Journal of Alloys and Compounds 591 (2014) 351–355

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jalcom

Phase identification on the intermetallic compound formed between eutectic SnIn solder and single crystalline Cu substrate

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ARTICLE INFO

Article history:
Received 13 September 2013
Received in revised form 3 December 2013
Accepted 30 December 2013
Available online 7 January 2014

Keywords:
Phase identification
Interface
IMC
Eutectic SnIn solder
Single crystalline Cu

ABSTRACT

The intermetallic compound (IMC) formed between eutectic SnIn solder and single crystalline Cu substrate during reflow and solid-state aging was investigated precisely utilizing electron microscope. Two kinds of crystal structures with different morphologies were identified, which are $Cu(In,Sn)_2$ at the solder side and the $Cu_2(In,Sn)$ at the Cu substrate side. The $Cu(In,Sn)_2$ layer with chunk-type morphology suffered spalling easily during slightly increased liquid soldering at 160 °C, and $Cu_2(In,Sn)$ was in the form of duplex structure with coarse-grain and fine-grain sublayers. During solid-state aging at 60 °C, the morphology of fine-grain $Cu_2(In,Sn)$ kept granule-type, while that of the coarse-grain $Cu_2(In,Sn)$ was substrate-dependent with elongated morphology.

1. Introduction

Sn–Pb solders have been widely used as a joining material for many years in modern microelectronic industry with good-wetting and low-temperature properties. However, due to the adverse effects of toxic Pb element on human health and its serious pollution to environment, the elimination of Pb usage in electronic components and devices is an inevitable trend [1]. Therefore, Sn-based lead-free solders have been widely focused on for electronic packaging applications, such as Sn–Bi [2], Sn–Ag–Cu [3,4] and Sn–Cu [5] alloys, in which Sn element acts as the main species and reacts with the substrates to form intermetallic compound (IMC) layers for joining. Besides the above-mentioned Sn-based lead-free solders, the binary eutectic Sn–In solder has the advantages of lower melting temperature, better wettability, better ductile properties and longer fatigue life [6], and exhibits particular and different characters such as the phase species of IMC owing to the participation of In element in the interfacial reactions between solder and substrates.

During soldering process, the phase species of formed interfacial IMC can affect the properties and service life of solder joints. Over the past decades, the phase identification on the interfacial reaction between eutectic SnIn solder and Cu has been studied during reflowing as well as long-term solid-state aging. For example, Kim and Jung [7] found two possible phases in this system: $Cu(In,Sn)_2$ adjacent to the solder and $Cu_6(In,Sn)_5$ at the substrate side, which was the dominant phase formed in the process of solid-state aging at a temperature range of 70–100 °C for 0–60 days. Chuang et al. [8] reported that $Cu_3(In,Sn)$ and $Cu_6(In,Sn)_5$ were the possible phases at the interface after soldering in the In–49Sn/Cu system during subsequent aging at 60–110 °C. More recent work was performed by Sommadossi et al. [9], who found that below 200 °C only the Cu–16In–27Sn (at.%) phase grew alone showing two different morphologies: large coarse-grains grew into the liquid In–48Sn due to the diffusion of Cu from the substrate and fine-grains grew into the solid Cu due to In and Sn diffusion through the Cu–16In–27Sn (at.%) phase. It can be clearly seen that the results of phase identification are not absolutely in agreement with each other. One reason comes from the complexity of binary phase diagrams between Sn/In and Cu, because both Sn and In can react with Cu to form IMC with close atomic percentage, such as Cu_2In, Cu_7Sn_3 and $Cu_{11}In_9$. Another reason is that the experimental methods used in previous studies mainly focused on the elemental analyses with electron probe microanalyzer (EPMA) or energy dispersive spectrometer (EDS), which are not very accurate to identify different crystal structures especially with similar compositions. Thus it is necessary to distinguish the IMC formed in SnIn/Cu solder joints more precisely using other method like electron microscopy.

