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Thermal change of SnI_2 thin films. Part 1. Thermogravimetry

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Abstract

Thermal change of tin iodide (SnI_2) evaporated film as-deposited on a glass substrate has been successfully detected by TG (heating rate, 10°C/min^{-1}); film mass about 0.5 mg, film area about 2 cm^2. A mass loss at 260–420°C in an argon flow is attributed to the evaporation of SnI_2. A mass loss at 180–290°C in an air flow is interpreted as oxidation of SnI_2 to form SnI_4 vapor and tin oxide.

The TG-DTA for SnI_2 and SnI_4 powders in a nitrogen flow (heating rate, 10°C min^{-1}) have been performed to understand the thermal change of SnI_2 thin films; an endothermic phenomenon without mass change attributed to melting at 319 and 144°C and an endothermic mass loss attributed to evaporation at 300–460 and 85–190°C were observed for SnI_2 and SnI_4 powders, respectively. A small mass loss (about 7%) at 85–150°C for SnI_2 powders is attributed to the evaporation of SnI_4 impurity.

INTRODUCTION

Tin oxide (SnO_2) films are used as transparent conductive films with the advantages of high transmittance in the visible range, chemical and physical durability, relatively low material cost, etc. However, SnO_2 films have been inapplicable to transparent electrodes for liquid crystal display devices since pattern formation by wet etching has been impossible. Kuku and Green [1] proposed an alternative lithography process via a photochemical reaction of tin iodide (SnI_2) film at relatively low temperature, for example at about 150°C. They proposed the following reaction:

$$2SnI_2(s) + O_2(g) + 2H_2O(g) \rightarrow 2SnO_2(s) + 4HI(g) \tag{1}$$

Kuku [2] also proposed the following photochemical reaction at about

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140°C in dry atmosphere:

$$SnI_2(s) + O_2(g) \rightarrow SnO_2(s) + I_2(g) \qquad (2)$$

Although their process is promising, it is known that tin iodide is unstable in the atmosphere at room temperature and elevated temperature even without the radiation of light. However, the stability of SnI_2, especially with regard to thermal change without the radiation of light has not been sufficiently clarified.

In the present study, SnI_2 thin films as-deposited on glass substrates (i.e. without separation from the substrate) have been successfully investigated by thermogravimetry. A novel oxidation mechanism is proposed following comparison of the results with those of TG–DTA for the powder specimens. The present results show that thermal analysis of thin films as-deposited on the substrates is useful for clarifying the formation process of the oxides, as emphasized previously [3, 4], recently with the example of DSC for the dip-coated process from indium(III)2-ethylhexanoate to In_2O_3 films [5], and high-temperature resistivity measurements for sputter-deposited InN films to In_2O_3 films [6].

EXPERIMENTAL

Film deposition

The SnI_2 films were deposited by vacuum evaporation. The bell jar was evacuated to about 8×10^{-6} Torr with an oil-diffusion pump backed up with a rotary pump. The SnI_2 powders (about 0.2 g) were heated in a capped molybdenum boat (BB-1-9 Furuuchi Chemical Co. Ltd.) whose temperature was maintained at about 400°C except for the first 30 s or so, when 60 W power was applied. The pressure was about 10^{-3} Torr during the complete evaporation for about 3 min to deposit a film about 1 μm thick on a room-temperature substrate placed approximately 10 cm above the boat. The film thickness was measured with a stylus profilometer (Dektak 3030).

The glass substrates used were Corning 7059 (75 mm × 25 mm × 0.7 mm) and micro coverglass (Matsunami Co. Ltd., 18 mm × 18 mm × (0.12–0.17) mm). The substrates were cleaned ultrasonically with Semico-Clean 56 (Furuuchi Chemical Co. Ltd.) in water for 10 min, rinsed with water and then with acetone and finally they were dipped in boiled acetone.

