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DSC of silver-added indium-tin-oxide (ITO) transparent conductive materials

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Abstract

Chemical state of silver in the sintered silver-added ITO (indium-tin-oxide, tin-doped In_2O_3) ceramics was investigated by X-ray diffraction analysis and high-temperature DSC. The X-ray diffraction peaks of metallic silver were detected for the specimens with >ca. 1 at.% Ag (as indicated by Ag/(Ag+Sn+In)). High-temperature DSC detected an endothermic peak at ca. 960°C, which agreed with the melting point of metallic silver, and the exothermic peak during the cooling for all specimens. Therefore, chemical state of silver in the sintered silver-added ITO ceramics was interpreted as metallic. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: ITO transparent conductive films; Sputtering target; Metallic silver; X-ray diffraction; High-temperature DSC

1. Introduction

Thin films of tin-doped In_2O_3 (indium-tin-oxide, ITO) are widely used as transparent conductive electrodes for display devices, such as liquid crystal displays. The ITO films were usually deposited by the sputtering method using a sintered ITO as a target.

The authors reported that addition of silver enhanced the doping efficiency (formation of carrier electrons by tin doping) in the ITO films [1]. The addition of silver increases the carrier concentration and the optical absorption in the visible range. Therefore, ca. 1 at.% of silver (as indicated by Ag/(Ag+Sn+In)) is recommended for application; in this case, the doping efficiency is approximately doubled compared with that in case of no silver addition.

Chemical state of the added silver, whether metallic (Ag) or oxide (AgO, Ag_2O, etc.) in the ITO sintered body, seems to provide important information for understanding the conduction mechanism of the ITO films and the sintering process of silver-added ITO targets. In the present work, silver-added In_2O_3 and ITO ceramics were prepared to investigate the chemical state of silver additive by thermal analysis and X-ray diffraction analysis.

2. Experimental

The powders of In_2O_3 (purity 99.99%, particle size ca. 1 μm), SnO_2 (99.99%, ca. 1 μm) and metallic silver (99.9%, ca. 2 μm) were mixed in predetermined

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atomic ratios; tin contents (as indicated by Sn/(In+Sn)) 0, 5 or 10 at.% and silver contents (as indicated by Ag/(In+Sn+Ag)) 0–20 at.%. These mixed powders were pressed and sintered at 1350°C for 5 h in air.

The sintered bodies were cooled in air and milled to powders for the compositional analysis by inductively coupled plasma emission spectrometry (ICP), X-ray diffraction analysis and thermal analysis. The phase identification of the specimens were performed by X-ray diffraction using monochromated 40 kV, 300 mA Cu*K*α radiation (Rigaku RINT 2500 V System). Thermal analysis was performed using high-temperature DSC (Rigaku, DSC8270). The specimens (ca. 100 mg) in platinum pans or alumina pans were heated at the heating rate of 10°C/min in static air or flowing argon (flow rate; 100 ml/min). The heating and cooling was repeated eight times between the temperature ranges of 600–1000, 600–1200 and 600–1400°C. Powder mixture of metallic silver and alumina (Ag 0.2–16 mass%) was prepared for reference.

3. Results and discussion

3.1. X-ray diffraction

Fig. 1 shows the X-ray diffraction (XRD) spectra for the sintered In_2O_3 and ITO ceramics with various silver contents. All samples showed the strong peaks which agree with those reported as In_2O_3 [2], although they were shifted slightly to the lower angles. For 5 at.% of tin content, absence of the peaks of SnO_2 [3] was interpreted as formation of the solid solution (ITO, i.e. tin-doped In_2O_3). The weak peaks of SnO_2 and $In_4Sn_3O_{12}$ [4] were observed in the ITO containing 10 at.% Sn which was interpreted to excess the solubility limit (9 at.%) [5] of tin in In_2O_3. The silver additive was detected as metallic silver [6]. Silver compound ($AgInO_2$ [7] etc.) was not found in the present study. Thus, trace of the reaction of silver with In_2O_3 or SnO_2 was not detectable.

The (111) diffraction peaks of metallic silver for the various specimens are shown in Fig. 2. The metallic silver was detected at >0.71 at.% Ag. Intensity of the peak increased along with the increase of silver content, and was independent of the tin content. Fig. 3 shows the X-ray diffraction spectra of the mixture of starting materials. Metallic silver for the various specimens was not detected in the case of $\leq$ ca. 1.0 at.% Ag. Therefore, it was impossible to determine the chemical state of added silver at $\leq$1.0 at.% Ag by X-ray diffraction analysis.