2. Experimental procedures

The solder used in this study was eutectic In–48Sn alloy, and the substrate was single crystalline Cu. The (100) and (111) Cu plates ($40 \times 4 \times 2$ mm^3) were commercially purchased with polished and clean surfaces (the roughness is below 0.5 nm). Wetting TEM samples were prepared by sandwiching eutectic SnIn thin

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http://dx.doi.org/10.1016/j.jallcom.2013.12.257

foil (~100 μm thick) into two copper sheets, while wetting SEM samples were prepared by putting eutectic SnIn thin foil on the polished Cu sheets. Then they were aligned, clamped together and heated to the reflow temperature to form a solder joint. The typical reflowing and aging temperatures are 160 °C and 60 °C, respectively. In order to clearly reveal the morphologies of the IMC formed between eutectic SnIn solder and Cu from the top, the unreacted solder should be removed completely. The surface excess solder was mechanically polished first, and then was carefully etched with the 20% H_2O_2 + 80% CH_3COOH (vol.%) etchant solution. All the clean samples were observed with a LEO super35 and Quanta600 scanning electron microscopes with an EDS system to study the morphologies of the IMC and to perform compositional analyses.

3. Results and discussion

3.1. Cross-sectional microstructure and phase identification

3.1.1. The composition and crystal structure of $Cu_2(In,Sn)$ compound

After reflowing at 160 °C for 5 s, the cross-sectional SEM image of the In–48Sn/Cu(1 1 1) interface was shown in Fig. 1. It could be seen that there are two distinct IMC layers on (1 1 1) Cu substrate, whose interface was indicated by horizontal arrows. Layer I is adjacent to Cu substrate, while layer II is at the solder side whose outer boundary was outlined with dashed line. The corresponding EDS analyses of these two layers were shown in Table 1, and layer I consists of 66.11%Cu, 15.53%In, and 18.36%Sn which could be described as 66Cu–16In–18Sn (at.%), while layer II consists of 33.05%Cu, 51.66%In, and 15.29%Sn which corresponds to 33Cu–52In–15Sn (at.%). The thickness of these two layers was measured from a wide range with an image analyzing software as depicted in detail by Shang et al. [10]. It was found that both layers are in thickness of around 1 μm after soldering, with a thickness ratio of about 1:1 between them. It is worth noticing that some grains with composition of 33Cu–52In–15Sn was observed within the solder as shown in Fig. 1 (top-left corner), which should come from the spalling of layer II during liquid reaction in reflowing.

As SEM observations could not provide sufficient information besides composition to determine the IMC species, the interfacial microstructure was investigated further using TEM (also equipped with EDS system). Fig. 2(a) shows a typical bright field image of the detailed interfacial microstructures between eutectic SnIn solder and (1 1 1) Cu. Different from the double-layer morphology in Fig. 1, three layers could be observed on Cu substrate: a fine-grain layer A, a coarse-grain layer B (B_1, B_2 and B_3 are different grains in the same layer), and a large-grain layer C. Elemental analyses using EDS revealed that layers A and B have similar composition of 66Cu–16In–18Sn (at.%), while layer C has a composition close to 33Cu–52In–15Sn (at.%). It implies that layer I in Fig. 1(a) is made of two sublayers A and B in Fig. 2(a), and layer II corresponds to layer C. Besides the similar composition, electron diffraction also revealed that sublayers A and B have the same crystal structure. The SAED patterns of these two sublayers were shown in Fig. 2(b and c) respectively, both of them can be indexed with the hexagonal Cu_2In structure with lattice constants of $a = b = 0.4292$ nm, $c = 0.5232$ nm, $\alpha = \beta = 90°$, and $\gamma = 120°$ [11]. The extra or scattered spots in Fig. 2(b) come from surrounding fine-grains in layer A, while Fig. 2(c) shows a perfect diffraction pattern from only one coarse-grain in sublayer B with the same zone axes of $[1\,1\,0]_{Cu2In}$. Therefore, the IMC species of layer I (including sublayers A and B) can be identified as $Cu_2(In,Sn)$ that has a hexagonal Cu_2In lattice dissolved with some Sn atoms for substituting In atoms, which agrees well with those observed on polycrystalline Cu substrate [12].

Many theoretical and experimental works have been tried to consummate the Cu–In–Sn ternary phase diagram [13,14]. Liu and his coworkers [13] studied the Cu–In–Sn isothermal section at 110 °C, which is the lowest available temperature in the literature for this ternary system. In their study, they pointed out that the η phase, which represents Cu_6Sn_5 and Cu_2In phases, continuously existed from the Cu–In to the Cu–Sn system. Lin et al. [14] studied the Cu–In–Sn isothermal section at 250 °C and found that η-(Cu_6Sn_5, Cu_2In) phase formed a continuous solid solution. However, they cannot distinguish the crystal structures between Cu_6Sn_5 and Cu_2In clearly, noticing that the η-Cu_6Sn_5 has a NiAs B8 crystal structure with dimensions of $a = b = 0.4200$ nm, $c = 0.5090$ nm, $\alpha = \beta = 90°$, $\gamma = 120°$ [15], which is similar to the crystal structure of Cu_2In. It is well known that η-Cu_6Sn_5 can exist stably above the temperature of 189 °C [15]. When the temperature is below 189 °C, the η-Cu_6Sn_5 will transform into η'-Cu_6Sn_5 which has a monoclinic structure with lattice constants of $a = 1.1033$ nm, $b = 0.7294$ nm, $c = 0.9830$ nm, $\alpha = 90°$, $\beta = 98.82°$, $\gamma = 90°$ [16,17]. In this study, the reflowing temperature (160 °C) is much lower than 189 °C, and none of three- or five-modulated superstructures were observed according to TEM investigations. Precise electron diffraction confirmed that neither η-Cu_6Sn_5 nor η'-Cu_6Sn_5 was formed during reflowing eutectic SnIn/Cu solder joint at 160 °C. The resulted IMC at substrate side is undoubtedly determined as $Cu_2(In,Sn)$ with hexagonal crystal structure.

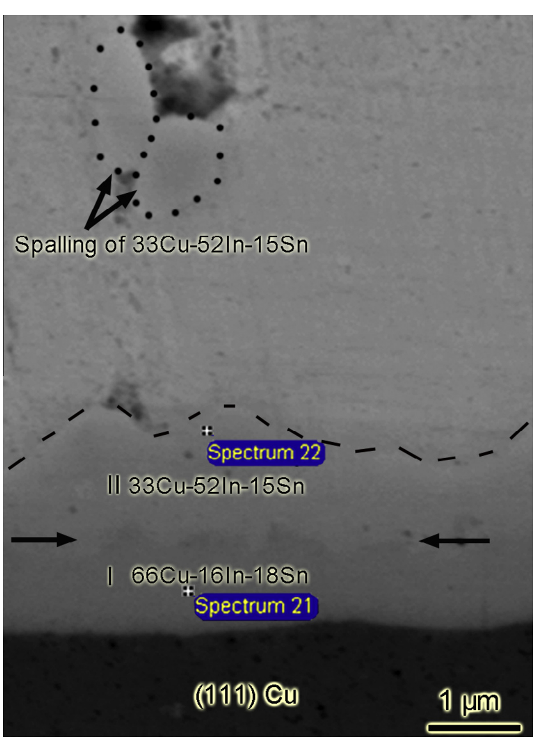

Fig. 1. Cross-sectional SEM images taken at the interface between eutectic SnIn solder and single crystalline (1 1 1) Cu after reflowing at 160 °C for 5 s.

Table 1
The content (at.%) of element in I and II IMC layers (see Fig. 1).

IMC layer	Content (at.%)		
	Cu	In	Sn
Layer I	66.11	15.53	18.36
Layer II	33.05	51.66	15.29

3.1.2. The composition and crystal structure of $Cu(In,Sn)_2$ compound

According to the EDS analyses in TEM, layer C in Fig. 2(a) has a similar composition to that of layer I in Fig. 1, which is about 33Cu–52In–15Sn (at.%). To identify its crystal structure, series of SAED patterns from the same grain in layer C were taken as shown in Fig. 2(d–g). These diffraction patterns can be indexed exactly with