Investigation of intermetallic compounds (IMC) in electrochemically stripped solder joints with SEM

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Abstract

In this work we compare the microstructures of intermetallic compounds (IMCs) in electrochemically stripped solder joints created by two different soldering methods (vapor phase soldering (VPS), and selective laser soldering with a CO₂ laser). After the selective removal of the Sn phase with amperometry, the microstructure and structural composition of the IMC can be revealed in a detailed way, which is unlike any other previously published methods. The differences between the IMC microstructures of the technologically different solder joints were analyzed with optical microscopy and scanning electron microscopy (SEM). Energy dispersive spectroscopy (EDS) measurements were utilized to identify the different intermetallic phases (Ag₃Sn, Cu₆Sn₅). Significant differences were observed in the IMC structures of solder joints prepared by different technologies.

1. Introduction

The rework process of circuits with high integration level cannot be imagined without any selective joining technology. Nowadays laser soldering process is one of the most emerging selective joining techniques [1], thanks to its big advantages compared to conventional technology (concentrated heat affected zone, precisely controllable heat profile) [2]. But on the other hand the application of significantly different heat profiles may demand the solution of new reliability issues. The rapid temperature rise and drop could alter the microstructure of the solder causing the variation of the mechanical properties [3-4]. The significant temperature gradients in the vicinity of the laser impact zone have effect on the diffusion processes similarly as the natural heat convection in the molten solder [5]. This is why the structural analysis of different solder joints is a widespread research area in the field of reliability.

The most common metallographic observation method, i.e. cross sectioning combined with optical microscopy can only provide information about the distribution of composing elements in the cross sectioning plane. Based on the results obtained from one sectioning plane the spatial orientation and distribution or the detailed microstructure of different phases cannot be observed. We have been developing a new observation method, which makes the selective removal of the interdendric elements possible. In such a way the spatial orientation of the dendric core of the alloying elements can be studied. The aim of this investigation is to compare the microstructure of solder joints created by different soldering methods with this unique technique. The differences between the microstructure of vapour phase soldered and selective laser soldered joints are engaged in research. Since the microstructure of SAC-based solder is a mixture of Sn and IMCs, such as Ag₃Sn and Cu₆Sn₅ [6] we were focusing on these intermetallic precipitations.

2. Experimental Procedures

The test layout was developed on FR4 glass-fiber reinforced epoxy single sided printed circuit board (PCB) with 35 µm copper layer and galvanic tin coating on it. Round pads were formed with 2 mm in
diameter and placed in 6 by 6 array arrangement. The cylindrical symmetric pads were in galvanic connection so they could have been easily connected as the working electrodes to the potentiostat. A commonly used lead free solder alloy, SENJU Sn96.5Ag3.0Cu0.5 was used during the investigation. The solder paste was printed onto the PCBs with 100 µm thick nickel stencils, through laser cut circular apertures, 1.9 mm in diameter.

Fig. 1 Schematic illustration of the test layout molded into acryl based resin. All pads were in galvanic connection with each other.

Synrad 48-2W CO₂ laser was used for the laser soldering experiments. The laser was operated in continuous mode and significant defocusing was applied in order to avoid any visible damage either on the PCB substrate or on the solder bumps. The diameter of the laser spot was approximately 2 mm (@1/e²) and it was positioned to the center of each pad. The heating profile was one staged, step excitation with an average optical power of 4.5 W. The wavelength of the laser beam was 10.6 µm. The solder was heated up to molten phase within 1 second and the time above liquidus was further 10 seconds.

For the metallographic inspections the samples were embedded in an acryl based (Technovit 4006) resin. First they were ground by SiC grinding papers (grit size: 80, 320, 500, 1200) and polished by 9 µm, 3 µm and 1µm and finally OP-S (0.04 µm) diamond and SiC suspensions. The optical microscopic images were taken by an Olympus BX51 upright microscope. SEM analysis was done by a FEI Inspect S50 scanning electron microscope with a Bruker Quantax EDX (energy dispersive X-ray analysis) system.

The selective electrochemical stripping of the Sn phase was done with a Voltalab PGZ 301 potentiostat in chrono-amperometry mode. The solder joints were immersed in 1% H₂SO₄ in a standard three electrode setup with an Ag/AgCl reference electrode and a stainless steel plate as counter electrode. The applied bias potential was ~350 mV for 2 minutes.

