

Active Soldering of ITO to Copper

Active soldering of indium-tin-oxide (ITO) sputtering targets to copper backing plates using an Sn56Bi4Ti(Ce, Ga) filler metal was investigated

S. Y. CHANG, M. H. LU, L. C. TSAO, AND T. H. CHUANG

ABSTRACT. An Sn56Bi4Ti(Ce, Ga) active solder was used for joining indium-tin-oxide (ITO) targets with copper backing plates at 180°C in air. The mechanism for such low-temperature (<200°C) soldering of ceramic/metal was investigated. The filler metal contains titanium that acts as a reactive agent to facilitate joining. The affinity of cerium for oxygen protects titanium from oxidation, allowing titanium to react with ITO and copper. Electron probe microanalyzer analysis (EPMA) elemental mapping revealed that titanium segregates effectively at the ITO/solder and copper/solder interfaces.

Introduction

Indium-tin-oxide (ITO) is the most commonly used of all transparent conductive oxides (TCO), whose application domain encompasses flat-panel displays, huge touch panels, photovoltaics, electrochromic devices, solar cells, heatable glass, etc. (Ref. 1). Sputtering is a widely used technique for the deposition of ITO thin-film layers onto desired substrates (Ref. 2). In recycling, the spent ITO targets are removed from their copper backing plates, and a soldering process is used to join a new ITO target to the recycled copper backing plate. The soldering temperature must be kept lower than 300°C in order to avoid the dissociation of oxygen from the ITO material. Furthermore, ITO and copper provide very different coefficients of thermal expansion at 8.2×10^{-6} and 17×10^{-6} (1°C), respectively. Therefore, it is necessary to find a low-melting-point solder to minimize the residual stresses generated from the aforementioned thermal mismatch and to prevent

breakage of the target material.

For ceramic to metal brazing, conventional active fillers such as Ag-Cu-Ti alloys have high melting temperatures in the range of 850–900°C (Ref. 3). Sn10Ag4Ti and Pb4In4Ti have been employed in the development of a low-melting-point active filler (Refs. 4, 5). Although the act of brazing, when using these filler metals, must also be conducted at temperatures above 850°C (similar to the case using traditional Ag-Cu-Ti active filler metals), the thermal stress can be alleviated by virtue of their lower solidification temperatures (221–300°C) (Ref. 6). More recently, there have been reports of new active solders by adding rare earth elements (Ce, La) and the wetting promoter (Ga) into Sn-Ag-Ti and Zn-Ag-Ti (Refs. 7, 8). With these active solders, the joining process in the case of ceramics can be done at temperatures lower than 450°C without flux and without the need for premetallization or a protective atmosphere.

This study employed a newly developed active filler metal Sn56Bi4Ti(Ce, Ga) with a low melting temperature of 148°C to join ITO targets with their copper backing plates. As electron probe microanalyzer (EPMA) analysis indicates, the addition of the rare-earth element (Ce) to this active solder can remove oxides at the reaction interfaces of the workpieces during joining, thereby facilitating the interaction between the active element (Ti) and the joining material.

Experimental

The active solder Sn56Bi4Ti(Ce, Ga) was prepared by melting metals of 99.99% purity in a high-frequency vacuum induction furnace. The cast ingots were rolled into 0.3-mm-thick foil. The contents of the trace elements cerium and gallium were 0.1 and 0.9 wt-%, respectively. Differential scanning calorimetry (DSC) was used to determine the melting temperature of the filler metal at a heating rate of 10°C/min under an argon atmosphere. The ITO target material used for joining, supplied by Thintech Materials Technology Co., Ltd., was a mixture of 90% In₂O₃ and 10% SnO₂. Figure 1 shows the geometry and dimensions of the soldered specimens subjected to shear testing. The bond surfaces of ITO and copper were ground and polished with a suspension containing 1- μm Al₂O₃. Prior to soldering, the ITO specimens were preheated to 180°C on a heating plate for 5 min in air. The active solder was then placed on the ITO surfaces to melt. After the molten solder was agitated for 30 s, the Cu specimen was set on the molten solder to join with an ITO specimen by sliding one over the other for 30 s. After sliding and repositioning, the joints were held firmly in place and cooled to solidify the molten solder. After joining, the specimens were cross sectioned. The microstructures and distribution of the elements were analyzed by an electron probe microanalyzer (EPMA) to investigate the joining mechanism and related interfacial reactions. The joining strengths were measured by shear testing. Fractured surfaces were observed by scanning electron microscopy (SEM) and inspected with energy dispersion X rays (EDX).

