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Thermal change during formation process of indium-tin-oxide transparent conductive films

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Abstract

Formation of tin-doped indium oxide (indium-tin-oxide; ITO) transparent conductive films via dip coating or spin coating was investigated by TG for the precursor materials, di-*n*-butyltin(IV) diacetate $(C_4H_9)_2Sn(CH_3COO)_2$, tin(II) acetate $Sn(CH_3COO)_2$ and indium diacetate monohydroxide $In(OH)(CH_3{}^{-}COO)_2$. Influence of the sample mass was examined on the thermal behavior of di-*n*-butyltin(IV) diacetate in He–20%O_2 atmosphere. The maximum mass (60 mg) inserted in the sample pan showed a remarkable mass loss (96.9%) via a single step which was interpreted as vaporization of di-*n*-butyltin(IV) diacetate while the minimum mass (0.3 mg) showed less mass loss (34.5%) to produce an SnO_2 film (estimated thickness, ~0.75 μm) on the bottom of the sample pan. Influence of the heating atmosphere was investigated for the foregoing three compounds by fixing the sample mass to the minimum value (0.3 mg) in He–20%O_2 and He atmospheres. Mass loss due to the vaporization of the metal-containing compounds was enhanced in the He atmosphere; the mass loss was most remarkable in case of di-*n*-butyltin(IV) diacetate and least so in case of indium diacetate monohydroxide. The yield of the residual metal oxide increased in the He–20%O_2 atmosphere; in case of indium diacetate monohydroxide, vaporization of indium-containing compound was negligible in forming an In_2O_3 film (estimated thickness, ~0.8 μm) on the bottom of the sample pan at 500°C. Coexistence of SnO_2 and SnO was observed when tin(II) acetate was heated in an oxygen-containing atmosphere. These results suggested that thermal analysis of the precursor materials should be performed with the sample mass corresponding to the film thickness. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Dip coating; Spin coating; Thermal gravimetry (TG); Di-*n*-butyltin(IV) diacetate; Tin(II) acetate; Indium diacetate monohydroxide

1. Introduction

Thin films of indium oxide, In_2O_3, usually doped with tin (indium-tin oxide, ITO) are widely used as transparent conductive films for liquid crystal displays, etc. [1] The dip coating process is advantageous

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for cost-saving mass-production of large-area ITO films, such as heat reflecting windows. The authors obtained ITO films (resistivity; $\approx 6.8\times10^{-4}$ and 7.9×10^{-4} Ω cm) using indium diacetate monohydroxide $In(OH)(CH_3COO)_2$ as a main precursor material and di-*n*-butyltin(IV) diacetate $(C_4H_9)_2Sn(CH_3COO)_2$ or tin(II) acetate $Sn(CH_3COO)_2$ as a dopant (Sn: ≈5–10 at.%) precursor material, respectively; the dip-coated films were heated at a heating rate of 10°C/min in air until 420°C, then in nitrogen until 650°C [2,3]. Heating conditions strongly influence the thermal processes, such as vaporization, decomposition, oxidation, crystallization, etc. Therefore, thermal analysis of the precursor materials is important in order to understand the oxide formation during which the structure and the properties of the ceramic film are determined. The authors reported that the temperature of an exothermic peak (combustion of the organic component) was dependent on the film thickness in case of indium(III) 2-ethylhexanoate, $In(C_8H_{15}O_2)_3$, coated on a glass substrate [4]. The different results between the film and the bulk suggested that thermal analysis of the film material should be performed with the sample mass corresponding to the actual film thickness. In the present work, the precursor materials (di-*n*-butyltin(IV) diacetate, tin(II) acetate and indium diacetate monohydroxide) for dip coating and spin coating of ITO films were analyzed by TG in He–20%O_2 and He flows, respectively.