The X-ray diffraction spectrum for the as-deposited thin film is shown in Fig. 1. Preferred orientation of α-SnI_2 and β-SnI_2 [8] was observed. Unidentified very weak peaks might be assigned to unreported peaks of α or β-SnI_2. The result is different from that of Green and Kuku [9] who

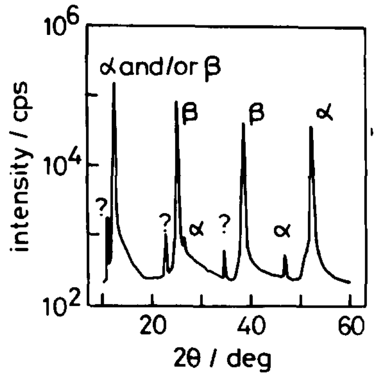

Fig. 1. X-ray diffraction spectrum for SnI_2 thin film. α, β and ? are α-SnI_2, β-SnI_2 and an unidentified peak, respectively.

reported α phase only at a substrate temperature of 100°C and β phase at room temperature and temperatures higher than 108°C.

Raw materials

Tin(II) iodide (SnI_2) produced by Kojyundo Chemical Laboratory Co. Ltd. was used as a raw material for film deposition (purity, 99.9%; Ca, 0.002%; Cu, 0.001%; Fe, 0.001%; Na, 0.003%; Pb, 0.02%, Si, 0.001%). Only α-SnI_2 [7] was detected by X-ray diffraction analysis for the powders ground with an agate mortar. The specimen after unsealing was preserved without the radiation of light in a vacuum desiccator (nitrogen at about 1 Torr); no significant change was observed by X-ray diffraction analysis up to 152 days when further analysis was abandoned. Tin(IV) iodide SnI_4 produced by Kojyundo Chemical Laboratory Co Ltd. was used for reference (purity, 99.9%; Ca, 0.001%; Cu, 0.001%; Fe, 0.001%; Na, 0.001%; Pb, 0.001%; Si, 0.001%).

Characterization and thermal analysis

The X-ray diffraction spectrum for the powders and the films were recorded with a conventional θ–2θ type diffractometer with nickel-filtered copper radiation, 40 kV 45 mA (Rigaku RAD-IIIC system). The specimen mass was measured with an ultramicrobalance (Sartorius S4) or a conventional balance (Shimadzu AEL-4SM) whose sensitivities were 0.1 and 10 μm, respectively.

The powders were analyzed by TG–DTA (Rigaku 8101D, twin holder type) in a nitrogen flow of 30 ml min^{-1} at a heating rate of 10°C min^{-1} with platinum containers and Al_2O_3 reference material. A Rigaku TAS-300 system (HP Apollo 9000/425e) was used for system control and data processing. The films deposited on the substrates were analyzed with TG (Shimadzu TGA-50) in an air and a nitrogen flow (20 ml min^{-1}) at the heating rate of 10°C min^{-1}; the substrate with the film was crushed before it was put into the platinum container. The blank subtraction of the baseline was performed.

RESULTS

Thin films

The TG results for SnI_2 thin films are shown in Fig. 2. It is clear that thermal analysis is possible for the as-deposited thin films whose masses and areas are as small as about 0.5 mg and 2 cm^2, respectively. The film is expected to evaporate almost completely in an argon flow (Fig. 2, curve A) since after analysis the specimen showed no optical interference by which the existence of transparent thin film could be examined qualitatively. The residual mass given by TG (10%) might be included in the experimental error, and is probably due to the reproducibility of baseline stability because the mass loss of 99.6% was obtained from the mass change measured with a conventional balance at room temperature before and after thermal analysis.

After analysis in an air flow the specimens were transparent (colorless) showing optical interference which changed depending on the geometrical relation between the light source, the film and the observer; formation of tin oxide films was suggested. The mass loss revealed by TG (about 86%) in Fig. 2, curve B agreed approximately with that (89.0%) measured with a conventional balance before and after the thermal analysis. It should be

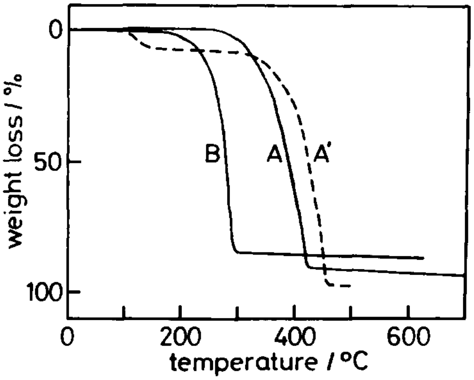

Fig. 2. TG for SnI_2 thin films. Curve A, film mass, 0.47 mg; film thickness, 0.58 μm; atmosphere, argon. Curve B, film mass, 0.58 mg, film thickness, 0.74 μm; atmosphere, air. Curve A', result for SnI_2 powders shown in Fig. 3 (in nitrogen flow, heating rate 10°C min^{-1}) for reference.

noted that the mass loss is more than the expected value for oxidation; 59.5% for reactions (1) and (2) and 63.8% for reactions (3) and (4).

$$SnI_2(s) + H_2O(g) \rightarrow SnO(s) + 2HI(g) \tag{3}$$

$$2SnI_2(s) + O_2(g) \rightarrow 2SnO(s) + I_2(g) \tag{4}$$

It should also be noted that the loss of mass in an air flow began at a much lower temperature (about 180°C) than in an argon flow (about 260°C).