Results and Discussion

The microstructure of the cast Sn56Bi4Ti(Ce, Ga) active solder consists of the lamellar structure of a β -Sn solid solution (gray) and the Bi-rich phase (white), as shown in Fig. 2. Compared with

KEYWORDS

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Sn56Bi4Ti(Ce, Ga) Filler
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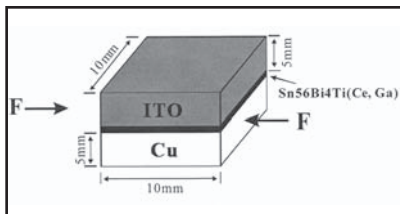


Fig. 1 — Schematic representation of the soldered specimens ready for shear testing in this study.

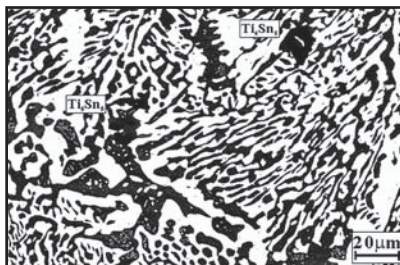


Fig. 2 — Microstructure of the Sn56Bi4Ti(Ce, Ga).

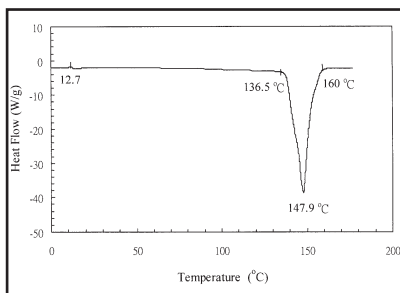


Fig. 3 — DSC analysis of the Sn56Bi4Ti(Ce, Ga).

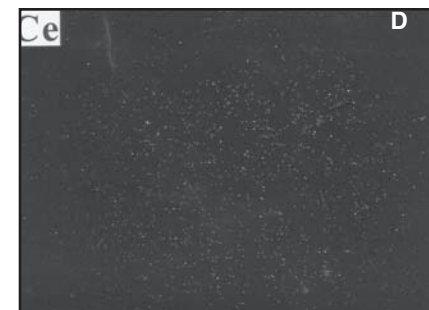
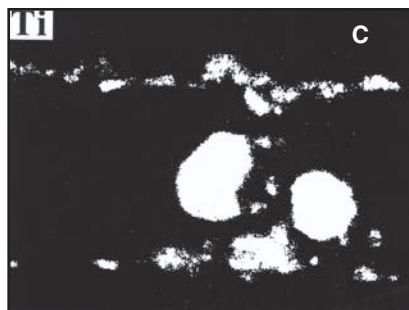
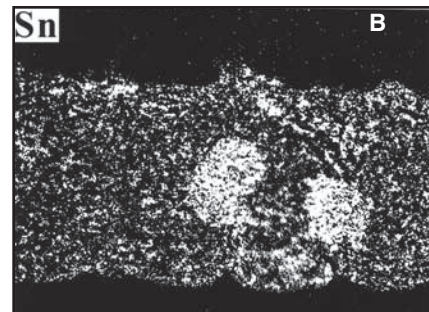
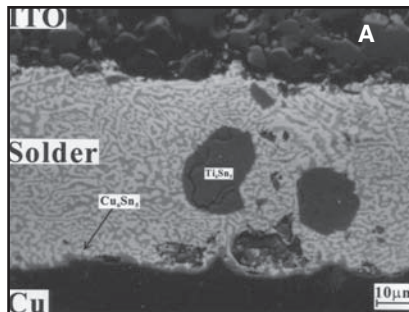


