

Formation Process of Indium Oxide Thin Films from Indium 2-Ethylhexanoate Monohydroxide, $\text{In}(\text{OH})(\text{O}_2\text{CCH}(\text{CH}_2\text{CH}_3)(\text{CH}_2)_3\text{CH}_3)_2$

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The thermal change of indium 2-ethylhexanoate monohydroxide, $\text{In}(\text{OH})(\text{O}_2\text{CCH}(\text{CH}_2\text{CH}_3)(\text{CH}_2)_3\text{CH}_3)_2$, to form indium oxide, In_2O_3 , thin film was investigated by TG-DTA-MS in a He-20% O_2 atmosphere with a minute amount of specimen (~ 0.1 mg) in order to clarify the formation process of the indium-tin-oxide transparent conducting films (thickness, ~ 240 nm). The total mass loss at 500°C (67.9%) approximately agreed with the value (66.8%) corresponding to the formation of In_2O_3 from $\text{In}(\text{OH})(\text{O}_2\text{CCH}(\text{CH}_2\text{CH}_3)(\text{CH}_2)_3\text{CH}_3)_2$. The main mass loss at approximately 250-350°C can be divided into two steps. In the first step, the evolution of 2-ethylhexanoic acid $\text{CH}_3(\text{CH}_2)_3(\text{CH}_2\text{CH}_3)\text{CHCOOH}$ was observed. The evolution of water vapor and carbon dioxide was observed in both steps and significant in the second step. A strong exothermic peak was also observed in the second step. A small amount of water vapor was detected at ~ 130 -190°C. The reaction mechanism was proposed.

Key words: thermal analysis, ITO films, TG-MS, indium 2-ethylhexanoate, indium oxide

1. INTRODUCTION

Thin films of indium-tin-oxide (tin-doped In_2O_3) are usually deposited by a PVD process such as the sputtering method in order to fabricate the transparent electrodes of flat-panel displays. Chemical processes such as dip coating, spin coating, spray pyrolysis, etc., are expected to be a less expensive way to manufacture ITO films as transparent heaters and/or infrared shielding of buildings and automobiles.

Indium 2-ethylhexanoate, $\text{In}(\text{O}_2\text{CCH}(\text{CH}_2\text{CH}_3)(\text{CH}_2)_3\text{CH}_3)_2$, is a typical precursor material for fabricating ITO films by the spin coating process as Xu et al. reported [1] and fluorine-doped In_2O_3 films by the CVD process as Maruyama and Fukui reported [2]. One of the authors investigated the thermal change in the same precursor material by DSC and demonstrated that the reactions for such films occurred at a lower temperature than that in the bulk specimen [3]. Recently, Ching and Hill [4] and Tsuchiya et al. [5] reported the photolytic formation of In_2O_3 thin films at

room temperature.

In the present study, the formation process of In_2O_3 thin films at elevated temperature in an oxygen-containing atmosphere was investigated mainly by TG-DTA-MS (simultaneous operation of thermogravimetry, differential thermal analysis and mass spectrometry) for a slightly different precursor material, indium 2-ethylhexanoate monohydroxide, $\text{In}(\text{OH})(\text{O}_2\text{CCH}(\text{CH}_2\text{CH}_3)(\text{CH}_2)_3\text{CH}_3)_2$ (basic salt), which is more stable than the normal salt, $\text{In}(\text{O}_2\text{CCH}(\text{CH}_2\text{CH}_3)(\text{CH}_2)_3\text{CH}_3)_2$. The specimen mass was reduced to the sensitivity limit of the thermal analysis in order to clarify the thermal change in the actual film condition which is often different from that of the bulk condition as pointed out by Sawada et al. [3], Gallagher et al. [6] and Seki et al. [7].