The study was focused on the influence of the sample mass with respect to the film thickness. Influence of the heating conditions, such as atmosphere (existence of oxygen), was also reported. However, the clarification of the reaction was abandoned in the present work, since the TG-DTA-MS study of the complicated reaction using minute amounts of samples found to be more difficult than our previous work (sample mass; ~7.4 mg) for indium diacetate monohydroxide $In(OH)(CH_3COO)_2$ [5].

2. Experimental

Tin(II) acetate $Sn(CH_3COO)_2$ (Kanto, reagent 1st grade) and di-*n*-butyltin(IV) diacetate $(C_4H_9)_2Sn(CH_3COO)_2$ (Tokyo Kasei, 1st grade) were used as received.

Indium diacetate monohydroxide $In(OH)(CH_3COO)_2$ was synthesized by the procedure similar to that reported previously [5]. The In_2O_3 powders (10 g, purity 99.999%, particle size <1 μm, Kojundo) were refluxed in an excess amount of acetic acid (150 ml, 99%, Wako) for 24 h; the color of the suspension changed from pale yellow to white after ~6 h. The powders filtered from the solution were heated at 70°C in vacuo ($\sim 2.7\times10^4$ Pa) for 24 h to evaporate the excess acetic acid and water to the obtain white powder of indium diacetate monohydroxide. The results of compositional analysis (18.77, 2.84 and 54.82% for carbon, hydrogen and residue, respectively) approximately agreed with the expected formula $In(OH)(CH_3COO)_2$ (19.22, 2.82 and 55.55%, respectively). The X-ray diffraction of unreacted In_2O_3 [6] was not detected. The sample mass was measured using a Sartorius S-4 microbalance (sensitivity; 0.1 μg) at room temperature before the thermal analysis.

A Rigaku 8101D thermal analyzer (TG-DTA) was used. The specimen powders were ground lightly in an agate mortar before filling in an aluminum container (5 mm Ø×2.5 mm, ~15 mg). Alumina was used as the reference material for the DTA. The specimen was heated from ambient temperature to 500°C at a heating rate of 10°C/min in He–20%O_2 or He flow. The flow rate of the gas was ~250 ml/min.

3. Results and discussion

3.1. Influence of sample mass

The results of TG for di-*n*-butyltin(IV) diacetate $(C_4H_9)_2Sn(CH_3COO)_2$ in He–20%O_2 atmosphere with various sample masses are shown in Fig. 1. The thermal behavior was influenced remarkably by the amount of sample mass. When the maximum amount of sample mass in the pan (60 mg in the present case) was heated, a mass loss proceeded via a single step at ~200°C suggesting vaporization of di-*n*-butyltin(IV) diacetate (boiling point 142–145°C at 10 mm Hg [7]). The residue was estimated to contain SnO_2 from the results of X-ray diffraction analysis for the bulk specimen heated in air at various temperatures. Formation of SnO_2 is supported by the report of Kosugi, et al. [8], who deposited SnO_2 films in air onto a glass substrate typically heated at 450°C by spray pyrolysis using ethanol solution of di-*n*-butyltin(IV)

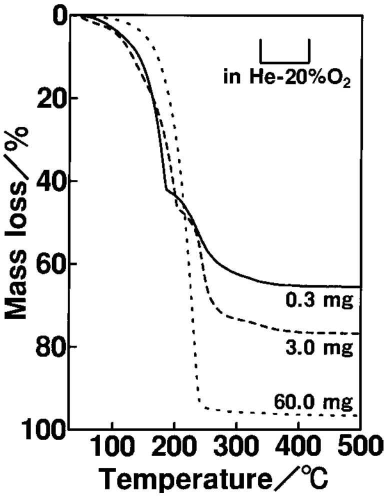

Fig. 1. TG of di-*n*-butyltin(IV) diacetate $(C_4H_9)_2Sn(CH_3COO)_2$ in He–20%O_2 atmosphere with various sample masses. Heating rate, 10°C/min; gas flow rate, 250 ml/min.