3. Results and Discussion

3.1. Effects of the electrochemical stripping

Figure 2 shows optical microscopic images of a cross-section of a solder joint created by VPS before and after the removal of the tin phase with electrochemical stripping. Fig. 3 shows higher magnification optical and SEM images of the highlighted area. In the optical microscopic images the intermetallic layer at the Cu-Sn interface and others small IMCs dissolved in the solder bulk can be identified, but no further structural information can be obtained. On the other hand it can be clearly seen, that the electrochemical stripping only removes the pure tin phase and other intermetallic structures are left intact and can be observed in detail.
**Fig. 2** Optical microscopic images before and after electrochemical stripping of a cross-sectional solder joint sample, created by VPS

**Fig. 3** Left: Optical microscopic image of the same solder joint presented in Fig 2. Right: SEM image of the highlighted area after the electrochemical stripping.

The microstructures are presumably formed by two different intermetallic phases. The Cu$_6$Sn$_5$ phase forms hexagonal tubes, while the Ag$_3$Sn phase is a thready net which envelops the Sn-phase by forming cellular structures. These hexagonal objects were also observed in previous works [7], but based on only the cross-sectional analysis, they could not be identified as hexagonal tubes. The two different phases can be easily identified and differentiated as demonstrated in Fig. 4 by EDS.
Fig. 4 Left: SEM image of a solder joint created by VPS technology. Right: EDS elemental map of the same area: red – Ag phase; blue – Sn phase.

3.2. Differences between the VPS and CO\textsubscript{2} soldering

The first difference between the intermetallic microstructures of solder joints created with CO\textsubscript{2} laser and VPS is the fineness of the Ag\textsubscript{3}Sn fibers and the average size of the cells. Although the soldering characteristics were set in a way that the time above liquidus was the same in both soldering techniques, the CO\textsubscript{2} laser soldering results in finer Ag\textsubscript{3}Sn fibers and smaller average cell size compared to the VPS as can be seen in Fig. 5. The plane of the etching front (still intact tin phase) can also be observed in Fig. 5 as vertical pattern between the Ag\textsubscript{3}Sn cells.

Fig. 5 SEM images of solder joints created with different soldering techniques. Left: CO\textsubscript{2} laser soldering, right: VPS.

The second significant difference is that the laser soldered joint completely lacks the Cu\textsubscript{6}Sn\textsubscript{5} phase and the corresponding microstructures (hexagonal tubes) from the bulk of the solder joint. In correspondence, the intermetallic Cu\textsubscript{6}Sn\textsubscript{5} layer is very thin in case of CO\textsubscript{2} soldering. Fig. 6 shows SEM images about the relevant areas, and it can be clearly seen, that the scallop-type Cu\textsubscript{6}Sn\textsubscript{5} intermetallic
layer did not form in the case of CO$_2$ laser soldering at the Cu-Sn interface. Based on our experimental results we can suspect two alternatives of Cu$_6$Sn$_5$ tube growing mechanism. First, the tubes can be originated from the elongated grains at the Cu-Sn interface. Secondly, we also observed Cu$_6$Sn$_5$ flakes in the solder bulk, which might also assemble closed tubes, given the condition during the soldering process. Fig. 7 presents images for both possible tube forming theory. Fig. 8 presents an EDS image of this relevant area.

Fig. 6 SEM images of solder joints created with different soldering techniques at the Cu-Sn interface. Left: CO$_2$ laser soldering, right: VPS.

Fig. 7 SEM image of a solder joint created with VPS technology. Left: Possible formations of Cu$_6$Sn$_5$ tubes from flakes. Right: Possible formations of Cu$_6$Sn$_5$ tubes from the elongated grains of the IM layer.

Furthermore the experimental results also proved the fact that the laser soldered joints contain many voids [8]. It can also be concluded that the Ag$_3$Sn IMCs tend to precipitate not only at grain boundaries and at the Cu$_6$Sn$_5$ structures, but at the wall of the voids as well (Fig. 6).
4. Conclusions

Electrochemical stripping was utilized to examine the spatial microstructure of intermetallic compounds in lead-free solder joints with SEM and EDS. The significant differences between the IMCs of two different soldering methods (vapor phase soldering, and selective laser soldering with a CO₂ laser) are the following: 1. the existence of Cu₆Sn₅ tubes in conjunction with the thicker and scallop-type Cu₆Sn₅ intermetallic layer at the Cu-Sn interface in the case of VPS; 2. the Ag₃Sn net is finer and the average cell size is smaller as well in the case of selective laser soldering; 3. the solder joint created with laser soldering contains voids at which the Ag₃Sn phase tends to precipitate. This novel examination method and the obtained structural data can be used to study and understand the reliability issues of solder joints in more detail.

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6. References


