ELSEVIER

Thermochimica Acta, 243 (1994) 95–100

thermochimica
acta

Thermal change of SnI_2 thin films. Part 3. Isothermal change under light radiation

Y. Sawada *, M. Suzuki [1]

Department of Industrial Chemistry, Faculty of Engineering, Tokyo Institute of Polytechnics,
1538 Iiyama, Atsugi-shi, Kanagawa 243-02, Japan

(Received 14 June 1993; accepted 21 January 1994)

Abstract

The influence of light radiation on the thermal change of SnI_2 thin films heated at 50, 100 and 150°C in air for 6 h was investigated using weight measurement and X-ray diffraction analysis. The thermal change was accelerated by heating and light radiation. Radiation with a tungsten lamp (500 W, 25 cm from the film) was more effective than room light (mainly from fluorescent lamps). Weight loss at 150°C stopped at 21.1% and 21.5%, based on specimen weight, under radiation from room light and from a tungsten lamp, respectively. These values approximately agree with the 20.2% expected for the reaction proposed in our previous papers (Thermochim. Acta, 232 (1994) 29–36; 37–45), $2SnI_2(s) + O_2(g) \rightarrow SnI_4(g) + SnO_2(s)$. This reaction mechanism is supported by the presence of diffraction peaks for SnO_2. The higher values of the apparent end point (25.0% and 25.5%) at 100°C are interpreted as indicating incomplete evaporation (sublimation) of SnI_4.

Keywords: Isothermal; Light; Radiation; Thin film; Tin oxide; XRD

1. Introduction

Kuku [1] and Kuku and Green [2] proposed a novel lithography process via the photo-oxidation of an SnI_2 film to produce a transparent conductive film of SnO_2. The isothermal and non-isothermal changes of SnI_2 films in air without light radiation were investigated in our previous papers [3, 4]. The oxidation reaction of

---

* Corresponding author.

[1] Present address: Kojundo Chemical Laboratory, Co., Ltd., 5-1-28 Chiyoda, Sakade-shi, 350-02, Japan.

SSDI 0040-6031(94)01735-Y

SnI_2 to form SnI_4 and SnO_2 was detected. In the present study, the influence of light radiation on the isothermal change is investigated.

2. Experimental

The SnI_2 films (thickness $\approx 0.5-1\ \mu m$) were deposited by vacuum evaporation onto substrates at room temperature, as previously described [3]. The films as deposited on the substrate were immediately placed on a hot plate heated at a predetermined temperature (50, 100 and 150°C; fluctuation $\pm \approx 7°C$).

The films were heated isothermally in air for a predetermined period under room light (mainly fluorescent lamps) or a tungsten lamp (500 W, 25 cm from the film). The heat treatment and the evaluation of the quenched films were repeated for a total heating time of 6 h. The film weight was measured using an ultra-microbalance (Sartorius S4; sensitivity, 0.1 μg). The X-ray diffraction spectra were recorded using a conventional $\theta-2\theta$ type diffractometer with Ni-filtered Cu radiation; 40 kV, 45 mA (Rigasku RAD-IIIC system). A film heated at 100°C for 6 h under a tungsten lamp was also analyzed using a thin-film type X-ray diffractometer with monochromated Cu radiation; 50 kV, 300 mA (Rigaku RINT-2000 system) at different incident angles (0.5 and 8.0 deg).

3. Results and discussion

3.1. Weight change

Isothermal weight changes for SnI_2 thin films in air under room light and tungsten lamp radiation are shown in Figs. 1 and 2, respectively. Weight loss

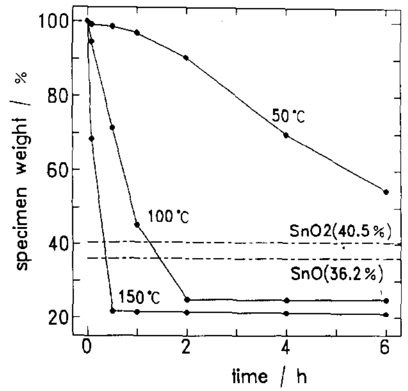


Fig. 1. Isothermal weight changes in air for SnI_2 thin films under room light radiation.

