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DSC OF AS-DEPOSITED THIN FILMS DIP-COATED ON THE SUBSTRATE
Thermal change of indium(III) 2-ethylhexanoate to form In_2O_3 thin films

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The formation process of a ceramic (indium oxide) thin film (thickness: approximately 20 nm to several microns) was investigated by thermal analyses. Thermal change of an organic precursor, indium(III) 2-ethylhexanoate, dip-coated on a glass substrate was successfully detected by DSC in air. Exothermic phenomena were observed at marked lower temperatures for the thin films than for the bulk material; thinner films had slightly lower peak temperatures. The reaction mechanism is discussed with reference to mass spectra of the evolved gases.

Keywords: dip-coating, indium oxide, thin films

Introduction

The dip-coating process is suitable for economical mass-production of large-area ceramic thin films with uniform thickness [1]; a substrate, for example a glass plate, is dipped into the solution containing an organic precursor of the ceramic material, raised slowly to evaporate the solvent, and then heated to form the oxide film. The thermal process (decomposition, oxidation etc.) exerts an important control on structure and properties of the ceramic film, since solid-state reactions are strongly influenced by topochemical factors such as thickness and microstructure of the film, and heating conditions such as heating rate and atmosphere. One of the authors has previously reviewed and emphasized the importance of thermal analyses of thin solid films and precursor materials [2]. The precursors are usually analysed using specimen containers with a diameter of a several millimeters (specimen weight: several milligrams) while dip-coated films are normally no thicker than 100 nm, so that the actual reactions in the films would be expected to occur at lower temperature than those in the bulk specimen.

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In the present study, differential scanning calorimetry was performed semi-quantitatively for an organic precursor deposited on a glass substrate. Indium(III) 2-ethylhexanoate was selected as the precursor material since In_2O_3, more precisely ITO (Indium Tin Oxide i.e. Sn-doped In_2O_3) film, is a typical transparent conductive film for liquid crystal displays etc. [3–5]. Improvement of the film conductivity was not attempted in the present investigation since the objective was direct detection of thermal change of the thin films.

Experimental

Specimen

Indium(III) 2-ethylhexanoate, $In(C_8H_{15}O_2)_3$ diluted with toluene (approx. 5 wt%, Nihon Kagaku Sangyou Co., Ltd.), was used; the NMR spectrum agreed with the expected composition. Thermal analyses were performed after evaporating the toluene at room temperature for one week during which the weight loss was 92–97%. The weight loss (73%) by TG at 800°C in air agreed approximately with the expected value (75%). Quantitative analysis of the unreacted excess of 2-ethylhexanoic acid $C_8H_{16}O_2$ was not attempted.

Film formation

The above precursor diluted with toluene was further diluted with toluene or xylene. Since dip-coating was inapplicable to a small substrate for DSC, the following methods were adopted. Method I: the further diluted solution was poured onto thin glass substrates (Matsunami Co., Ltd., 5 mm × 5 mm × 0.07 mm, approx. 5 mg) placed on the bottom of a vessel. The solvent (toluene) was evaporated for one week. A small amount of the specimen deposited on the opposite side (lower side) of the substrates was mechanically removed. Method II: the further diluted solution was dropped from a pipette into an aluminium pan (5 mm diameter, approx. 13.4 mg) or onto a tilted glass substrate (15 mm × 15 mm), the opposite side of which was pre-cracked in order to obtain the 5 mm × 5 mm substrate. The In_2O_3 film thickness was estimated on the basis of the following hypotheses: (1) area was 0.25 cm^2 when using the glass substrate (0.196 cm^2 when using an aluminium pan), (2) the weight loss during heating was 75%, (3) the density of the In_2O_3 film was 7.0 g/cm^3, and (4) the thickness was uniform.

Thermal analyses

A Rigaku TAS-300 system was used; an 8240D ultra-high-sensitivity DSC and 8101D differential-type-TG/DTA were driven by EWS (HP Apollo 9000/425e). The specimens were weighed using Sartorius S4 ultramicrobalance before and after thermal analysis. The DSC data were blanked by the uncoated glass sub-

strate. A Rigaku TG-DTA/MS system was used to analyse the evolved gases. The heating rate was fixed at 10 deg·min^{-1}.

Results and discussion

Bulk specimen

TG/DTA results for the bulk specimen are shown in Fig. 1. The weight loss between 200°–350°C is accompanied by multiple DTG peaks. Two small endothermic peaks at 205° and 248°C match a small DTG peak and a corresponding shoulder on the DTG curve, respectively. An exothermic peak ar 332°C is observed after the weight loss is almost complete. No DTA peak corresponds to the largest DTG peak at 290°C, probably because of the strong endothermic peak.

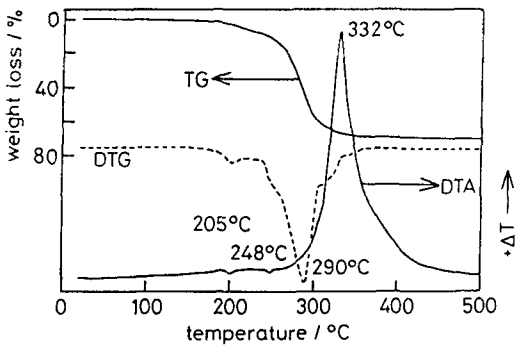

Fig. 1 TG/DTA curves of In(III) 2-ethylhexanoate bulk specimen. Specimen weight, 1.892 mg; reference material, alumina; sample pan, platinum

Thin films

DSC results for the dip-coated films are shown in Fig. 2. Thermal change was successfully detected; the detection limit was equivalent to a film thickness approximately 20 nm in the present work. The effect of film thickness on the exothermic peak temperature is shown in Fig. 3. The exothermic phenomena occurred at markedly lower temperatures for the thin films than for the bulk material. The thinner films had lower peak temperatures. A discontinuity seemed to exist at a thickness of approximately 500 nm. Only one exothermic peak was observed for a very thick film (> 10 μm).

