TEM Observation of Interfacial Compounds of SnAgCu/ENIG Solder Bump after Laser Soldering and Subsequent Hot Air Reflows

Baolei Liu, Yanhong Tian*, Wei Liu, Weiwei Wu, Chunqing Wang

State Key Lab of Advanced Welding and Joining, Harbin Institute of Technology, Harbin, China, 150001.

Email: tianyh@hit.edu.cn, Tel: +86-451-86418359

Abstract

In three-dimensional (3D) packaging and assembly technology, Lead-free SnAgCu solder joints inevitably experience multiple reflows. The interfacial compounds of Sn3.0Ag0.5Cu (SAC305)/Electroless Ni-P/Immersion Au (ENIG) solder bump after laser soldering and subsequent hot air reflows were observed by transmission electron microscopy (TEM), respectively. The initial laser soldering played a key role in interfacial compound evolution during the subsequent multiple reflows. After laser soldering, a thin P-rich layer and an ultrafine scallop-type (Ni, Cu)₃Sn₄ layer formed at the interface of SAC305/ENIG. The valleys of ultrafine (Ni, Cu)₃Sn₄ grains served as rapid channels for Ni diffusion, which contributed to the formation of dendritic η -(Cu, Ni)₆Sn₅ + (Ni, Cu)₃Sn₂ intermetallic compounds after the first hot air reflow. However, with the number of reflow times increasing, the η -(Cu, Ni)₆Sn₅ totally transformed to noodle-like (Ni, Cu)₃Sn₂ owing to their similarly hexagonal lattice structure and the limited Cu supply in solder.

Keywords: Laser soldering; Intermetallic alloys and compounds; ENIG; Lead-free; Diffusion.

1 Introduction

Recently, laser soldering, as a new and unique soldering process has been introduced into the electronic packaging industry [1, 2]. Compared with the conventional reflow soldering processes, laser soldering shows obvious advantages for solder bumping in ball grid array (BGA) electronic packages, due

to its unique properties such as localized and noncontact heating, fast heating and cooling. [1-4]. By laser soldering, lead-free SnAgCu solder balls are melted and metallurgically soldered to metallic pads to form solder bumps, which inevitably experiences subsequent multiple reflows during multi-assembly in 3D packaging and assembly technology [5, 6]. However, after the hybrid and multiple reflows, the undefined interfacial microstructures of solder joint maybe cause reliability problems.

The Electroless Ni-P/Immersion Au (ENIG) finish is widely used as a surface treatment on Cu pad for its advantages of good solderability, low-cost, and antioxidation [7-9]. During soldering process, SnAgCu solder and ENIG/Cu pad react with each other and form various intermetallic compounds (IMCs) like, Au_4Sn , $(\text{Ni}, \text{Cu})_3\text{Sn}_4$, $(\text{Ni}, \text{Cu})_{48}\text{Sn}_{52}$, $(\text{Cu}, \text{Ni})_6\text{Sn}_5$, $(\text{Ni}, \text{Cu})_3\text{Sn}_2$. Most IMCs are brittle, and excessive IMCs would degenerate the mechanical integrity of the solder joints. The interfacial reactions of SnAgCu/ENIG under laser soldering [6, 9, 10] and hot air reflow [8, 11-13] have been extensively studied, respectively. However, the evolution of interfacial microstructures of SnAgCu/ENIG after hybrid and multiple reflows seems not sufficient.

In this paper, the interfacial microstructure evolution of Sn3.0Ag0.5Cu/ENIG after laser soldering and subsequent multiple hot air reflows were investigated. To identify the interfacial compound phases, TEM was mainly used, and crystal structures and compositions of these interfacial compounds were analyzed.