Fig. 4 — Micrograph and EPMA of the ITO/Cu joint soldered with Sn56Bi4Ti(Ce, Ga) active solder. A — The interfacial microstructure; B–F — elemental mappings of Sn, Ti, Ce, Ga, and O, respectively.

the Bi-rich phase with a Ga content of 0.45 at.-%, the regions of the β -Sn solid solution demonstrate the formation of a higher Ga concentration (about 3 at.-%). Figure 2 also illustrates the appearance of cluster-shaped α -Ti₆Sn₅ precipitates in the matrix (black). Figure 3 displays the results of the DSC analysis, indicating that this active solder has a eutectic point of 147.9°C. An exothermic peak (12.7°C) can also be found in the DSC curve, which may be attributed to the existence of a low-melting-point, Ga-rich eutectic phase in the active solder.

After soldering, satisfactory joining interfaces are formed in the ITO/solder and solder/Cu joints as shown in Fig. 4A. It can also be seen in Fig. 4A that Cu dissolves irregularly at the Cu/solder interface to form scallop-shaped Cu₆Sn₅ intermetallic compounds. Figure 4B and C shows some Sn-Ti-rich clusters in the solder matrix. As analyzed by EPMA, the coarse clusters are Ti₆Sn₅ intermetallic compounds. Ti segregates at both the

ITO/solder and Cu/solder interfaces (Fig. 4C), as suggested by EPMA elemental mapping of the ITO/Cu joint joined with Sn56Bi4Ti(Ce, Ga) active solder. The trace amount of Ce distributes uniformly in the solder matrix (Fig. 4D), while Ga segregates slightly at the interfaces — Fig. 4E. The enrichment of Ga at the interfaces may be responsible for the wetting of this solder on the surfaces of Cu and ITO. Attracted to the active rare-earth element Ce (Fig. 4F), the oxygen in ITO seems to diffuse into the solder. Evidently, it is the affinity of Ce for oxygen that promotes the reaction of the active element Ti with ITO at such a low soldering temperature.

The shear strengths of Cu/Cu, ITO/ITO, and ITO/Cu joints obtained with one specimen of each, as shown in Fig. 5, are 8.7, 1.5, and 1.2 MPa, respectively. Fractography of the specimens after shear tests reveals that the soldered Cu/Cu joint fractures along the Cu₆Sn₅ intermetallic layer — Fig. 6. Since the ITO

material is of a brittle nature and exhibits quite low strength, this study consequently also reports low joining strengths for the ITO/ITO and ITO/Cu joints. Such findings can be confirmed by the fractography in Fig. 7 of the soldered ITO/Cu joint region after shear testing. Figure 7A shows the fractured surface of a Cu specimen covered with an ITO layer, which shows that the ITO/Cu joint was fractured in the ITO material. Figure 7B provides a contrasting example of the fractured ITO specimen. That reveals the soldered Cu/ITO joint fractures on the ITO side.

Conclusions

The joining of indium-tin-oxide (ITO) with ITO and Cu was achieved at 180°C in air using a newly developed active solder Sn56Bi4Ti(Ce, Ga). It is believed that the affinity of Ce for oxygen enabled the Ti to partition and to react with ITO and Cu at such temperatures near 180°C. Electron probe microanalyzer analysis elemental

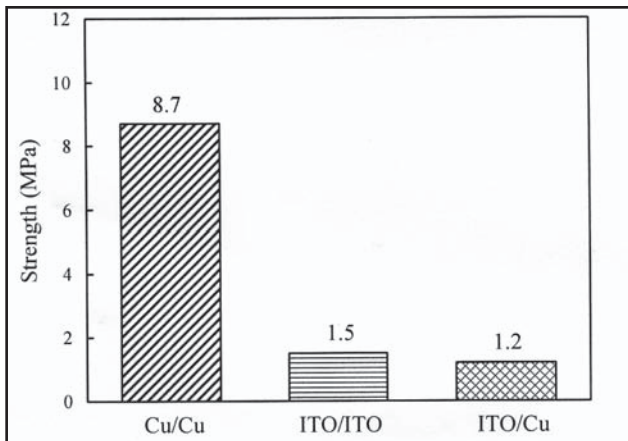


Fig. 5 — Shear strengths of Cu/Cu, ITO/ITO, and ITO/Cu joints joined with Sn56Bi4Ti(Ce, Ga) active solder.

