Thermal change of SnI$_2$ thin films.
Part 4. TG–DTA and DSC

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Abstract

A thermal change of a tin iodide (SnI$_2$) evaporated film as deposited on a glass substrate has been successfully detected by TG–DTA and evaluated semiquantitatively by DSC in nitrogen and air (heating rate 10°C min^{-1}); the film area was ≈ 0.5 and ≈ 0.25 cm^2 for TG–DTA and DSC, respectively. In nitrogen, a sharp endothermic peak at 317.9°C was interpreted as denoting the melting of SnI$_2$; an endothermic weight loss at 260–420°C was interpreted as the sublimation and evaporation of SnI$_2$. An exothermic weight loss at 180–290°C in air was interpreted as the oxidation reaction proposed in our previous papers [Thermochim. Acta, 232 (1994) 29–36; 232 (1994) 37–45; 243 (1994) 95–100], namely 2SnI$_2$(s) + O$_2$(g) → SnO$_2$(s) + SnI$_4$(g).

Keywords: Coupled technique; DSC; DTA; TG; Thin film; Tin iodide

1. Introduction

Tin oxide (SnO$_2$) films are used as transport conductive films. Kuku and Green [1] proposed a lithographic process for their formation via photochemical reaction of tin iodide (SnI$_2$) film at relatively low temperature in a moist atmosphere, for example at ≈ 150°C. They proposed the reaction

$$2SnI_2(s) + O_2(g) + 2H_2O(g) \rightarrow 2SnO_2(s) + 4HI(g)$$

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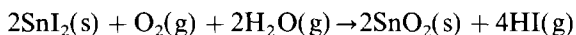
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Kuku [2] also proposed the photochemical reaction at $\approx 140°C$ in a dry atmosphere

$$SnI_2(s) + O_2(g) \rightarrow SnO_2(s) + I_2(g)$$
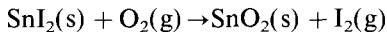
The thermal change of SnI_2 thin films as deposited on glass substrates (i.e., without separation from the substrate) was investigated successfully by thermogravimetry in our previous paper [3], in which a novel oxidation mechanism different from those reported was proposed

$$2SnI_2(s) + O_2(g) \rightarrow SnI_4(g) + SnO_2(s)$$
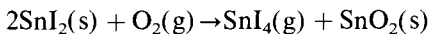
This hypothesis was supported by the results of weight measurement and X-ray diffraction analysis of specimens quenched from isothermal heating at 50, 100 and 150°C in air with [4] and without [5] light irradiation. In the present work, to confirm the previous hypothesis more completely, endothermic and exothermic phenomena of the films were investigated by TG–DTA and, semiquantitatively, by DSC.

2. Experimental

The SnI_2 films ($\approx 0.51 \mu m$ thick) were deposited by vacuum evaporation as previously reported [3] on the surface of a micro cover glass (Matsunami Co. Ltd. 18 mm × 18 mm × 0.12–0.17 mm). An ultramicrobalance (Sartorius S4, sensitivity 0.1 μg) was used to measure the substrate weight before and after film deposition and thermal analysis. The thermal analyses were performed at a heating rate of 10°C min^{-1} in static air and in flowing nitrogen (30 ml min^{-1}). The nitrogen was introduced after evacuation with an oil rotary pump. A Rigaku 8101D (twin-holder type) TG–DTA apparatus was used with platinum containers (5 mm diameter × 2.5 mm, ≈ 126 mg) and alumina as reference material. The substrate (≈ 5 mm × 5 mm) bearing the film was crushed lightly using an agate mortar before placing it in the platinum container; film weight was ≈ 0.35 mg. Baseline subtraction was performed by a blank measurement with an uncoated substrate. The film for DSC was deposited on a substrate whose opposite surface was pre-cracked in order to obtain a smaller specimen (5 mm × 5 mm, film weight ≈ 0.1 mg). The substrate was cut after film deposition and placed on the detector of the DSC apparatus with the film surface up. A Rigaku 8240D instrument (heat-flux type) was used with an uncoated substrate as the reference material. DSC was calibrated with bulk In, Sn and Pb. Baseline subtraction using a blank measurement was not performed in the present DSC analyses because the quality of the data was not thereby improved in the present case. A Rigaku TAS-300 system (HP Apollo 9000/425e) was used for system control and data processing.