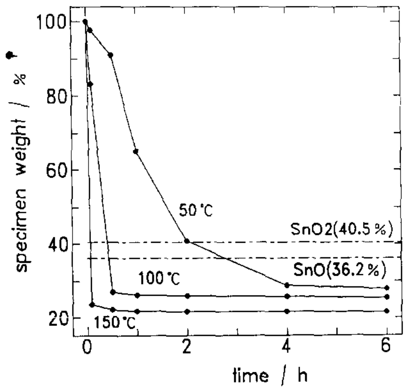


Fig. 2. Isothermal weight changes in air for SnI_2 thin films under tungsten lamp radiation.

was accelerated by heating as well as by light radiation when compared with the previous results without light radiation [4] (not shown in the figures). Significant photo oxidation was observed. Radiation from a tungsten lamp was more effective under the present experimental conditions. In these figures, the expected weights for the reactions $SnI_2(s) + O_2(g) \rightarrow SnO_2(s) + I_2(g)$, and $SnI_2(s) + 0.5O_2(g) \rightarrow SnO(s) + I_2(g)$ are indicated for reference. Weight loss at 150°C stopped at 21.1% and 21.5%, as determined from the weight of the film under room light and tungsten lamp radiation, respectively. These values agree approximately with that expected (20.2%) for the reaction proposed in our previous papers [3, 4]

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

The thermal change was accelerated by heating; the weight loss proceeded more slowly at lower temperatures. At 100°C, the apparent end points (25.0% and 25.5%) were higher than those at 150°C. Sigmoidal curves were observed at 50°C. The higher values of the apparent end point at ≤100°C can be attributed to the incomplete evaporation (sublimation) of SnI_4.

3.2. X-ray diffraction analysis

X-ray diffraction spectra for a thin film of SnI_2 heated at 50, 100 and 150°C under room light and then quenched are shown in Figs. 3–5, respectively. The spectrum for the film heated at 50°C for 5 min and then quenched (Fig. 3) was approximately identical with the as-deposited pattern [3] (not shown). The preferred crystal orientations of α- [5] and β-SnI_2 [6] were observed, except for very weak peaks of randomly oriented α-SnI_2. An unknown peak was attributed to

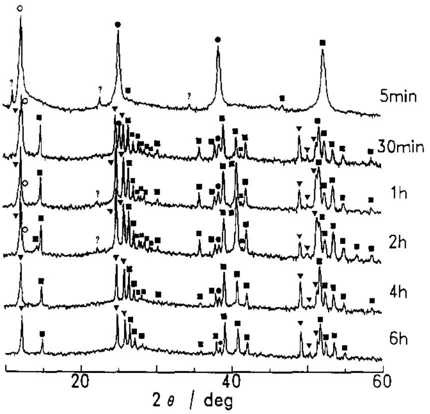


Fig. 3. X-ray diffraction spectra for an SnI_2 thin film heated at 50°C under room light radiation and then quenched: ■, α-SnI_2; ●, β-SnI_2; ○, α- and/or β-SnI_2; ▼, SnI_4; ?, unreported peak of α- or β-SnI_2. The $\log_{10}$ (diffraction intensity) is plotted to emphasize the minor phases.

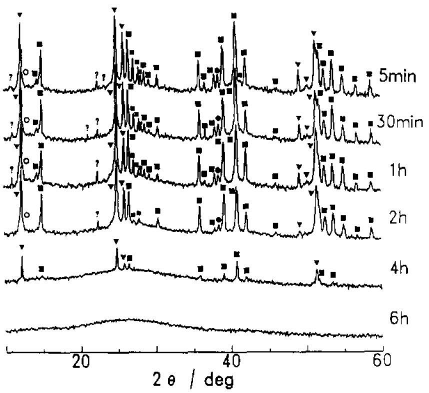


Fig. 4. X-ray diffraction spectra for an SnI_2 thin film heated at 100°C under room light radiation and then quenched. Symbols as in Fig. 3.