3.2. High-temperature DSC

A typical DSC of silver-added ITO ceramics (Ag, 0.02 mass%) is shown in Fig. 4. A clear endothermic

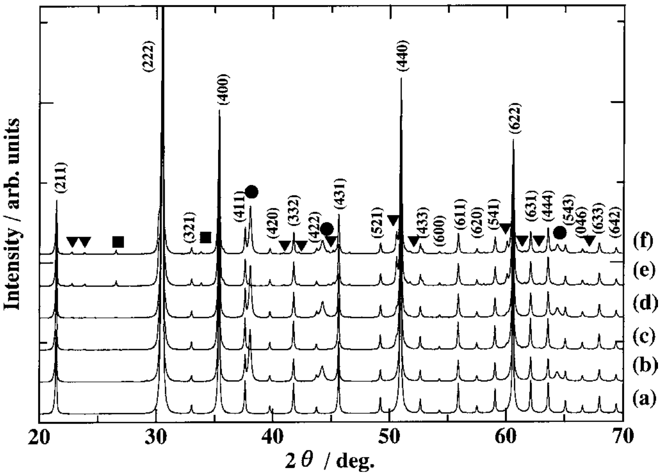

Fig. 1. X-ray diffraction spectra of the specimens. (a) In_2O_3, (b) In_2O_3-Ag (Ag, 22.6 at.%), (c) ITO (Sn, 5 at.%), (d) ITO-Ag (Sn, 5 at.%, Ag, 18.8 at.%), (e) ITO (Sn, 10 at.%); and (f) ITO-Ag (Sn, 10 at.%, Ag, 18.8 at.%). Peaks of Ag (●), SnO_2 (■) and $In_4Sn_3O_{12}$ (▼), respectively. The indexes of the peaks as In_2O_3 are indicated in parentheses.

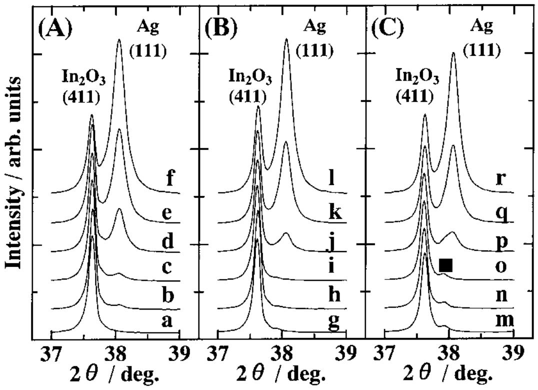

Fig. 2. The (111) diffraction peaks of the metallic silver for the various specimens. (A), In_2O_3-Ag, (B) ITO (Sn, 5 at.%)-Ag and (C) ITO (Sn, 10 at.%)-Ag. ■; the peak of SnO_2. Curves a, g, m represent C_{ag}=0 at.%; and curves b, c, d, e, f, h, i, j, k, l, n, o, p, q and r represent 0.71, 0.96, 4.55, 10.3, 22.6, 0.14, 0.43, 4.94, 10.0, 18.8, 0.11, 0.34, 4.73, 10.1 and 18.8 at.% Ag, respectively.

peak at 957°C agreed approximately with the melting point (960°C) of pure metallic silver suggesting the presence of metallic silver that was undetectable by the X-ray diffraction analysis.

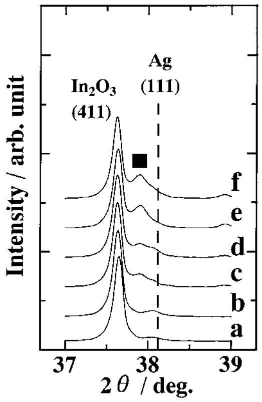

Fig. 3. The (111) diffraction peak of the metallic silver of the mixture of starting materials before sintering: Curves a and b represent In_2O_3-Ag; curves c and d represent ITO (Sn, 5 at.%); and curves e and f represent ITO (Sn, 10 at.%). ■;, the peak of SnO_2. Curves a, c, e, represent Ag, 0.5 at.%, and curves b, d, f represent Ag, 1.0 at.%, respectively.

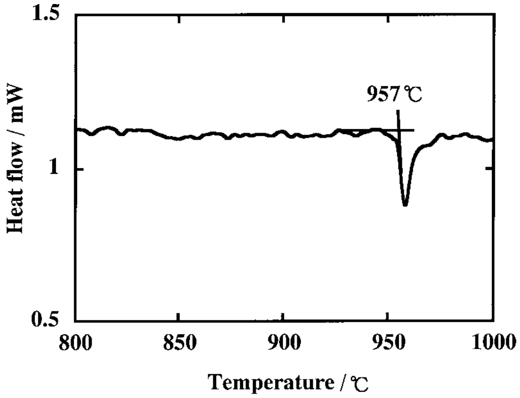

Fig. 4. A typical DSC curve of silver-added ITO ceramics. Sn, 10 at%; Ag, 0.02 mass%; sample mass, 100 mg, heating atmosphere, static air; and heating rate, 10°C/min.