diacetate. When smaller amounts of the specimen mass (3.0 and 0.3 mg) was heated, less mass loss (76.9 and 65.5%, respectively) at 500°C was observed. Formation of a decomposition intermediate was suggested by a shoulder appearing at 150–200°C. In case of the minimum sample mass (0.3 mg) in the present case, the mass loss at 500°C (65.5%) agreed, apparently, with the estimated value (65.9%) for the formation of metallic tin which was rather improbable, so that formation of SnO_2 and vaporization of tin-containing compounds was expected to proceed simultaneously; for example, 20.1% of the tin vaporized at <500°C as tin-containing compounds before the rest of tin remained as SnO_2 film (thickness ~0.75 μm) on the bottom of the sample pan at above ~450°C. Vaporization and/or reaction of the intermediate seemed to occur at a temperature slightly higher than that of the di-*n*-butyltin(IV) diacetate and terminate at ~400°C. Thus, the formation of the intermediate was highly dependent on the sample mass. Thermal analysis of the vaporizable precursors are effective to understand the influence of the film thickness, since vaporization of metal-containing compounds during the heating process is disadvantageous for dip-coating or spin-coating process to produce films with uniform thickness and composition (Sn/In ratio in case of ITO films). These results also suggests that thermal analysis of the precursor materials should be performed with the sample mass corresponding to the film thickness; thermal analysis of the sample with an excess amount of mass may result in misleading interpretation.

3.2. Influence of heating atmosphere

3.2.1. Di-n-butyltin(IV) diacetate

The result of TG for di-*n*-butyltin(IV) diacetate $(C_4H_9)_2Sn(CH_3COO)_2$ in He atmosphere is shown in Fig. 2. The result in the He–20%O_2 atmosphere is plotted in this figure for reference; the sample mass was fixed at 0.3 mg. The heating atmosphere did not seem to influence the appearance of the shoulder at ~150°C. Mass loss at ~300°C in He atmosphere was interpreted as evaporation of the intermediate whose vaporization temperature was assumed to be higher than that of di-*n*-butyltin(IV) diacetate. In the He–20%O_2 atmosphere, oxidation seemed to suppress the evaporation of the intermediate and enhanced the formation of SnO_2. Fig. 3 shows the dependence of residual mass on the initial sample mass when heated at 10°C/min up to 500°C. In this figure, logarithm of the initial sample mass was scaled on the abscissa for convenience. If the initial sample mass is ~0.1 mg, vaporization of tin-containing compounds will be negligible for the deposition of SnO_2 thin film (thick-

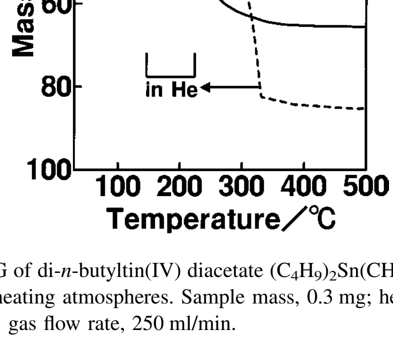

Fig. 2. TG of di-*n*-butyltin(IV) diacetate $(C_4H_9)_2Sn(CH_3COO)_2$ in different heating atmospheres. Sample mass, 0.3 mg; heating rate, 10°C/min; gas flow rate, 250 ml/min.