Powders

The results of TG–DTA for SnI_2 and SnI_4 powders in a nitrogen flow are shown in Figs. 3 and 4, respectively, as reference materials to understand the thermal change of SnI_2 thin films. A mass loss and the corresponding endothermic phenomenon at 300–460°C and 85–190°C for SnI_2 and SnI_4, respectively, should be attributed to the evaporation of the respective iodides. The total mass loss (96.7% and 96.9% for SnI_2 and SnI_4, respectively) showed that the specimens evaporated almost completely. The initiation of mass loss was observed at about 300 and 85°C for SnI_2 and SnI_4, respectively. Dependence of the vapor pressure on the temperature

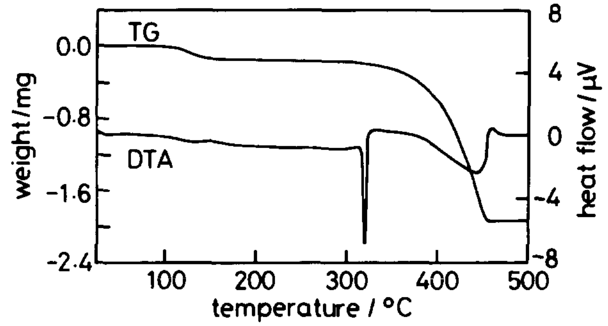

Fig. 3. TG–DTA for SnI_2 powders in flowing nitrogen.

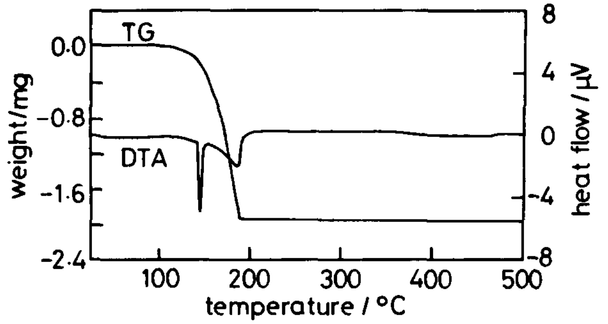

Fig. 4. TG–DTA for SnI_4 powders in flowing nitrogen.

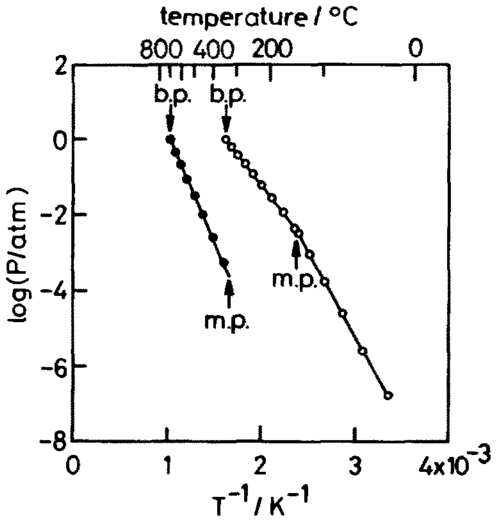

Fig. 5. Dependence of vapor pressure on the temperature for SnI_2 and SnI_4. ●, SnI_2 after Zhamskaya et al. [10] and ○, SnI_4 after Zhamskaya et al [11]; m.p., melting point; b.p., boiling point.

for SnI_2 [10] and SnI_4 [11] is shown in Fig. 5; the equilibrium vapor pressure of SnI_4 is about 5×10^{-5} atm, corresponding to the initiation temperature of mass loss. Although the vapor pressure versus the solid is not reported for SnI_2, a vapor pressure in approximately the same order is expected from the rough extrapolation of the data versus the liquid. A small amount of mass loss (about 7%) at 85–150°C for SnI_2 (Fig. 3) swill be discussed later. A sharp endothermic peak without mass change should be attributed to melting; the observed peak temperatures (318.6 and 143.9°C) are in good agreement with the reported values (320 and 144.5°C [12]) for SnI_2 and SnI_4, respectively. The observed mass loss at a temperature lower than the melting point, as shown in Fig. 4, shows sublimation of SnI_4. The phase transition from α to β-SnI_2 at 108°C reported by Green and Kuku [9] was not detected in the present DTA study.