When DSC of silver-added ITO (Ag 10 at.%, Sn 5 at.%) was repeated at 600–1400°C in static air at 10°C/min in a platinum pan, the endothermic peak decreased gradually before disappearing at the 8th cycle. The X-ray diffraction analysis indicated disappearance of metallic silver; no extra phase was detected except that of In_2O_3 (ITO). In case of the cyclic DSC at the lower temperature range (600–1000 and 600–1200°C), the endothermic peak remain unchanged suggesting the evaporation of silver was negligible at temperatures <1200°C.

The influence of the heating atmosphere (static air and flowing argon) and the sample pans (platinum and alumina) are shown in Fig. 5. The temperature of the endothermic peak was independent of the heating conditions. The exothermic peak during the cooling appeared at the lower temperature (ca. 830–780°C). These results are equal to those of the reference specimens (powder mixture of metallic silver and alumina). The temperature of the exothermic peak was also independent of the heating conditions. These reversible peaks should be regarded as melting and solidification of metallic silver. Small exothermic peaks or shoulders observed during the cooling were not fully understandable at the present. All specimens showed an endothermic peak at ca. 960°C which agreed with that of metallic silver. Therefore, chemical state of silver additive was interpreted as metallic. That is, reaction of silver additive with In_2O_3 or ITO was negligible.

Fig. 6 shows the dependence of the melting temperature on the silver content in the pan. The results of alumina (powder mixture of metallic silver and alumina) agree with that measured with a small grain of

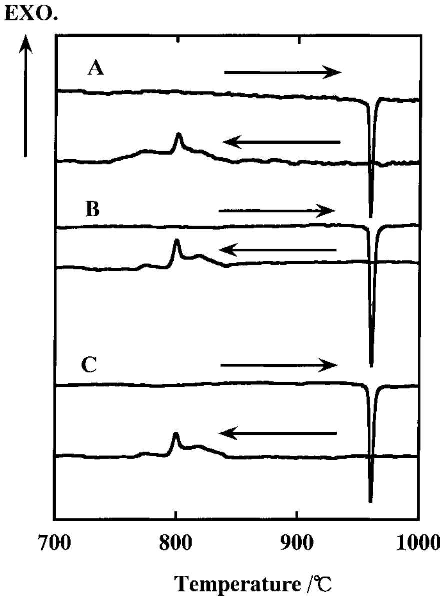

Fig. 5. DSC of silver-added ITO with various heating conditions. A, with platinum pans in static air, B with platinum pans in flowing argon and C, with alumina pans in static air, respectively. Sn, 10 at.%; Ag, 6 mass%; sample mass, ca. 100 mg; and heating rate, 10°C/min.

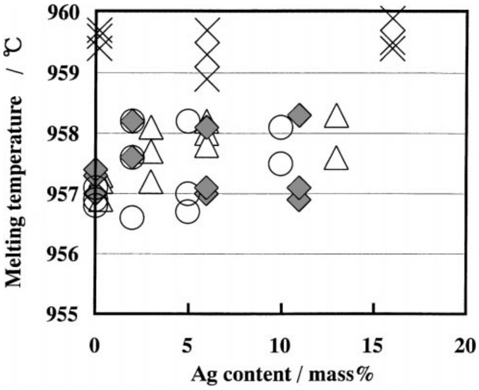

Fig. 6. Dependence of the melting temperature on the silver content in the pan. (△), silver-added In_2O_3, (◆) silver-added ITO (Sn, 5 at.%), (○) silver-added ITO (Sn,10 at.%) and (×) powder mixture of silver and alumina, respectively. Sample pan, platinum; heating atmosphere, static air; and heating rate, 10°C/min.

metallic silver. In case of the silver-added In_2O_3 and ITO, the peak temperature was ca. 1–3°C lower. The deviation was explained tentantively by the formation of silver alloy containing small amount of indium and for tin although the detail remained unexplained.

4. Conclusions

ITO ceramics with silver additive was investigated using X-ray diffraction analysis at room temperature and high-temperature DSC in static air and flowing argon. The diffraction peaks indicating only metallic silver were detected for the specimen with >ca. 1 at.% Ag, while these were not detected for the sample with less silver content. The endothermic peak at ca. 960°C was independent of the silver content in the ceramics, and agreed approximately with the melting point (960°C) of pure metallic silver. Therefore, the chemical state of silver in the sintered silver-added ITO ceramics was interpreted as metallic; no indication of the reaction of silver with In_2O_3 or S_nO_2 was detected by X-ray diffraction analysis.

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