2. EXPERIMENTAL

The dip coating solution was supplied from Asahi Denka Kogyo Co., Ltd. This solution contained indium 2-ethylhexanoate monohydroxide,

$\text{In}(\text{O}_2\text{CCH}(\text{CH}_2\text{CH}_3)(\text{CH}_2)_3\text{CH}_3)_2$ (2.0 mass%), ethanol (20 mass% of the solvent) and xylene (mixture of *o*-, *m*- and *p*-). Results of the compositional analysis (45.79 and 7.07 mass% for C and H, respectively) after evaporating the solvent at room temperature agreed approximately with the calculated values (45.95 and 7.47 mass%) for $\text{In}(\text{O}_2\text{CCH}(\text{CH}_2\text{CH}_3)(\text{CH}_2)_3\text{CH}_3)_2$.

The dip coating solution was inserted into an aluminum pan (5 mm ϕ \times 2.5 mm) for thermal analysis before evaporating the solvent sufficiently at room temperature for approximately 15 h. The specimen (\sim 0.1 mg) that remained on the bottom of the pan was analyzed by TG-DTA-MS at the heating rate of 10°C/min in a He-20%O₂ atmosphere; a Rigaku TG-8120 was coupled with a JEOL AutoMS via a gas interface system made by Rigaku. The specimen mass was measured before and after the thermal analysis using a conventional balance (sensitivity 0.1 μ g; Sartorius S4); an In₂O₃ thin film (thickness \sim 240 nm) was fabricated on the bottom of the pan during the TG-DTA-MS analysis. The evolved gases were identified by TG-DTA-CG-MS (specimen mass, \sim 1 mg) in a He-20%O₂ atmosphere (Rigaku TG-8120 coupled with Shimadzu QP5050 via a gas interface system made by Rigaku).

3. RESULTS AND DISCUSSION

The results of a conventional balance (67.9%) measured before and after the thermal analysis agreed approximately with the calculated value (66.81 %) for the conversion of $\text{In}(\text{OH})(\text{O}_2\text{CCH}(\text{CH}_2\text{CH}_3)(\text{CH}_2)_3\text{CH}_3)_2$ into (1/2)In₂O₃.

The results of the TG-DTA are shown in Fig. 1. The mass change in the film specimen was comparable with the baseline shift of the TG curve so that the ordinate of the figure is calibrated with reference to the results determined using a conventional balance. The main mass loss was observed at between 250 and 350°C. The mass loss was divided into two steps. An exothermic peak (320°C) was observed only in the second step. The absence of an endothermic peak in the first step was explained by the minute amount of the specimen.

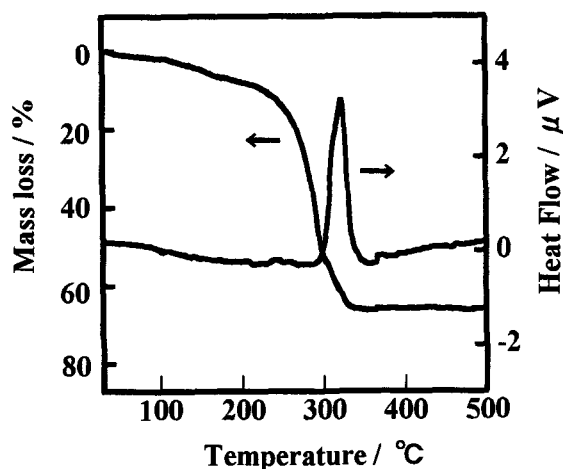


Fig. 1 TG-DTA of $\text{In}(\text{OH})(\text{O}_2\text{CCH}(\text{CH}_2\text{CH}_3)(\text{CH}_2)_3\text{CH}_3)_2$ in He-20%O₂. Specimen mass, 0.1mg; heating rate, 10°C/min; heating atmosphere, He-20%O₂; no reference material for DTA was used.

