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Effective suppression of interfacial intermetallic compound growth between Sn–58 wt.% Bi solders and Cu substrates by minor Ga addition

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ABSTRACT

Overgrowth of the intermetallic compound (IMC) layer between Sn–58 wt.% Bi (Sn–58Bi) solders and Cu substrates significantly degrades the reliability of electronic products. Doping active elements into Sn–58Bi solders is a common approach for improving joint properties. In this study, minor amounts of Ga, ranging from 0.25 to 3.0 wt.%, were doped into Sn–58Bi solders. The interfacial reactions between the Ga-doped Sn–58Bi solders and Cu substrates at 200 °C were investigated using electron probe microanalysis (EPMA) and CALPHAD thermodynamic modeling. Four IMCs, namely θ-$CuGa_2$, γ_1-Cu_9Ga_4, η-Cu_6Sn_5, and ε-Cu_3Sn phases, were observed. For longer reaction time or lower doping levels of Ga in the solders, the diffusion paths across the Ga-doped Sn–58Bi/Cu couples changed from L/θ/γ_1/Cu to L/γ_1/ε/Cu and L/γ_1/η/ε/Cu. The dense γ_1-Cu_9Ga_4 layer acted as a native diffusion barrier. The growth of the IMC layer was effectively suppressed with minor Ga addition.

1. Introduction

Soldering is the most important interconnection technology for various levels of electronic packaging [1–6]. Pb-free solders have been introduced in the electronic industry due to the prohibition of Pb in consumer electronic products [7]. In order to avoid thermal damage in step-soldering processes and eliminate the mismatches between different materials in packaging modules, low-temperature Pb-free solders with low cost and high reliability are in demand in the electronic industry [8,9]. Eutectic Sn–58 wt.% Bi (Sn–58Bi) alloy, with its low melting temperature at 139 °C [10], has drawn a lot of attention as a candidate for low-temperature soldering applications [1,11,12]. Sn–58Bi alloy has high joint strength, large creep resistance, low coefficient of thermal expansion, good wettability, and most importantly, low cost [11,13]. Cu is the most commonly used substrate material in electronic products. However, the major drawback of applying Sn–58Bi solder is the excessive growth of the η-Cu_6Sn_5 layer in Sn–58Bi/Cu joints, which degrades joint strength [14,15]. The reactions between Sn–58Bi and Cu have been extensively studied [2,14–20]. The η-Cu_6Sn_5 and ε-Cu_3Sn phases form between molten Sn–58Bi solders and Cu substrates. The growth of the scallop-type η-Cu_6Sn_5 phase is governed by the grain-boundary diffusion mechanism, which has been reported to be responsible for the rapid consumption of the Cu substrate and the overgrowth of intermetallic compounds (IMCs) [15,21].

Various alloying elements, including Al, Cr, Cu, Si, