Corrosion Characterization of Sn37Pb Solders and With Cu Substrate Soldering Reaction in 3.5wt.% NaCl Solution

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Abstract

The electrochemical corrosion behavior of Sn37Pb solder, Cu_6Sn_5, Cu_3Sn and Cu in 3.5% NaCl solution was investigated by using Galvanic corrosion testing, potentiodynamic polarization methods. The galvanic current densities for Sn37Pb solder in 3.5wt.% NaCl solution are 38, 16 and 5μA/cm^2 for Cu_3Sn, Cu, and Cu_6Sn_5, respectively. Polarization studies revealed that an increase in Cu content and formation of IMCs shifted the corrosion potential ($E_{corr.}$) towards more noble values and increased the corrosion current density ($I_{corr.}$).

1 Introduction

Solder is extensively used for the electronics industry for packaging applications. Especially, lead-tin solder is widely used for chip-to-package connection. It has very excellent properties, with a unique combination of electrical, chemical, physical, thermal and mechanical behavior [1-2]. According to the International Technology Roadmap for Semiconductors (ITRS), it has been projected that the pad pitch may fall below 20μm by the year 2016 [3]. In some flip chip packages, solder balls of 20μm in size are used to connect the pads on the chip and the print circuit board (Fig.1). In connected metals, all the common base materials, coatings, and metallizations such as Cu, Ni, Ag, Ag-Pd, and Au, form intermetallic compounds (IMCs) with Sn, which is the major element in Sn solders. Cu is the material most frequently used for leads and pads on flip chip substrates and printed wiring boards. It is now known that in the Cu/solder interfacial reaction, Sn reacts rapidly with Cu to form Cu_3Sn (ε) and Cu_6Sn_5 (η) [4-5]. These intermetallic compounds are generally more brittle than the base metal, which can have an adverse impact on the solder joint reliability [6-7]. In addition to air, the solder is exposed to moisture and other corrosives such as chlorine and sulfur compounds. Therefore, many researchers have studied the corrosion behavior of Pb-free solders [8-14], but few have studied the galvanic corrosion properties of Sn-Ag solder, Sn-Al-Zn solder, and Sn37Pb solder with respect to electroless Ni-P, Ni-Cu-P deposits and Cu substrate [15]. No literature is available on the effect of Cu_6Sn_5 and Cu_3Sn on the corrosion resistance of Sn37Pb/Cu solder. In the present study, 3.5wt.% NaCl solution was used to simulate sea water, and the corrosion properties of Sn37Pb solder, Cu_6Sn_5, Cu_3Sn, and Cu substrate in this solution were studied through potentiodynamic polarization and galvanic corrosion tests.

2 Experimental

In the present study, alloys containing Sn37Pb, Cu_6Sn_5, and Cu_3Sn were made by weighing and melting commercially purity metals (nominally 3N) on the vacuum quartz tube by 10mm in diameter, and then quenched to water at room temperature. The intermetallic compounds ingot was homogenized temperature at 670°C (Cu_3Sn) and 415°C (Cu_6Sn_5) in 40 days.

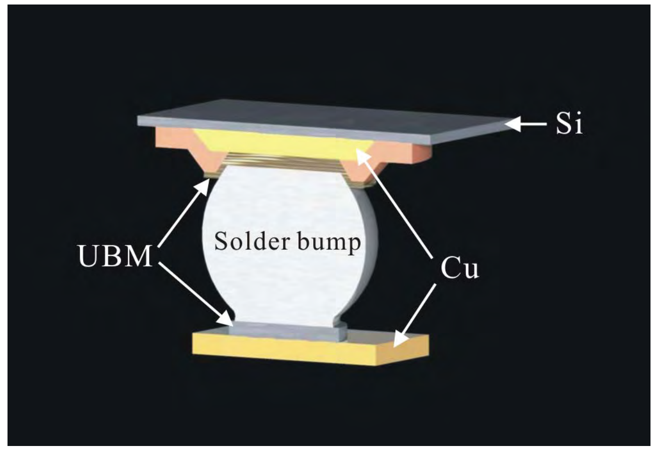

Figure 1 Schematic structure of solder joint in a flip chip package.

The electrochemical measurement experiments was measured with a typical three-electrode cell, no stirring, and degassing of the solution at room temperature by an EG & G M273A potentioset. The reference potential was a saturated calomel electrode (SCE) and platinum (Pt) counter electrode (Φ 1.5mm by 20cm). All electrolytes were prepared by dissolving high-grade chemicals in high purity deionized water (Millipore Milli-Q SP, 18MΩ.cm). The area of the specimens in the experiment was 0.2829cm^2. For dynamic polarization testing, the specimen was immersed in the electrolyte for 1 hour, and then the potential began at -800mV$_{SCE}$ and scanned in the noble direction to an anodic 1V$_{SCE}$ at a scanning rate of 1mV/s. Galvanic corrosion current densities were measured with a zero resistance meter and A/D recorder for Cu, Cu_6Sn_5 and Cu_3Sn. The electrode area was 2.83cm^2. The specimens were cut from rod-shaped ingots rod and wet polished with 240-grit to 2000-grit silicon carbide (SiC), rinsed with acetone and deionized water, and cleaned with ultrasonic cleaning.

The phases of the alloy as observed in the microstructure were identified with energy-dispersive spectroscopy (EDS) and scanning electron microscopy.

3 Results and discussion

Many studies have shown that Sn solders and Cu substrate interfacial reactions result in Cu_6Sn_5 and Cu_3Sn intermetallic compounds. Figure 2 is an optical micrograph showing the microstructure of Sn37Pb solder and copper substrate at the interfacial reactions formed at 420°C for 10 min. Multiple layers can be clearly seen in the micrograph.

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The layers are in the order of solder, Cu_6Sn, Cu_3Sn, and Cu, respectively.

The joining of materials with Sn37Pb solders generally results in a multi-layer structure in which intermetallic compounds are formed between substrate and solders (Fig.2). Such a structure in a flip chip packaging is a galvanic couple. The galvanic corrosion behavior of the solder bump structures has a great effect upon reliability. The galvanic current densities of the Sn37Pb solder with respect to the intermetallic compounds Cu_6Sn_5 and Cu_3Sn, and base Cu were investigated (Fig. 3). It appears that Sn37Pb solder has a greater galvanic current density, and thus is very subject to corrosion, especially more so in coupling with the formation of Cu_3Sn layers than with Cu_6Sn layers. The galvanic current densities for the Sn37Pb solders with respect to Cu_3Sn, Cu, and Cu_6Sn_5 are about 38, 16, and 5 ($\mu A/cm^2$), respectively. It can be seen that the galvanic corrosion behavior of Cu_3Sn is generally greater than that of Cu_6Sn for the flip chip packaging in a 3.5wt.% NaCl solution environment. This indicates that the formation of Cu_3Sn and Cu_6Sn_5 layers causes many problems with corrosion behavior and reliability.

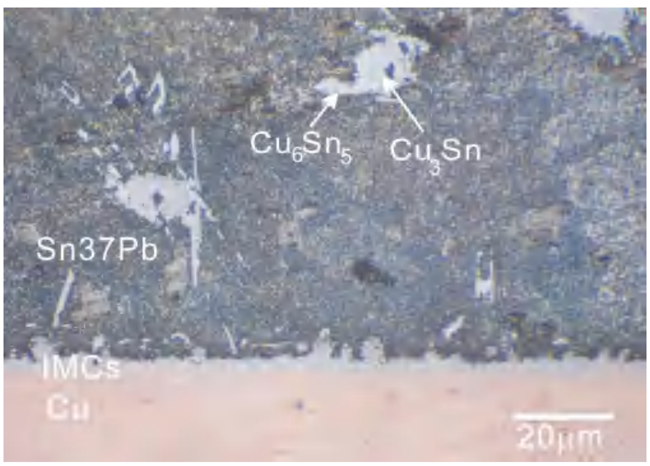

Figure 2 Typical optical micrograph images of Sn37Cu solder joints with Cu substrate at 420°C for 10 min.

