Thermochimica Acta, 232 (1994) 37–45
Elsevier Science B.V., Amsterdam
SSDI 0040-6031(93)01455-C

Thermal change of SnI_2 thin films. Part 2. Isothermal change without exposure to light radiation

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(Received 18 May 1993; accepted 8 June 1993)

Abstract

The isothermal change of SnI_2 films in air without exposure to light was investigated by weight change and X-ray diffraction analysis for films treated at room temperature or quenched from 50, 100 and 150°C. At room temperature, α- and β-SnI_2 peaks (preferred orientation) similar to those of the as-deposited films were observed after 1–3 h; then, randomly oriented α-SnI_2 and SnI_4 peaks appeared after 4–5 h. Heating accelerated the thermal change. α-SnI_2 (random orientation) and SnI_4 were also detected for films quenched from 50, 100 and 150°C. The weight loss at 150°C stopped at 20.4% of the sample weight, which agrees approximately with the value of 20.2% proposed by Sawada and Suzuki (Thermochim. Acta, 232 (1994) 29–36) for the reaction $2SnI_2(s) + O_2(g) \rightarrow SnI_4(g) + SnO_2(s)$. Weak diffraction peaks for SnO_2 were detected after the SnI_4 peaks disappeared.

INTRODUCTION

Tin oxide (SnO_2) films cannot be applied to transparent electrodes for liquid-crystal display devices because pattern formation by wet-etching has proved impossible. Kuku and Green [1] proposed an alternative lithography process via a photochemical reaction of a tin iodide (SnI_2) film at a relatively low temperature, e.g. ≈150°C. Although their process is promising, SnI_2 is unstable in air at room temperature and at the elevated temperature, even without exposure to light. However, there have been no systematic investigations concerning the thermal analysis of SnI_2.

In our previous paper [2], TG–DTA analysis of SnI_2 and SnI_4 powders in

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a nitrogen flow (heating rate 10°C min^{-1}) showed an endothermic weight loss attributed to evaporation at 300–460 and 85–190°C, respectively. Thermal change of SnI_2 evaporated film, as-deposited on a glass substrate, i.e. without separating from the substrate, was detected successfully by TG (heating rate 10°C min^{-1}). A weight loss between 260 and 420°C in an argon flow was attributed to the evaporation of SnI_2. A weight loss at 180–290°C in an air flow was interpreted as oxidation of SnI_2 to form tin oxide (SnO_2 or SnO) and SnI_4 vapor.

In the present study, the isothermal change of SnI_2 thin films in air without exposure to light radiation was investigated with a microbalance and an X-ray diffractometer; the results support the reaction mechanism proposed in our previous paper.

EXPERIMENTAL

The SnI_2 films (thickness $\approx$0.5–1 μm) were deposited by vacuum evaporation onto substrates at room temperature, as described elsewhere [2]. The film as deposited on the substrate was placed immediately on a hot plate heated at pre-determined temperatures (50, 100 and 150°C; fluctuation $\pm\approx7$°C). The room temperature treatment was performed without the hot plate. Room light was shielded during the isothermal heating for a pre-determined period before the sample was removed for room temperature evaluation by weight measurement and X-ray diffraction analysis. The heat treatment and the evaluation was repeated until a total heating time of 6 h was attained. The film was weighted using an ultra-microbalance (Sartorius S4; sensitivity 0.1 μg). The X-ray diffraction patterns were recorded with a conventional θ–2θ-type diffractometer with Ni-filtered Cu radiation, 40 kV and 45 mA (Rigaku RAD-IIIC system).