3. Results and discussion

3.1. Nitrogen atmosphere

The result of TG–DTA for a SnI_2 thin film in a nitrogen atmosphere is shown in Fig. 1. It is clear that TG–DTA is applicable to an as-deposited thin film with
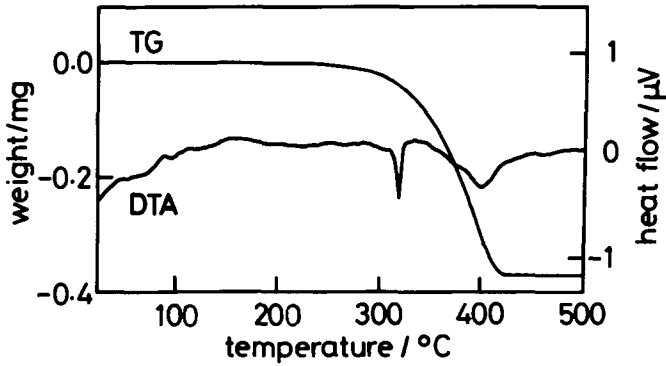
Fig. 1. TG-DTA of SnI$_2$ thin film in flowing nitrogen.

weight and area as small as ≈ 0.35 mg and ≈ 0.5 cm^2, respectively. The weight loss at 260–420°C agreed with that in flowing argon using a different TG apparatus (Shimadzu TGA-50) at the same heating rate, as reported in our previous paper [3]. Baseline stability in the present TG system was superior to that with the previous apparatus, probably because the mass change was detected by the weight difference between a pair of specimen holders disposed closely and symmetrically. The apparent weight loss by TG (107 and 90% in the present analyses and the previous analyses, respectively) should include the experimental error due to the small amount of the specimen, because the weight change measured with an ultramicrobalance before and after the thermal analyses showed that the film was expected to evaporate completely in an inert gas atmosphere. The broad endothermic peak at ≈ 400°C could be attributed to the evaporation of SnI$_2$. A sharp endothermic peak was attributed to the melting of SnI$_2$; the peak temperature (317.9°C) was slightly lower than the reported values (320°C [6] and 318.6°C [3]) for the bulk specimen. A small amount of weight loss before the melt could be understood as the sublimation of SnI$_2$.
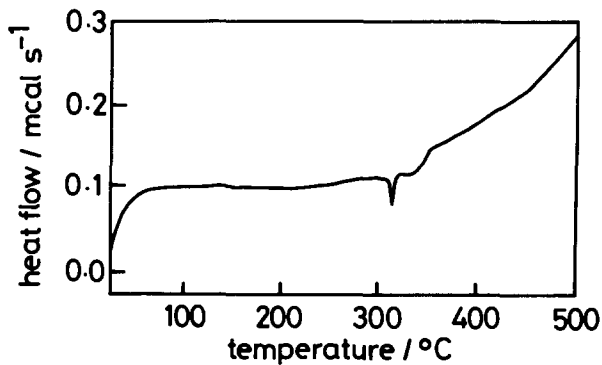

Fig. 2. DSC of SnI$_2$ thin film in flowing nitrogen.

The result from the DSC of a SnI_2 thin film in flowing nitrogen is shown in Fig. 2; it is clear that DSC is applicable to an as deposited film having weight and area as small as ≈ 0.1 mg and 0.25 cm^2, respectively. A sharp endothermic peak at 312.7°C agreed approximately with the result from DTA; the lower peak temperature was tentatively attributed to the minute difference in the conditions of specimen preparation and preservation. The transition of SnI_2 from the β to the α phase at ≈ 100°C [4,5] was not detected, probably because the enthalpy change for the transition is small.