2 Experimental Materials and Methods

The BT (Bismaleimide Triazine) substrate with SAC305 solder balls (760 μm in diameter) was used. The surface finish on Cu pads (60 μm thick) was electroless Ni-8 wt. % P/immersion Au in thickness of 7 μm and 0.075 μm respectively. After ultrasonically cleaning the pads and BT substrate in acetone, the Lead-free no-clean flux (AMTECH NC-559-ASM) was applied. The solder balls were bumped on ENIG/Cu pads by laser soldering for 1 s in ambient atmosphere. The laser system was a continuous wave

type Nd: YAG laser (1064 nm in wavelength) with a beam diameter of 0.6 mm and laser power of 4W.

Then the solder bumps were remelted with different times by the subsequent hot air reflows. In every hot air reflow, the peak reflow temperature was 255 °C, and the reflow time was 100 s. The interfacial compounds of SAC305/ENIG after the laser soldering and subsequent multiple reflows were respectively analyzed by scanning electron microscope (SEM, FEI Quanta 200 FEG) and TEM (FEI Tecnai G2 F30, 300KV) equipped with energy dispersive spectrometer (EDS). The thin foils for TEM observation were prepared by focused ion beam (FIB, FEI Helios Nanolab 600i).

3 Results and discussion

3.1 Interfacial microstructures of SAC305/ENIG bumps after laser soldering

After laser soldering for 1 s, sound SAC305/ENIG bumps (Fig. 1a) were obtained with fine Ag₃Sn particles distributing uniformly in solder matrix and thin compound layer adhering well onto the Ni-P plating (Fig. 1b). Fig. 1c clearly shows the compound layer consists of two layers: a continuous P-rich layer and an ultrafine scallop-type Cu-Ni-Sn IMC layer. The Ni-P plating was identified as fine polycrystalline FCC-Ni with 8 wt. % P dissolved, because of the continuous Debye rings in Fig. 1d. The similar diffraction pattern of polycrystalline Ni-8 wt. % P has been reported by Torazawa [14]. Based on the selected area electron diffraction (SAED) pattern in Fig. 1e and EDS (20~25 wt. % P), the ultrathin P-rich layer was identified as polycrystalline Ni₃P+Ni. It was reported that the stable Ni₃P phase initially formed during conventional reflow process when the P contents was lower than 9 wt. % [11, 13]. Nevertheless, in this study, the laser heating time was short, and only a small quantity of Ni atoms in the surface of Ni-P plating diffused into the molten solder, which induced the formation of ultrathin Ni₃P+Ni layer.

Fig. 1f shows that the SAED pattern of grain A in Fig. 1c matches the lattice structure of Ni₃Sn₄.

However, EDS analysis suggested that the IMC layer contained a small amount of Cu. Therefore, this Cu-Ni-Sn IMC layer was $(\text{Ni}, \text{Cu})_3\text{Sn}_4$ because some Ni atoms were substituted by Cu atoms. Besides, several Ag_3Sn particles distributed randomly at the top surface of $(\text{Ni}, \text{Cu})_3\text{Sn}_4$ grains, and the corresponding SAED pattern of grain B was shown Fig. 1g. However, no Au-Sn IMCs were detected at the interface of SAC305/Ni-P plating. In our previous reports, the needle-like AuSn_4 IMCs usually formed at the interfaces of solder and pads during laser soldering [5, 6, 10]. But in this study the Au layer was far thinner than that in our previous reports with relatively longer laser heating time, the ultrathin Au layer has sufficient time to dissolve into the molten solder.

Fig. 1 Interfacial microstructures of SAC305/ENIG bump after laser soldering: (a) cross-sectional SEM image of solder bump; (b) interfacial SEM image; (c) interfacial TEM image; (d) and (e) are diffraction patterns of Ni-8 wt. % P and $\text{Ni}_3\text{P}+\text{Ni}$, (f) and (g) are SAED patterns of A and B grains in (c).