RESULTS

Weight measurement

Isothermal weight changes for SnI_2 thin films measured in air without light radiation are shown in Fig. 1. Weight loss at 150°C stopped at 24.3% of the specimen weight, which agreed approximately with the value expected (20.2%) for the reaction proposed in our previous paper [2]

$$2SnI_2(s) + O_2(g) \rightarrow SnI_4(g) + SnO_2(s) \qquad (1)$$

At the lower temperatures, the weight loss proceeded more slowly so that

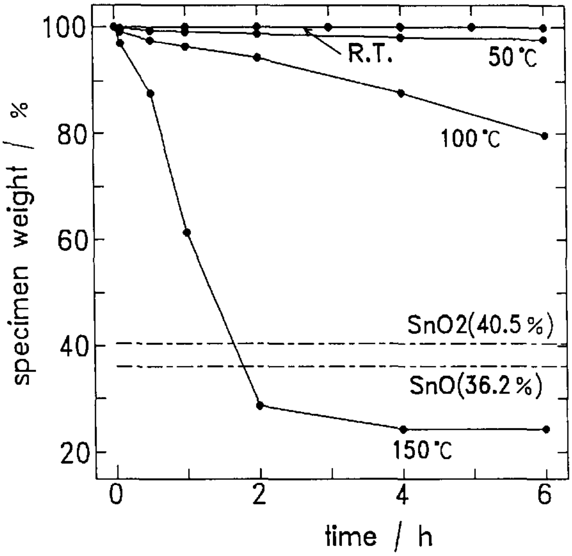

Fig. 1. Isothermal weight changes in air for SnI_2 thin films.

it is impossible to discuss the reaction mechanism up to the end point of the weight loss.

X-ray diffraction analysis

X-ray diffraction patterns for an SnI_2 thin film treated at room temperature are shown in Fig. 2. The patterns are identical with that of the as-deposited thin film up to 3 h of treatment; preferred crystal orientations of α-SnI_2 [3] and β-SnI_2 [4] were observed. The unidentified very weak peaks could be assigned to unreported peaks of α- or β-SnI_2. The intensities of these peaks remained almost unchanged during the present investigation. Randomly oriented α-SnI_2 and SnI_4 appeared at 4 and 5 h. respectively, at increasing diffraction intensities.

X-ray diffraction patterns for an SnI_2 thin film quenched from 50°C are shown in Fig. 3. The pattern after 5 min is identical with that of the as-deposited film. The changes were enhanced by heating; α-SnI_2 (random orientation) and SnI_4 are observed after 30 min while these appeared after 4 or 5 h for the room temperature specimens. The preferred orientations of α- and β-SnI_2 peaks became insignificant after 2 h (specimen weight 99%).

X-ray diffraction patterns for an SnI_2 thin film quenched from 100°C are shown in Fig. 4. The as-deposited spectrum with preferred orientation was not observed at 5 min (specimen weight, 99%). The predominant phases detected were α-SnI_2 (random orientation) and SnI_4. A very weak β-SnI_2 peak was observed.

X-ray diffraction patterns for an SnI_2 thin film quenched from 150°C are shown in Fig. 5. The predominant peaks changed from being randomly

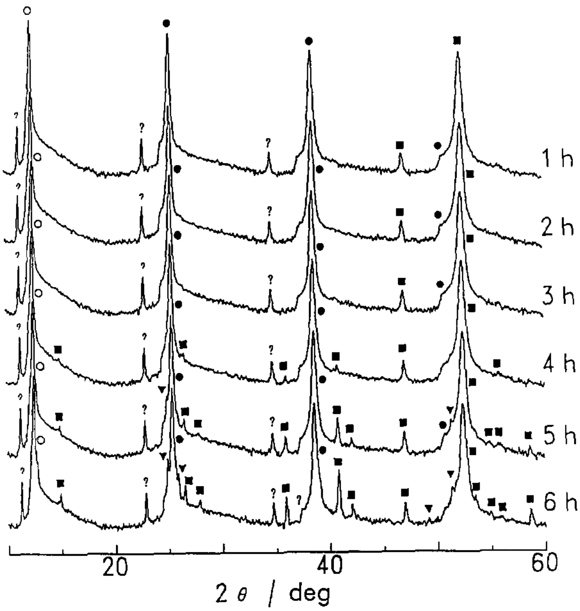

Fig. 2. X-ray diffraction patterns for an SnI_2 thin film treated at room temperature: ■, α-SnI_2; ●, β-SnI_2; ○, α- and/or β-SnI_2; ▼, SnI_4; and ?, an unreported peak of α- or β-SnI_2, respectively. The $\log_{10}$(diffraction intensity) is plotted to emphasise the minor phases.