The mass spectrum of the gases evolved from the specimen is shown in Fig. 2. Detection of mass numbers *m/z* 16, 31, 32 and 48 was intentionally eliminated in the present analysis because of the strong background of oxygen in the carrier gas. In this figure, the results of 2-ethylhexanoic acid, $\text{CH}_3(\text{CH}_2)_3(\text{CH}_2\text{CH}_3)\text{CHCOOH}$, are also indicated for reference; this spectrum agreed with the database [8]. The spectra of water vapor [9] and carbon dioxide [10] are also indicated in the figure. The 2-ethylhexanoic acid, water vapor and carbon dioxide were detected in the present study. Other compound such as the solvent (ethanol and xylene) was not detected. The results were confirmed by TG-DTA-GC-MS. The evolution of 2-ethylhexanoic acid was mainly observed in the first step.

The detections corresponding to Re^+ (*m/z* 185 and 187), ReO^+ (201 and 203), ReO_2^+ (217 and 219), ReO_3^+ (233 and 235) and ReHO_4^+ (250 and 252) [11] were neglected in Fig. 2 because they should be attributed to the rhenium filament of the mass spectrometer. The intensity of the oxides were synchronized with that of 2-ethylhexanoic acid; 2-ethylhexanoic acid promoted the oxide formation in

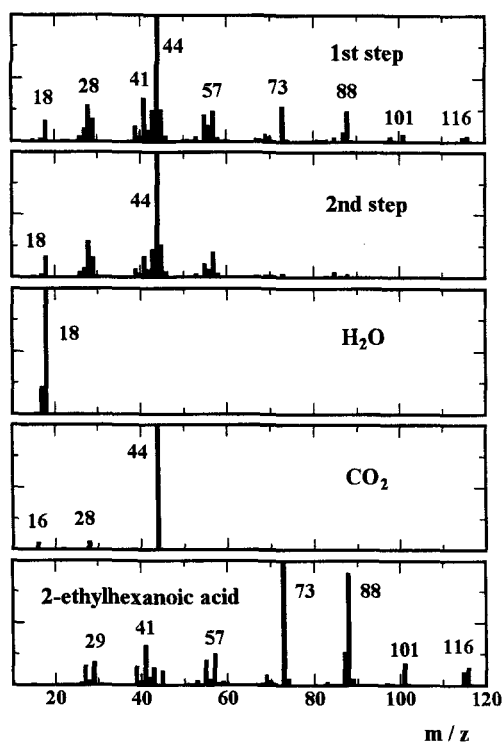


Fig. 2 Mass spectrum of the evolved gases during the first and second step of TG-DTA of $\text{In}(\text{OH})(\text{O}_2\text{CCH}(\text{CH}_2\text{CH}_3)(\text{CH}_2)_3\text{CH}_3)_2$ in $\text{He-20}\%\text{O}_2$.

an oxygen atmosphere.

Fig. 3 shows the thermogram of the evolved gases. Water vapor, carbon dioxide and 2-ethylhexanoic acid were represented by the m/z 18, 44 and 73, respectively. The m/z 41, 57, 73, 88, 101 and 116, which were assigned to 2-ethylhexanoic acid, were approximately synchronized to each other. The evolution of 2-ethylhexanoic acid was initiated at 270°C , which is slightly higher than its boiling point (226.9°C [9]). The evolution of 2-ethylhexanoic acid was terminated when the simultaneous evolution of carbon dioxide and water vapor occurred remarkably along with an exothermic peak. In case of water vapor and carbon dioxide, the baselines were higher compared with their peak height and the baselines decreased upon heating. For 2-ethylhexanoic acid, the baseline (back ground pressure) was low and constant.

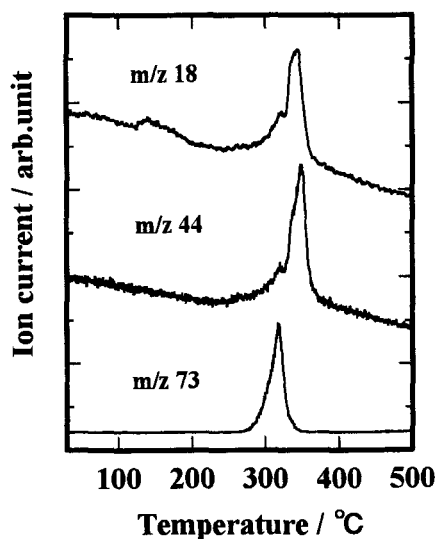
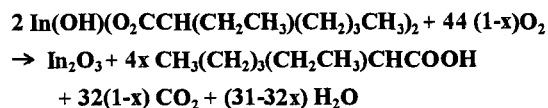


Fig. 3 Thermogram of the evolved gases during TG-DTA of $\text{In}(\text{O}_2\text{CCH}(\text{CH}_2\text{CH}_3)(\text{CH}_2)_3\text{CH}_3)_2$ in $\text{He-20}\%\text{O}_2$.