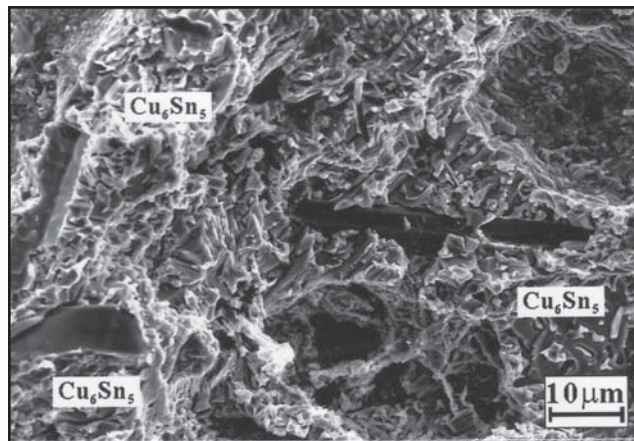


Fig. 6 — Fractograph of the Cu/Cu joint soldered with Sn56Bi4Ti(Ce, Ga) active solder after shear testing.

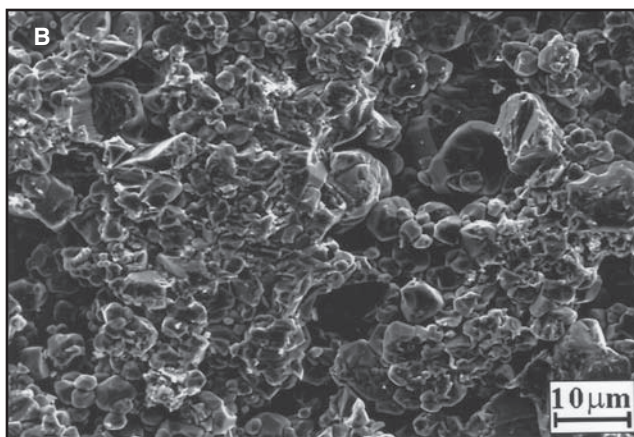
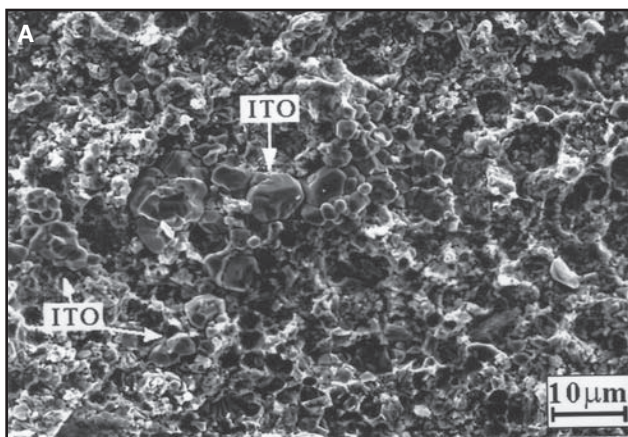


Fig. 7 — Fractographs of the ITO/Cu joint soldered with Sn56Bi4Ti(Ce, Ga) active solder after shear testing. A — The Cu side; B — the ITO side.

mapping revealed a strong tendency of Ti to segregate at the ITO/solder and solder/Cu interfaces. During soldering, Cu was found to dissolve and diffuse into Sn56Bi4Ti(Ce,Ga) solder forming scallop-shaped Cu_6Sn_5 intermetallic compounds. The bond shear strengths of Cu/Cu, ITO/ITO, and ITO/Cu joints were measured to be 8.7, 1.5, and 1.2 MPa, respectively. Fractography of the shear-tested specimens showed that the Cu/Cu joint fractured along the Cu_6Sn_5 intermetallic layer, while ITO/Cu joint failure occurred in the ITO matrix.

Acknowledgment

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