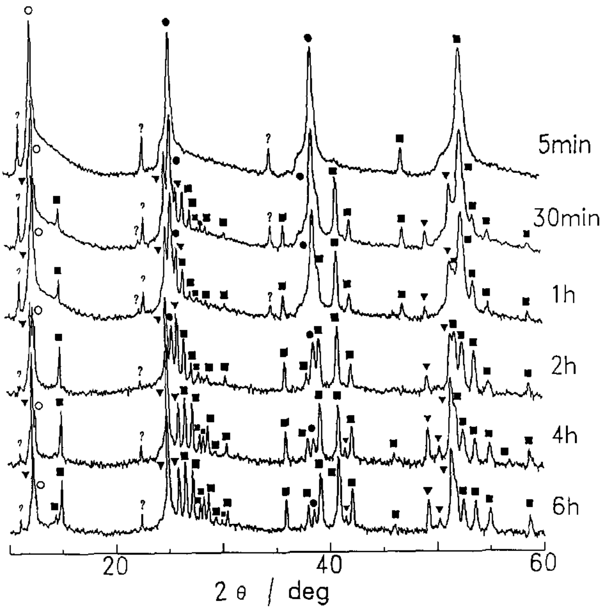

Fig. 3. X-ray diffraction patterns for an SnI_2 thin film quenched from 50°C; notations as in Fig. 2.

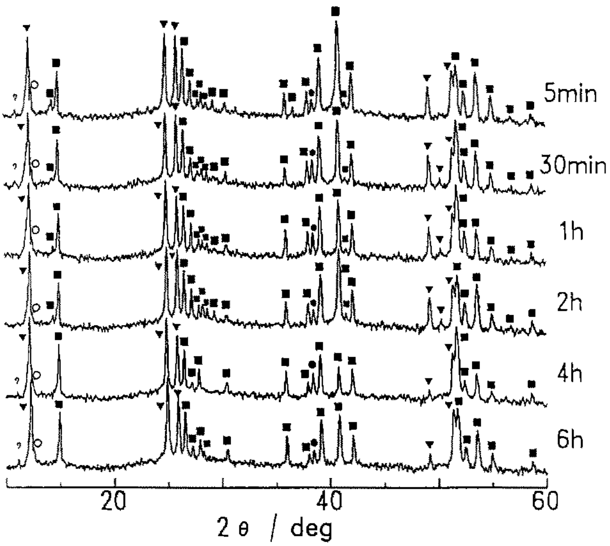

Fig. 4. X-ray diffraction patterns for an SnI_2 thin film quenched from 100°C; notations as in Fig. 2.

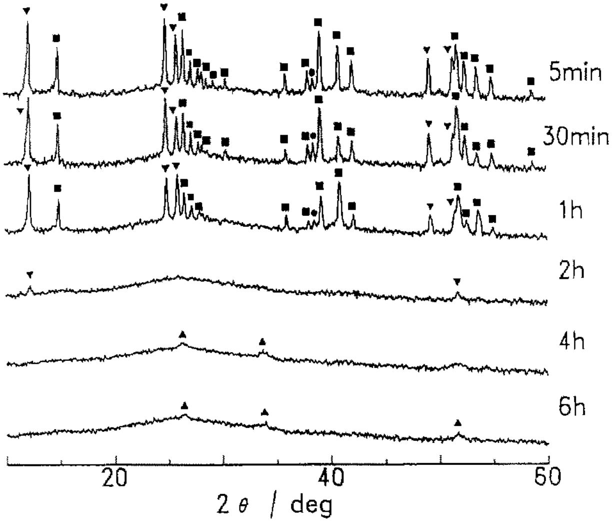

Fig. 5. X-ray diffraction patterns for an SnI_2 thin film quenched from 150°C; ■, α-SnI_2; ●, β-SnI_2; ▼, SnI_4; and ▲, SnO_2, respectively.