Figure 4 shows the polarization curves of the Sn37Pb solders, Cu_3Sn, Cu_6Sn_5, and base Cu in a 3.5wt.% NaCl solution. The corrosion current densities of all specimens were calculated through the Tafel method and are summarized with other corrosion parameters in Table 1. The corrosion potential ($\Phi_{corr.}$) and corrosion passivation current density ($I_{corr.}$) of the Sn37Pb solder were -584.4mV_{SCE} and 6.48$\mu A/cm^2$, respectively. In the solder/Cu interface, Sn reacts rapidly with Cu to form Cu-Sn intermetallic compounds (IMCs), thus leading to a signification shifting of the equilibrium corrosion potential towards noble values, -457.7 and -309.0mV_{SCE} for the IMC Cu_6Sn_5 and Cu_3Sn, respectively. The Cu substrate exhibits the highest equilibrium corrosion potential, -192.1m V_{SCE}. Also, the maximum corrosion current density of the base Cu is 391.6$\mu A/cm^2$, which is higher than that of 48.17, and 2.61$\mu A/cm^2$ for the IMC Cu_3Sn and Cu_6Sn_5, respectively. The corrosion current densities of the Sn37Pb solder and IMC Cu_6Sn_5 are very similar. Figure 5 presents the effects of Cu content on both $\Phi_{corr.}$ and $I_{corr.}$ values during polarization of the Sn37Pb solder, Cu_6Sn_5, Cu_3Sn, and Cu substrate in 3.5% NaCl solution. These IMCs exhibit corrosion potentials shifting toward noble as the amount of Cu increases. This indicates that the corrosion resistance of Sn solder increases with increasing Cu content.

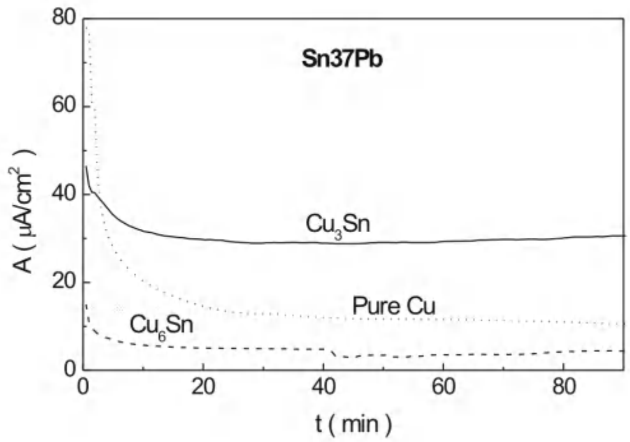

Figure 3 The galvanic current densities of the Sn37Pb solder with respect to intermetallic compound Cu_6Sn_5, Cu_3Sn and Cu substrate in a 3.5wt.% solution.

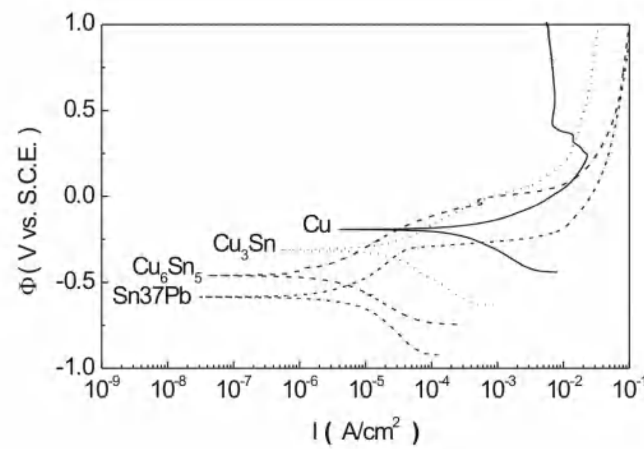

Figure 4 The potentiodynamic polarization curves of Sn37Pb solder, Cu_6Sn_5 IMC, Cu_3Sn IMC and pure Cu samples in a 3.5% NaCl solution.