Mass spectra

Mass spectra for the evolved gases are shown in Fig. 4. Sharp peaks at 320° and 335°C were observed in the total ion current (Fig. 4-A) and in the detection

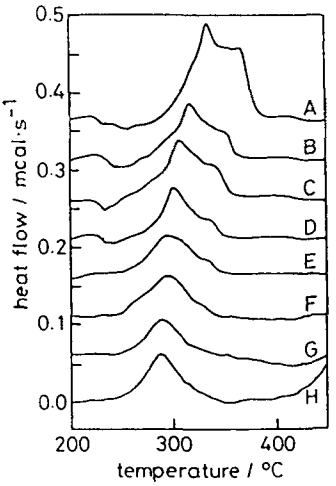

Fig. 2 DSC curves of dip-coated In(III) 2-ethylhexanoate films. A glass substrate was used for C, E, F, G and H. An aluminium pan was used for A, B and D. Estimated In_2O_3 film thickness (and measured weight of In(III) 2-ethylhexanoate) for A, B, ..., G and H are: 3920 nm (2.154 mg), 1360 nm (0.747 mg), 700 nm (0.491 mg), 470 nm (0.259 mg), 230 nm (0.158 mg), 90 nm (0.063 mg), 30 nm (0.021 mg) and 20 nm (0.015 mg). DSC data were normalized to 100 nm (0.070 mg). No reference material was used

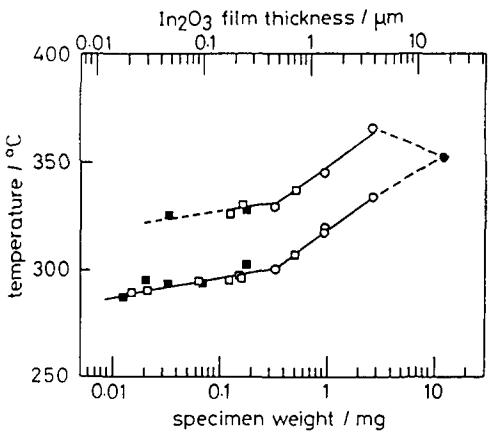

Fig. 3 Effect of film thickness on exothermic peak temperature for In(III) 2-ethylhexanoate. □ and ■: deposited on a glass substrate by methods I and II, respectively, then measured by DSC. o and •: deposited on the bottom of an aluminium pan by method II and measured by DSC and TG/DTA, respectively. Data are plotted by estimated In_2O_3 thickness, i.e. the specimen weight is the measured value when deposited on a 5 mm x 5 mm substrate

of m/e = 57 (Fig. 4-B). The former had no corresponding TG/DTA peak. The latter corresponds to the DTG peak. The detected mass spectra for the evolved gases were basically identical with those of 2-ethylhexanoic acid (m/e = 45, 57, 58, 73, 87, 88, 89, 101, 115, 116 and 144) whose peak temperature was 143°C. These results suggest that the weight loss corresponds to evolution of organic gases whose composition is identical or similar to those evolved on heating 2-ethylhexanoic acid. The m/e = 44 peak which should be attributed to carbon dioxide is shown in Fig. 4-C; the peak temperature (352°C) corresponds to the exothermic peak. This suggests that the exothermic peak can be attributed to the combustion of the organic compounds contained in the evolved gas. Mass spectra for the evolved gas from the specimen heated in helium (not indicated in the figures) were basically identical with those shown in Fig. 4 except that the peak for m/e = 44 (carbon dioxide) was very weak and at a higher temperature (430°C). The exothermic phenomenon in helium could also be attributed to combustion, consuming a small amount of oxygen contained as an impurity.

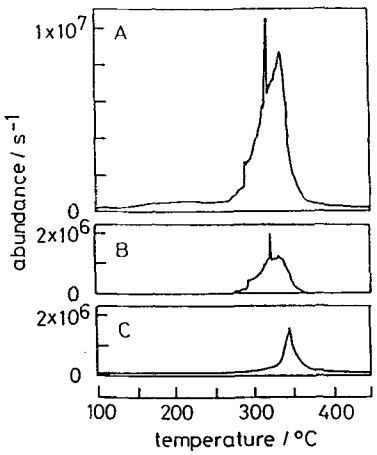

Fig 4 Mass spectra of evolved gases from In(III) 2-ethylhexanoate. A, total ion current; B, m/e 57; C, m/e = 44. Specimen weight, 9.28 mg; atmosphere, helium–20% oxygen

Conclusion

Thermal change of indium(III) 2-ethylhexanoate as deposited on a glass substrate has been detected semi-quantitatively by DSC. Dependence of peak temperature on film thickness for the exothermic reaction was clearly observed. The evolved gases were identical or similar to those detected when 2-ethylhexanoic acid is heated.

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Zusammenfassung — Mittels Thermoanalyse wurde der Bildungsprozeß einer Keramikdünnschicht (Indiumoxid, Schichtdicke ca. 20 nm bis einige Mikron) untersucht. Die thermische Veränderung eines auf Glassubstrat tauchaufgeschichteten organischen Präkursors (Indium(III) 2-ethylhexanoat) wurde mittels DSC in Luft erfolgreich detektiert. Für die Dünnschichten werden exotherme Erscheinungen bei deutlich niedrigeren Temperaturen beobachtet als für Kompaktmaterial; dünnere Filme haben leicht niedrigere Peaktemperaturen. Unter Einbeziehung der Massenspektren der freigesetzten Gase wurde auch der Reaktions- mechanismus diskutiert.