oriented α-SnI_2 and SnI_4 peaks after 5 min–1 h, to being weak SnI_4 peaks after 2 h, and then weak SnO_2 peaks after 4–6 h. Crystallization of SnI_2 was observed after disappearance of the iodides. A very weak β-SnI_2 peak was observed. The patterns from 5 min to 1 h (specimen weight 97%–61%) are analogous to those at 100°C from 5 min to 6 h (specimen weight 99%–79%), as shown in Fig. 4.

The results of the X-ray diffraction analyses are summarized in Table 1. The predominant phases detected for the quenched films changed in the approximate order: α-SnI_2 (preferred orientation), β-SnI_2 (preferred orientation), α-SnI_2 (random orientation), SnI_4, and SnO_2 (only observed for the films treated at 150°C). Heating accelerated the change.

TABLE 1

Phases detected by X-ray diffraction analysis for films quenched from various temperatures

Peaks observed	Treatment time					
	5 min	30 min	1 h	2 h	4 h	6 h
Room temperature						
α-SnI_2 prefer.	s	s	s	s	s	s
β-SnI_2 prefer.	s	s	s	s	s	s
α-SnI_2 random					s	s
SnI_4 random					w	w
SnO_4 random						
50°C						
α-SnI_2 prefer.	s	s	s			
β-SnI_2 prefer.	s	s	s	s	w	w
α-SnI_2 random		s	s	s	s	s
SnI_4 random		s	s	s	s	s
SnO_2 random						
100°C						
α-SnI_2 prefer.						
β-SnI_2 prefer.	w	w	w	w	w	w
α-SnI_2 random	s	s	s	s	s	s
SnI_4 random	s	s	s	s	s	s
SnO_2 random						
150°C						
α-SnI_2 prefer.						
β-SnI_2 prefer.	w	w	w			
α-SnI_2 random	s	s	s			
SnI_4 random	s	s	s	w		
SnO_2 random					w	w

Key: prefer., preferred orientation; random, random orientation. Intensity of the diffraction peaks: s; strong; w, weak.

DISCUSSION

α- and β-SnI_2

Green and Kuku [5] reported that β-SnI_2 was stable above the transition temperature (≈108°C), and that the substrate temperature should be maintained at ≈100°C during film deposition in order to obtain pure α-SnI_2. In the present investigation, the high-temperature phase (β-SnI_2) coexisted with α-SnI_2 for films deposited on a room-temperature substrate. These results suggest that rapid cooling of SnI_2 vapor on the room-temperature substrate forms metastable β-phase which transforms extremely slowly to stable α-phase at room temperature. The formation of α-SnI_2 (random orientation) at room temperature or 50°C can be explained by rearrangement of the as-deposited preferred orientation (α- or β-SnI_2), or of the possibly coexistent amorphous SnI_2; it is impossible at present to determine precisely which is the major originating phase. Heating accelerated the reorientation. The absence of β-SnI_2 peaks, except a very weak one, for the films quenched from 150°C (Fig. 5) can be explained by the reverse transition (from β- to α-phase) taking place during quenching.