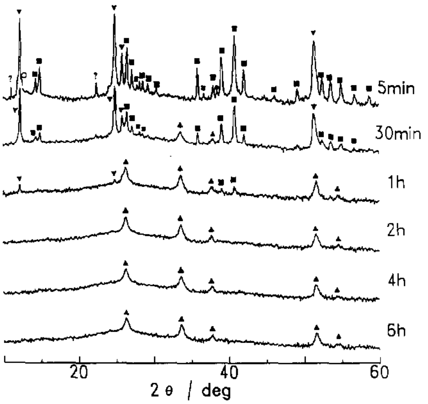
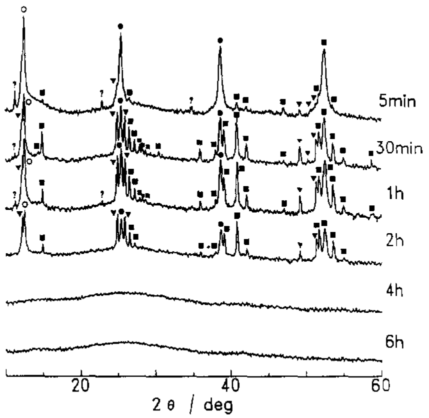


Fig. 5. X-ray diffraction spectra for an SnI_2 thin film heated at 150°C under room light radiation and then quenched: ■, α-SnI_2; ●, β-SnI_2; ○, α- and/or β-SnI_2; ?, unreported peak of α- or β-SnI_2; ▼, SnI_4; ▲, SnO_2.

unreported peaks of α- and/or β-SnI_2; see our previous paper [3]. Strong diffraction peaks for randomly oriented α-SnI_2 and SnI_4 appeared after 30 min. Their peak intensities increased up to 2 h (relative weight; 90.3%) before decreasing. A very weak β-SnI_2 peak was observed up to 6 h when further evaluation was abandoned. As shown in Fig. 4, the predominant phases detected for the film quenched from 100°C were α-SnI_2 (random orientation) and SnI_4, up to 4 h; a very weak β-SnI_2 peak was observed up to 2 h. The predominant peaks for the film quenched from 150°C (Fig. 5) changed from randomly oriented α-SnI_2 and SnI_4 peaks to weak SnO_2 [7] peaks.



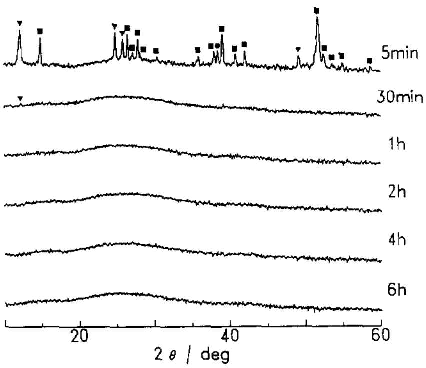


Fig. 6. X-ray diffraction spectra for an SnI_2 thin film heated at 50°C under tungsten lamp radiation and then quenched. Symbols as in Fig. 3.

Fig. 7. X-ray diffraction spectra for an SnI_2 thin film heated at 100°C under tungsten lamp radiation and then quenched: ■, α-SnI_2; ●, β-SnI_2; ▼, SnI_4.

X-ray diffraction spectra for the films heated at 50 and 100°C under tungsten lamp radiation and then quenched are shown in Figs. 6 and 7, respectively. Peaks were observed up to 2 h for the film quenched from 50°C (Fig. 6); the α- and β-SnI_2 peaks (preferred orientation) were stronger than those formed under room light conditions. Peaks were observed only up to 5 min for the film quenched from 100°C (Fig. 7); a halo with no diffraction peak was also confirmed using a thin-film type diffractometer for the film heated at 100°C for the longest heating period (6 h). The film heated at 150°C showed broad SnO_2 peaks (not shown), even for the shortest heating period (5 min).