3.2 Interfacial microstructure evolution during followed multiple hot air reflows

The interfacial microstructures of SAC305/ENIG after the first subsequent hot air reflow is shown in Fig. 2. The thickness of $\text{Ni}_3\text{P}+\text{Ni}$ layer and Ni-Cu-Sn IMC layer both increased, meanwhile, the Ni-Cu-Sn

IMC shape changed from scallop-type to dendritic type (Fig. 2a and b). The diffraction pattern of $\text{Ni}_3\text{P}+\text{Ni}$ is shown in Fig. 2d and the increased $\text{Ni}_3\text{P}+\text{Ni}$ layer means that the Ni diffused to solder continuously. As seen in Fig. 2e, the SAED pattern of grain A in Fig. 2c shows that the Ni-Cu-Sn IMC is either $\eta\text{-Cu}_6\text{Sn}_5$ or Ni_3Sn_2 , both of which have the space groups of $\text{P6}_3/\text{mmc}$ and similar hexagonal lattice parameters [14]. However, the EDS analysis showed that the Cu, Ni and Sn contents were about 41 at. %, 14 at. % and 45 at. %, respectively. So it was reasonable to conclude the Ni-Cu-Sn IMC was $\eta\text{-(Cu, Ni)}_6\text{Sn}_5$. We also noticed that some Ni-Cu-Sn IMC particles with low Sn content (about 37 at. %) decorated at the $\eta\text{-(Cu, Ni)}_6\text{Sn}_5$ grain boundaries (Fig. 2b and c). Theoretically, the solubility ranges of intermediate Ni_3Sn_2 and Cu_6Sn_5 were about 37~40 at. % and 43~44 at. %, respectively [11]. Thus, it was reasonable to believe those Ni-Cu-Sn particles with low Sn content are $(\text{Ni, Cu})_3\text{Sn}_2$.

Fig. 2 Interfacial microstructures of SAC305/ENIG after the first subsequent hot air reflow: (a) SEM image, (b) TEM image; (c) TEM image of white rectangle in (b); (d) diffraction pattern of $\text{Ni}_3\text{P}+\text{Ni}$; (e) and (f) are SAED patterns of A and B grains in (c), respectively.

Fig. 3 shows the interfacial microstructures of the SAC305/ENIG after three times of subsequent reflows. The thickness of P-rich layer increased nearly to 1 μm (Fig. 3a~c). The P-rich compounds were

considered as $\text{Ni}_3\text{P}+\text{Ni}_2\text{P}$, based on the SAED pattern in Fig. 3d and EDS (25~29 wt. % P). After one laser soldering and three hot air reflows, the Ni_3P layer was thick enough, and Ni started diffusing from Ni_3P to the solder matrix, which induced the transformation of Ni_3P into Ni_2P [13]. In addition, two long striped voids penetrated the whole $\text{Ni}_3\text{P}+\text{Ni}_2\text{P}$ layer (Fig. 3c) because of the black pad failure in ENIG process [7]. Interestingly, we noted that the dendritic $\eta\text{-(Cu, Ni)}_6\text{Sn}_5 + (\text{Ni, Cu})_3\text{Sn}_2$ compounds totally transformed into noodle-like $(\text{Ni, Cu})_3\text{Sn}_2$ after the third hot air reflow. The corresponding SAED patterns of grain A and B in Fig. 3b are shown in Fig. 3e and f respectively.

Fig. 3 Interfacial microstructures of SAC305/ENIG after the third subsequent hot air reflow: (a) SEM image, (b) TEM image; (c) TEM image of P-rich layer; (d) diffraction pattern of $\text{Ni}_3\text{P}+\text{Ni}_2\text{P}$; (e) and (f) are SAED patterns of A and B grains in (b), respectively.

After the third followed reflow, the $\eta\text{-(Cu, Ni)}_6\text{Sn}_5$ transformed into $(\text{Ni, Cu})_3\text{Sn}_2$, which was mainly caused by the continuous diffusion of Ni from Ni-P plating, similar hexagonal lattice structures of $(\text{Cu, Ni)}_6\text{Sn}_5$ and $(\text{Ni, Cu})_3\text{Sn}_2$, and the limited Cu supply of solder. Under conventional reflow condition, $(\text{Ni, Cu})_3\text{Sn}_4$ and $(\text{Cu, Ni)}_6\text{Sn}_5$ were the mainly IMCs phases formed at SAC/ENIG interface as reported in previous reports [7, 8, 12-14]. However, in this study, after one laser soldering and subsequent multiple

hot air reflows, the single reaction layer of $(\text{Ni}, \text{Cu})_3\text{Sn}_2$ formed. Clearly, the initial laser soldering played a crucial role in microstructure evolution and transformation during the followed multiple reflows.