On the other hand, the breakdown potential (Φ_b) of IMC becomes much more noble after the Cu/solder interface reaction forms Cu-Sn IMCs, and the larger value of $\Delta\Phi$ (=Φ_b-$\Phi_{corr.}$; $\Phi_{corr.}$=corrosion potential) for the Cu_6Sn_5 specimens reveals a characteristic of more stable passivation. This indicates that the pitting corrosion tendency of Cu-Sn IMC at the solder/Cu interface can be alleviated after solder packaging. The Cu substrate exhibits a passivation behavior at above 239mV_{SCE} with current densities of 22.3mA/cm^2. However, the passive behavior of other specimens does not present a prominent peak. The passivation current densities of all specimens at above 460mV_{SCE} are around $10^{-1}A/cm^2$ with the declining sequence of Sn37Pb≥Cu_6Sn_5>Cu_3Sn>Cu.

Table 1 Corrosion properties in a 3.5wt.% NaCl solution for the Sn37Pb solder with different heat treatments.

Specimens	Φ_{corr} (mV_{SCE})	Φ_b (mV_{SEC})	$\Delta\Phi$ (mV)	I_{corr} ($\mu A/cm^2$)	I_p (mA/cm^2)
Sn37Pb	-584.4	-303.0	281	6.48	67.7
Cu_6Sn_5	-457.7	-45	412	2.61	56.9
Cu_3Sn	-309.0	-8.9	300	48.17	18.3
Cu	-192.1	236	428	391.6	6.5

$\Phi_{corr.}$: corrosion potential; $I_{corr.}$: corrosion current density; Φ_b: breakdown potential;
$\Delta\Phi = \Phi_{corr.} - \Phi_b$; Φ_p: passivation range of solder alloy;
I_p: passivation current density at above $460mV_{SCE}$.

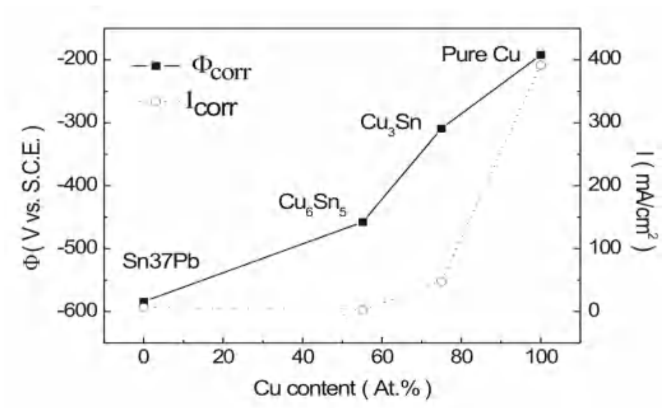

Figure 5 Effect of Cu content on the both Φ_{corr}. and I_{corr}. value during polarization of the Sn37Pb solder, Cu_6Sn_5, Cu_3Sn and Cu substrate in 3.5% NaCl solution.

Conclusions

The corrosion behavior of Sn37Pb solder, Cu_3Sn, Cu_6Sn_5, and base Cu were studied by means of galvanic corrosion and potentiodynamic polarization in 3.5 wt.% NaCl solution. The galvanic current densities of Sn37Pb solder in 3.5wt.% NaCl solution are 38, 16, and $5\mu A/cm^2$ for Cu_3Sn, Cu, and Cu_6Sn_5, respectively. Increasing the copper content, which reacts with Sn to form IMCs, led to a significant improvement in the corrosion resistance of solders and increased the corrosion current density ($I_{corr.}$). The passivation current densities of all specimens at above 460 mV_{SCE} were around $10^{-1}A/cm^2$, with the declining sequence of Sn37Pb $\geq$ Cu_6Sn_5 > Cu_3Sn > Cu.

Acknowledgments

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