The results of the X-ray diffraction analysis are summarized in Table 1, together with the results of our previous paper [4]. The predominant phases detected for the quenched films changed approximately in the following order; α-SnI_2 (preferred orientation), β-SnI_2 (preferred orientation), α-SnI_2 (random orientation), SnI_4 and SnO_2. Crystallization of SnO_2 was observed only for the films treated at 150°C at ≤24.4 wt%, which corresponds to ≈5% of the SnI_4 that remained unevaporated. No diffraction peak was detected after the disappearance of the iodides at ≤100°C so that formation of amorphous lower oxides such as SnO may be possible at low temperature. Heating and light radiation, especially with a tungsten lamp, accelerated the change.

Table 1
Phases detected using X-ray diffraction analysis for the films quenched from various temperatures

Treat. temp.	XRD peaks detected for the quenched films	Condition of light radiation and treatment period																	
		Dark (no light)						Room light						Tungsten lamp					
		5 min	30 min	1 h	2 h	4 h	6 h	5 min	30 min	1 h	2 h	4 h	6 h	5 min	30 min	1 h	2 h	4 h	6 h
50°C	α-SnI_2 p	■	■	■				■	□					■	■	■	■		
	β-SnI_2 p	■	■	■	■	□	□	■	□	□	□	□	□	■	■	■	□		
	α-SnI_2 r		■	■	■	■	■	□	■	■	■	■	■	□	■	■	■		
	SnI_4		■	■	■	■	■		■	■	■	■	■	□	■	■	■		
	SnO_2																		
100°C	α-SnI_2 p							□						■					
	β-SnI_2 p	□	□	□	□	□	□	□	□	□	□			□					
	α-SnI_2 r	■	■	■	■	■	■	■	■	■	■	□		■					
	SnI_4	■	■	■	■	■	■	■	■	■	■	□		■	□				
	SnO_2																		
150°C	α-SnI_2 p							□	□										
	β-SnI_2 p	□	□	□				□											
	α-SnI_2 r	■	■	■				■	■	□									
	SnI_4	■	■	■	□			■	■	□									
	SnO_2					□	□		□	□	□	□	□	□	□	□	□	□	□

Key: p, preferred orientation; r, random orientation; ■, strong; □, weak.

4. Conclusions

The influence of light radiation on the thermal change of SnI_2 thin films was investigated. The thermal change was accelerated by heating and light radiation. Radiation with a tungsten lamp was more effective than using room light (mainly from fluorescent lamps).

Weight loss at 150°C stopped at 21.1% and 21.5%, as found from the specimen weights, under room light and tungsten lamp radiation, respectively. These values agree approximately with the 20.2% expected for the reaction proposed in our previous papers [3, 4], $2SnI_2(s) + O_2(g) \rightarrow SnI_4(g) + SnO_2(s)$. This reaction mechanism was supported by the presence of SnO_2 diffraction peaks. The higher values of the apparent end point (25.0% and 25.5%, respectively) at 100°C were interpreted as indicating incomplete evaporation (sublimation) of SnI_4.

Acknowledgments

The authors thank the Ministry of Education, Science and Culture for a Grant-in-Aid for Scientific Research (C) 03650264 and Mr. T. Kubo, Rigaku Co. for the X-ray analysis using a thin-film type diffractometer.

References

[1] T.A. Kuku, Thin Solid Films, 142 (1986) 241.
[2] T.A. Kuku and M. Green, Thin Solid Films, 144 (1986) L119.
[3] Y. Sawada and M. Suzuki, Thermochim. Acta, 232 (1994) 29–36.
[4] Y. Sawada and M. Suzuki, Thermochim. Acta, 232 (1994) 37–45.
[5] Joint Committee for Powder Diffraction File 25-975.
[6] Joint Committee for Powder Diffraction File 40-877.
[7] Joint Committee for Powder Diffraction File 13-111.