SnI_4 and tin oxide

The detection of SnI_4 in the film treated at room temperature supports the hypothesis proposed previously [2] that SnI_4 impurity is formed in SnI_2 powders during their preparation or storage at room temperature in air, via one of the following reactions

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

$$8SnI_2(s) + O_2(g) + 4H_2O(g) \rightarrow 2SnI_4(s) + 6SnO(s) + 8HI(g) \quad (3)$$

$$2SnI_2(s) + O_2(g) \rightarrow SnI_4(s) + SnO_2(s) \quad (4)$$

$$4SnI_2(s) + O_2(g) \rightarrow 2SnI_4(s) + 2SnO(s) \quad (5)$$

Reactions (2) and (3) have a weight loss of 34.3%. It is impossible, at present, to determine which phases of SnI_2, i.e. α-SnI_2 (preferred orientation), β-SnI_2 (preferred orientation) or amorphous SnI_2, participate in these reactions. The oxide (SnO_2 or SnO) is expected to be amorphous. The absence of any weight loss (Fig. 1) can be explained by the very low vapor pressure (≈1×10^{-7} atm) [6] of SnI_4 at room temperature for reactions (4) and (5). SnI_4 is detected approximately simultaneously with the appearance of randomly oriented α-SnI_2. This suggests that the oxidation reaction is initiated when the ions or molecules can move.

The results of X-ray diffraction analysis for the specimen quenched from 150°C corroborate reaction (1); SnO_2 was detected after the disappearance of SnI_4 in Fig. 5. At the lower temperatures, crystallization of SnO_2 was not observed, so that the oxidation state of tin is unknown. In Fig. 1, the expected values for the other oxidation reactions without evaporation of SnI_4 are indicated for reference, i.e. formation of SnO_2 (40.5%) by reaction (6) or (7), and of SnO (36.2%) by reactions (8) and (9)

$$2SnI_2(s) + O_2(g) + 2H_2O(g) \rightarrow 2SnO_2(s) + 4HI(g) \tag{6}$$

$$SnI_2(s) + O_2(g) \rightarrow SnO_2(s) + I_2(g) \tag{7}$$

$$SnI_2(s) + H_2O(g) \rightarrow SnO(s) + 2HI(g) \tag{8}$$

$$2SnI_2(s) + O_2(g) \rightarrow 2SnO(s) + 2I_2(g) \tag{9}$$

The final specimen weight (24.3%) at 150°C is slightly greater than the value expected (20.2%) for reaction (1); the deviation can be explained by the fact that reactions (6)–(9) occur simultaneously. The weight loss proceeded slowly at lower temperatures so that it is impossible to discuss the reaction up to the end point; the presence of liquid SnI_4 (melting point, ≈144°C [2, 7]) may accelerate the reaction at 150°C. The final specimen weight (11%–14%) as determined by TG in air [2] was smaller than the expected value for reaction (1); evaporation of unreacted SnI_2 might occur at the higher temperature (180–290°C) during the non-isothermal heating (heating rate, 10°C min^{-1}).

CONCLUSION

The isothermal changes in SnI_2 films in air without light radiation were investigated from the weight changes and X-ray diffraction patterns of films treated at room temperature or quenched from 50, 100 and 150°C.

At room temperature, α- and β-SnI_2 peaks (preferred orientation), similar to those of the as-deposited films, were observed after 1–3 h; then randomly oriented α-SnI_2 and SnI_4 peaks appeared after 4–5 h. This supports the hypothesis proposed in our previous paper [2] that SnI_4 impurity is formed in the SnI_2 powders during preparation or storage at room temperature in air. The absence of any weight loss can be explained by the very low vapor pressure ($\approx 1 \times 10^{-7}$ atm) [8] of SnI_4 at room temperature.

α-SnI_2 (random orientation) and SnI_4 were also detected for films quenched from 50, 100 and 150°C; changes were accelerated by heating.

The weight loss at 150°C stopped at 20.4% of the original weight which agrees approximately with the value expected (20.2%) for the reaction proposed previously [2], i.e. $2SnI_2(s) + O_2(g) \rightarrow SnI_4(g) + SnO_2(s)$. Weak diffraction peaks for SnO_2 were detected after the SnI_4 peaks disappeared.

ACKNOWLEDGMENT

The authors thank the Ministry of Education, Science and Culture for Grant-in-Aid for Scientific Research (C) 03650264.

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