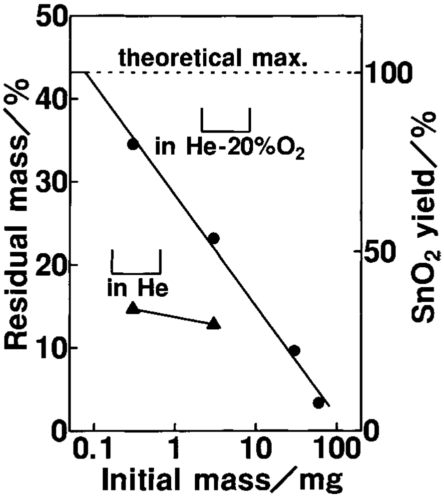

Fig. 3. Dependence of the residual mass on the initial sample mass for TG of di-*n*-butyltin(IV) diacetate $(C_4H_9)_2Sn(CH_3COO)_2$ with various heating conditions. Heating rate, 10°C/min; gas flow rate, 250 ml/min.

ness ~0.1 μm) on the bottom of the sample pan after the heating. In He atmosphere, the yield of SnO_2 was much smaller than in the He–20%O_2 atmosphere, which was attributed to the vaporization of the tin-containing compounds.

3.2.2. *Tin(II) acetate*

Fig. 4 shows TG of tin(II) acetate $Sn(CH_3COO)_2$ in different heating atmospheres. In the present case, the sample mass was fixed at 0.3 mg which corresponded to an SnO_2 film of 1.4 μm thickness in case no evaporation of tin-containing compounds occurred. Many shoulders were observed on the TG curve. In the He–20%O_2 atmosphere, the mass loss at 500°C (39.1%) was between the expected value for SnO_2 (36.13%) and that of SnO (42.86%). Coexistence of SnO_2 and SnO was supported by our result of X-ray diffraction analysis for the bulk specimen heated in a crucible in air at various temperatures. Formation of SnO was reported by Kawamata, et al. [9] who oxidized the amorphous films deposited by vacuum evaporation of tin(II) acetate at 400–700°C in air. In the He atmosphere, mass loss was observed remarkably at ~100–180°C. This temperature range agrees approximately with the vaporizing temperature (140–160°C) used by Maruyama and Tabata [10] who deposited ITO films by CVD using tin(II) acetate in N_2 atmosphere. The fact that mass loss at 500°C (47.4%) was lower than the expected value for SnO suggested the vaporization of tin(II) acetate.

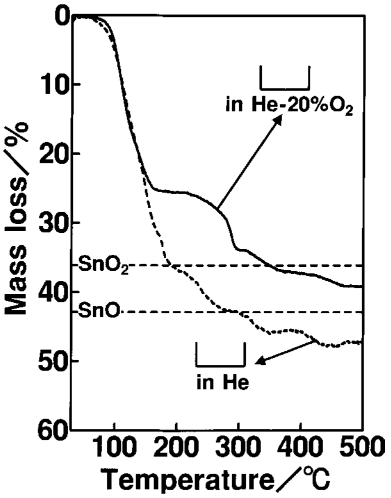

Fig. 4. TG of tin(II) acetate $Sn(CH_3COO)_2$ in different heating atmospheres. Sample mass, 0.3 mg; heating rate, 10°C/min; and gas flow rate, 250 ml/min.

3.2.3. *Indium diacetate monohydroxide*

Fig. 5 shows TG of indium diacetate monohydroxide $In(OH)(CH_3COO)_2$ with different heating atmo-

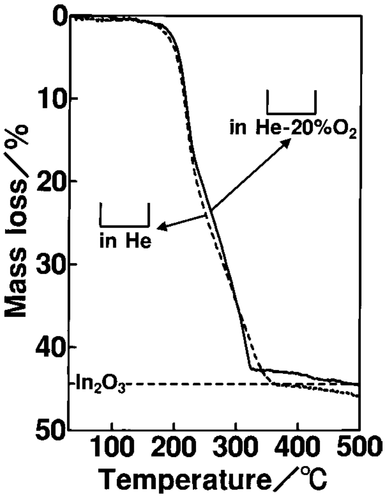

Fig. 5. TG of indium diacetate monohydroxide $In(OH)(CH_3COO)_2$ in different heating atmospheres. Sample mass, 0.3 mg; heating rate, 10°C/min; and gas flow rate, 250 ml/min.

spheres. The sample mass was fixed at 0.3 mg which corresponded to In_2O_3 film with the thickness of 0.8 μm. When sufficient oxygen was supplied to the sample in He–20%O_2 atmosphere, the mass loss at 500°C (44.5%) agreed excellently with the expected value (43.52%) for the formation of In_2O_3; moreover, vaporization of indium-containing compounds was negligible.