In Fig. 2, the result of TG–DTA for the powder specimen in a nitrogen flow (Fig. 3) is also plotted with a broken line (curve A′) for comparison. The thin film evaporated in an argon flow at about 40°C lower than the powder specimen in a nitrogen flow.

DISCUSSION

A small amount of mass loss at 85–150°C in Fig. 3 was observed for SnI_2 powders in a nitrogen flow; the corresponding mass loss was not detected for the film specimen in an argon flow in Fig. 2. This should be attributed to the evaporation of SnI_4; the corresponding endothermic peak was observed very slightly. The temperature (85°C) at which the mass loss was initiated in Fig. 3 was in excellent agreement with that of SnI_4 powders (85°C) the TG–DTA data for which are shown in Fig. 4. The formation of SnI_4 impurity is proposed to occur by one of the following reactions during preservation at room temperature:

$$4SnI_2(s) + 2O_2(g) + 2H_2O(g) \rightarrow SnI_4(s) + 3SnO_2(s) + 4HI \quad (5)$$

$$8SnI_2(s) + O_2(g) + 4H_2O(g) \rightarrow 2SnI_4(s) + 6SnO(s) + 8HI \quad (6)$$

$$2SnI_2(s) + O_2(g) \rightarrow SnI_4(s) + SnO_2(s) \quad (7)$$

$$4SnI_2(s) + O_2(g) \rightarrow 2SnI_4(s) + 2SnO(s) \quad (8)$$

Neither SnI_4 nor tin oxide was detected by X-ray diffraction analysis for the present SnI_2 powders, probably because a small amount of less crystallized impurities were not detectable. Although SnO_2 is thermodynamically more stable than SnO at any temperature of the present experimental conditions (partial pressure of oxygen, 0.2 atm [13], it is impossible to determine at present which oxide is actually predominant.

The oxidation in air seems to accompany the formation of SnI_4 vapor since the evaporation at 180°C in Fig. 2 was impossible for SnI_2 as shown in Fig. 3 but possible for SnI_4 as shown in Fig. 4. These results suggest one of the following reactions is expected in air at the elevated temperatures (above about 180°C).

$$4SnI_2(s) + 2O_2(g) + 2H_2O(g) \rightarrow SnI_4(g) + 3SnO_2(s) + 4HI \quad (9)$$

$$8SnI_2(s) + O_2(g) + 4H_2O(g) \rightarrow 2SnI_4(g) + 6SnO(s) + 8HI \quad (10)$$

$$2SnI_2(s) + O_2(g) \rightarrow SnI_4(g) + SnO_2(s) \quad (11)$$

$$4SnI_2(s) + O_2(g) \rightarrow 2SnI_4(g) + 2SnO(s) \quad (12)$$

The expected mass losses are 69.6%, 72.9%, 79.7% and 81.9% for reactions (9), (10), (11) and (12), respectively. The present result (86–89%) can be more successfully approximated by reactions (11) or (12) than by reactions (9) or (10).

CONCLUSIONS

The results of TG for SnI_2 thin films in an argon flow (heating rate, 10°C min^{-1}) showed a mass loss at 260–420°C attributed to the evaporation of SnI_2 which occurred at a temperature about 40°C lower than that for the powder specimen in a nitrogen flow. The results of TG for SnI_2 thin films in an air flow (heating rate, 10°C min^{-1}) showed a mass loss at 180–290°C. The thermal change in air was interpreted as the oxidation reaction of SnI_2 to form SnI_4 vapor and tin oxide.

The results of TG–DTA for SnI_2 and SnI_4 powders in a nitrogen flow (heating rate, 10°C $\min^{-1}$) showed an endothermic phenomenon without mass change attributed to melting at 319°C and 144°C and an endothermic mass loss attributed to evaporation at 300–460°C and 85–190°C, respectively. A small amount of mass loss (about 7%) at 85–150°C for SnI_2 powders was attributed to the evaporation of SnI_4 impurity.

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