4 Conclusions

The interfacial microstructure evolution of SAC305/ENIG after laser soldering and subsequent multiple hot air reflows were observed by TEM. After laser soldering, a $\text{Ni}_3\text{P}+\text{Ni}$ layer and an ultrafine scallop-type $(\text{Ni}, \text{Cu})_3\text{Sn}_4$ layer formed at the interface of SAC305/ENIG. Because of the out-diffusion of Ni, the thickness of P-rich layer increased with the number of subsequent reflows, and the $\text{Ni}_3\text{P}+\text{Ni}$ layer changed into $\text{Ni}_3\text{P}+\text{Ni}_2\text{P}$ layer after the third hot air reflow. In addition, after the first hot air reflow, the scallop-type $(\text{Ni}, \text{Cu})_3\text{Sn}_4$ transformed into dendritic $\eta\text{-(Cu, Ni)}_6\text{Sn}_5$ due to sufficient Cu supply from solder. Meanwhile, $(\text{Ni}, \text{Cu})_3\text{Sn}_2$ formed at the $\eta\text{-(Cu, Ni)}_6\text{Sn}_5$ grain boundaries for the valleys of ultrafine scalloped $(\text{Ni}, \text{Cu})_3\text{Sn}_4$ grains formed after laser soldering served as rapid channels for Ni diffusion. However, with the number of reflows increasing, the $\eta\text{-(Cu, Ni)}_6\text{Sn}_5$ totally transformed into noodle-like $(\text{Ni}, \text{Cu})_3\text{Sn}_2$ because of their similar hexagonal lattice structure and the limited Cu supply in solder.

Acknowledgements

The authors are grateful for financial support from the National Science Foundation of China (Grant No. 51522503) and support from Program for New Century Excellent Talents in University (NCET-13-0175).

References

- [1] Nishikawa H, Iwata N. J Mater Process Tech 2015;215:6-11.
- [2] Nishikawa H, Iwata N, Takemoto T. Transactions of JWRI 2012;41:33-6.
- [3] Lee JH, Lee YH, Kim YS. Scr Mater 2000;42:789-93.
- [4] Liu W, Tian YH, Wang CQ, Sun L. J Mater Sci-Mater El 2013;24:217-23.

- [5] Tian YH, Wang CQ, Ge X, Liu P, Liu D. Mater Sci Eng B 2002;95:254-62.
- [6] Tian YH, Wang CQ, Zhang X, Liu D. Solder Surf Mt Tech 2003;15:17-21.
- [7] Wojewoda BJ, Huber Z, Litynska DL, Sobczak N, Zieba P. Mater Chem Phys 2013;139:276-80.
- [8] Tseng CF, Lee TK, Ramakrishna G, Liu KC, Duh JG. Mater Lett 2011;65:3216-8.
- [9] Chen HT, Wang CQ, Li MY, Tian DW. Mater Lett 2006;60:1669-72.
- [10] Liu W, An R, Wang CQ, Tian YH. Solder Surf Mt Tech 2015;27:45-51.
- [11] Hwang CW, Suganuma K, Kiso M, Hashimoto S. J Mater Res 2003;18:2540-3.
- [12] Jeon YD, Nieland S, Ostmann A, Reichl H, Paik KW. J Electron Mater 2003;32:548-57.
- [13] Lin YC, Wang KJ, Duh JG. J Electron Mater 2010;39:283-94.
- [14] Torazawa N, Arai S, Takase Y, Sasaki K, Saka H. Mater Trans 2003;44:1438-47.