The result of TG up to 600°C using platinum pans in the same atmosphere supported this hypothesis. When heated in He atmosphere, a greater mass loss was observed; formation of In_2O_3 without the trace of metallic indium suggested the vaporization of indium-containing compounds. Maruyama and Tabata [10] reported that indium diacetate monohydroxide was applicable to CVD deposition of ITO films in N_2 atmosphere if the vaporization was performed in the very vicinity of the substrate.

3.2.4. Oxidation and vaporization

The influence of the heating atmosphere was most remarkable in case of di-*n*-butyltin(IV) diacetate in the present work. Indium diacetate monohydroxide was least sensitive although it was impossible to neglect the influence of the atmosphere. In any case, oxygen can restrain the vaporization of the metal-containing compound to increase the production yield of the metal oxide when it is possible to oxidize prior to vaporization. This gives us the leading principle for the film production of the ceramic films that oxidation at relatively low temperatures (mostly <200°C) must be performed by slow heating in an oxygen-containing atmosphere. The influence of the sample mass in He–20% O_2 atmosphere can be interpreted by insufficient supply of oxygen when the gaps between the sample particles were filled by the vapor of the metal-containing compounds in case of the large amount of sample being filled in the container.

4. Conclusions

Di-*n*-butyltin(IV) diacetate $(C_4H_9)_2Sn(CH_3COO)_2$, tin(II) acetate $Sn(CH_3COO)_2$, and indium diacetate monohydroxide $In(OH)(CH_3COO)_2$ were analyzed by TG in He–20%O_2 and He atmospheres. The sample mass influenced the thermal change of di-*n*-butyltin(IV) diacetate. Mass loss was remarkable when a large amount of sample was heated in He atmosphere. Vaporization of the sample and/or the decomposed intermediate was estimated. These results supported the hypothesis that thermal analysis of the precursor materials should be performed with the sample mass corresponding to the film thickness. The influence of the heating atmosphere was also reported for tin(II) acetate $Sn(CH_3COO)_2$, and indium diacetate monohydroxide $In(OH)(CH_3COO)_2$; the residual oxide decreased when heated in the He atmosphere.

References

[1] Y. Shigesato, I. Yasui, Oyo Butsuri 64 (12) (1995) 1225–1229.

[2] F. Yamaguchi, Abstract for The 9th Symposium, The Materials Research Society of Japan, Kawasaki, Japan 1997, pp. 113.

[3] F. Yamaguchi, Master Thesis, Tokyo Institute of Polytechnics 1998, pp. 19–73.

[4] Y. Sawada, K. Omika, Y. Ito, F. Muta, M. Momota, J. Thermal Anal. 40 (1993) 1145–1150.

[5] Y. Sawada, T. Shigaraki, S. Seki, M. Ogawa, T. Senda, T. Nishide, J. Matsushita, J. Spectrom. Soc. Jpn. 46 (4) (1998) 292–295.

[6] Joint Committee for Powder Diffraction Standards 44–1087.

[7] Dictionary of Organic Compounds, Soc. Org. Synth. Edition, Kodansha, Tokyo 1991, 342 pp.

[8] T. Kosugi, N. Kamiya, I. Yagi, K. Murakami, S. Kaneko, Trans. Mater. Res. Soc. Jpn. 20 (1996) 530–533.

[9] E. Kawamata, S. Kambe, K. Ohshima, Oyo Butsuri 44 (7) (1975) 742–749.

[10] T Maruyama, K. Tabata, Jap. J. Appl. Phys. 29 (2) (1990) 355–357.