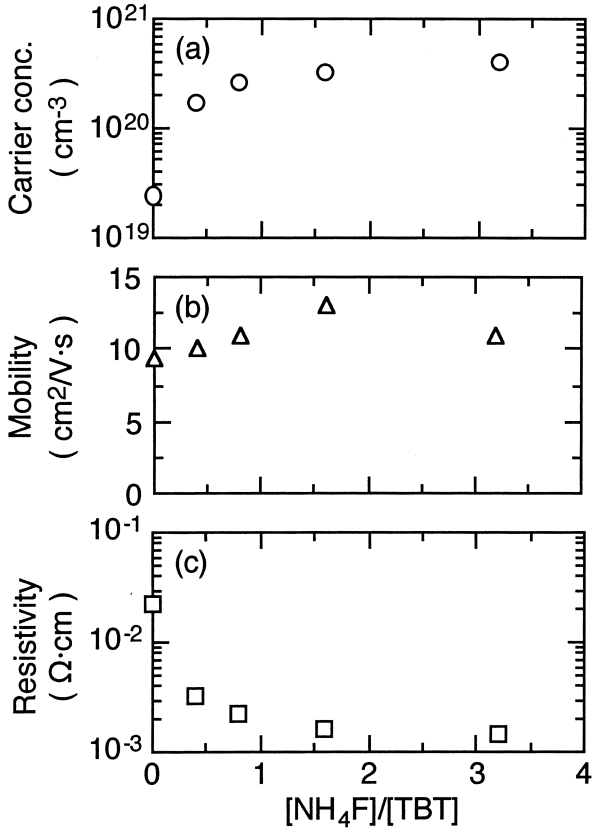

Fig. 3. Carrier concentration (a), mobility (b) and electrical resistivity (c) of SnO_2 thin films as a function of $[NH_4F]/[TBT]$ molar ratio in the source solution. Hydrogen peroxide was added to all solutions at $[H_2O_2]/[TBT]=0.4$. The film deposition was carried out at the substrate temperature of 340°C.

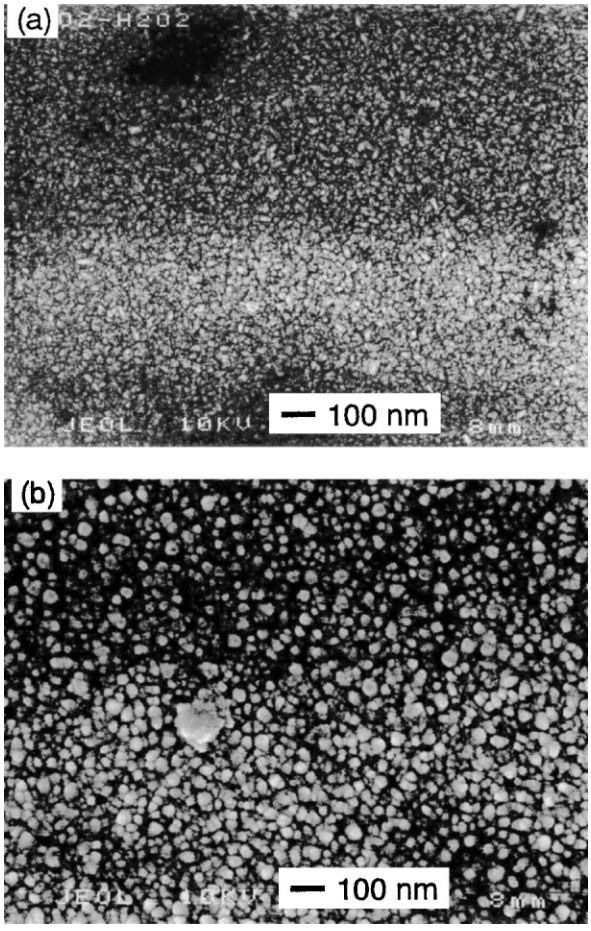

Fig. 4. Surface morphology of SnO_2 thin films deposited from the TBT solution with (a) $[H_2O_2]/[TBT]=0.4$, and (b) $[H_2O_2]/[TBT]=0.4$ and $[NH_4F]/[TBT]=1.6$. Both films were deposited at the substrate temperature of 340°C.

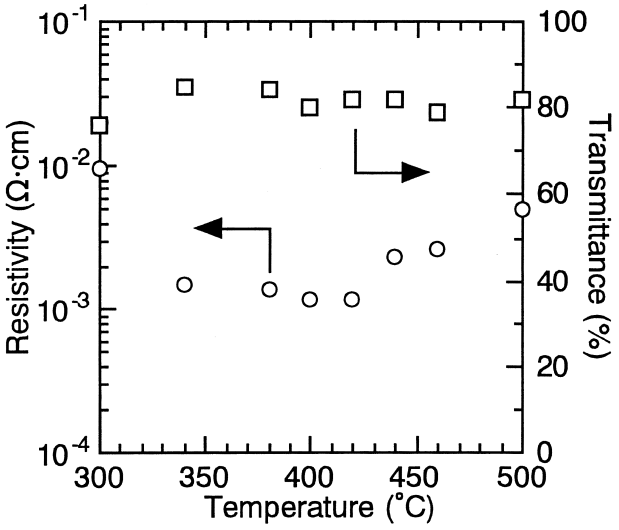

Fig. 5. Electrical resistivity and average transmittance of SnO_2 thin films deposited from the TBT solution with $[H_2O_2]/[TBT] = 0.4$ and $[NH_4F]/[TBT] = 1.6$ as a function of the deposition temperature. The film thickness is 120 nm for all films.

Fig. 5 shows the substrate temperature dependence of the electrical resistivity and the average transmittance of SnO_2 thin films with the thickness of 120 nm synthesized from TBT source solution with $[H_2O_2]/[TBT] = 0.4$ and $[NH_4F]/[TBT] = 1.6$. The film synthesized at the substrate temperature of 300°C showed the highest resistivity attributed to the amorphous crystal structure. While, at the substrate temperature between 340 and 420°C, the electrical resistivity was the lowest, approximately 1.5×10^{-3} Ω cm, and almost independent of the substrate temperature. However, the average transmittance in the visible light region exceeded 80% for all films except the one deposited at 300°C. Although the electrical resistivity was not reduced below 1.0×10^{-3} Ω cm in this study, the results lead to the possibility of low temperature synthesis of a SnO_2 transparent electrode.

4. Summary

Tin(IV) oxide thin films with high transparency, high conductivity and high crystallinity were synthesized from tetra-*n*-butyltin(IV) by a SPD technique. The substrate temperature was successfully reduced as low as 340°C by adding hydrogen peroxide in the source solution. These findings would make it possible to employ low melting point materials such as soda lime glass and plastic for substrates of a transparent electrode.

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