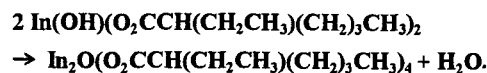
The Following reaction scheme is tentatively proposed for the present case;



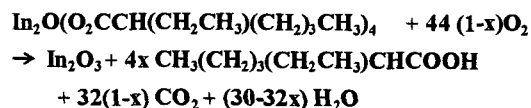
where the value x is between zero and $31/32$ and decreases upon increasing the temperature, i.e., the oxidation reaction becomes predominant at high temperature. This hypothesis was supported by the fact that simultaneous evolution of water vapor and carbon dioxide occurred more significantly in the second step than in the first step as shown in Fig. 3. This equation shows that the molar ratio between the evolved carbon dioxide and water vapor is approximately equal for any given x . This was supported by the synchronized evolution of carbon dioxide and water vapor shown in Fig. 3.

A small amount of water vapor was detected at approximately $130\text{-}190^\circ\text{C}$ which corresponded to the minute decrease in the TG. Although this is not fully clarified at the present, this might be explained by the

hygroscopic nature of the specimen or formation of an intermediate compound such as $\text{In}_2\text{O}(\text{O}_2\text{CCH}(\text{CH}_2\text{CH}_3)(\text{CH}_2)_3\text{CH}_3)_4$ via the reaction tentatively proposed as follows.

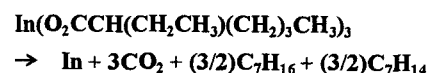


The apparent mass loss by TG seemed much larger than the calculated value (2.15%) for the above reaction although we must be careful because the mass loss was comparable with the baseline shift of the TG curve in the present case. Assuming the above reaction, the following reaction can also be tentatively proposed.



Except that the value x is between zero and 15/16, the situation is the same as that without assuming the intermediate compound.

Ching and Hill [2] detected m/z 44, 98 and 100 during the decomposition of $\text{In}(\text{O}_2\text{CCH}(\text{CH}_2\text{CH}_3)(\text{CH}_2)_3\text{CH}_3)_2$ films with irradiation of an ArF excimer laser at the room temperature in vacuo. They proposed the following reaction:



They assumed that the metallic indium was oxidized in air to form amorphous In_2O_3 . Tsuchiya et al. [5] reported the oxide film by a similar method. In the present study, heptane, C_7H_{16} (m/z 100 [12]), and 3-heptene, C_7H_{14} (m/z 98 [13]), were not detected by TG-DTA-MS and TG-DTA-GC-MS. The difference should be attributed to the decomposition mechanism (photolysis and pyrolysis) and the atmosphere (in vacuo and He-20% O_2).

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4. CONCLUSIONS

The TG-DTA-MS of indium 2-ethylhexanoate monohydroxide in a He-20% O_2 atmosphere was performed in order to understand the formation mechanism of indium-tin-oxide transparent conducting films. The mass loss at 500°C approximately agreed with the theoretical value for the heating from $\text{In}(\text{O}_2\text{CCH}(\text{CH}_2\text{CH}_3)(\text{CH}_2)_3\text{CH}_3)_2$ to form (1/2) In_2O_3 . A mass loss occurred at 250~350°C accompanying evolution of 2-ethylhexanoate acid, $\text{CH}_3(\text{CH}_2)_3(\text{CH}_2\text{CH}_3)\text{CHCOOH}$, carbon dioxide and water vapor.

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