3.2. Air atmosphere

The results of TG–DTA and DSC for SnI_2 thin films in static air are shown in Figs. 3 and 4, respectively. The weight loss at 180–290°C agreed with that reported in our previous paper using a different TG instrument (Shimadzu TGA-50) [3]. The weight loss (79.3%) agreed approximately with the expected value (79.7%) for the following reaction, as proposed in our previous papers [3–5]
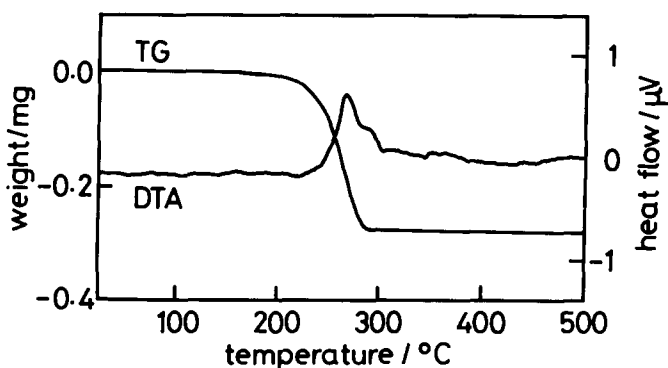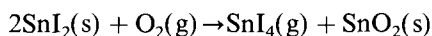
$$2SnI_2(s) + O_2(g) \rightarrow SnI_4(g) + SnO_2(s)$$
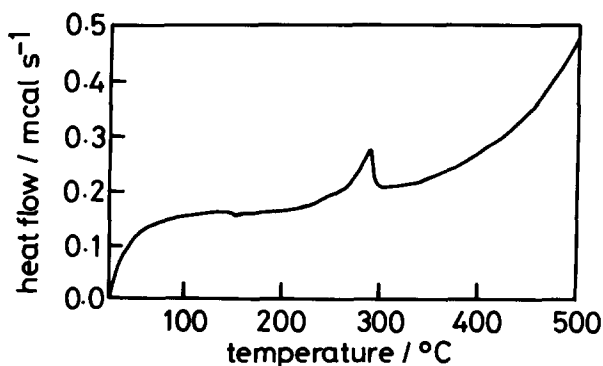

Fig. 3. TG–DTA of SnI_2 thin film in static air.

Fig. 4. DSC of SnI_2 thin film in static air.

An exothermic DTA peak in Fig. 3 (265.5°C) accompanied a shoulder at higher temperature (≈ 289°C), and an exothermic DSC peak in Fig. 4 (288.5°C) accompanied a shoulder at lower temperature (≈ 250°C). These complicated exothermic peaks suggest an inhomogeneous reaction or a reaction via multiple steps which are influenced by the minute differences in the formation or preservation conditions of the films. A small endothermic peak was detected at 152.5°C. This might be attributable to the melting (144.5°C [6]) or evaporation of SnI_4 which could have been formed during heating in air, as reported in our previous papers [3,5], although a definite conclusion should be obtainable after high-temperature X-ray diffraction analysis and cyclic (heating and cooling) DSC operations.

3.3. Enthalpy change

The enthalpy change detected for the melting of SnI_2 (13.4 kJ mol^{-1}) corresponded to 75% of the value (17.991 kJ mol^{-1}) reported for the bulk material [7], on the assumption that 9% of the SnI_2 had evaporated before melting, as shown by the TG–DTA results in Fig. 1.

The enthalpy change detected for the reaction mentioned above (139.4 kJ mol^{-1}) was ≈ 61–65% of the reported values (215.6 and 229.8 kJ mol^{-1} at 500 and 600 K, respectively, for the bulk [7,8]), where the partial pressure of oxygen and of SnI_2 vapor was assumed to be equal to that of air (0.2 atm; 1 bar is 1 atm) and the equilibrium vapor pressure (0.06 atm at 500 K and 0.6 atm at 600 K), respectively.

The deviation from the literature values may be attributed mainly to the positioning of the baseline and to the lack of an appropriate standard for the minute enthalpy change.

4. Conclusions

A thermal change of a SnI_2 film as deposited on a glass substrate has been successfully detected by TG–DTA and evaluated semiquantitatively by DSC in nitrogen and in air. In nitrogen, a sharp endothermic peak at 317.9°C was interpreted as the melting of SnI_2; an endothermic weight loss at 260–420°C was interpreted as the sublimation and evaporation of SnI_2. In air, an exothermic weight loss at 180–290°C was interpreted as the oxidation reaction proposed in our previous papers [3–5]: $2SnI_2(s) + O_2(g) \rightarrow SnO_2(s) + SnI_4(g)$.

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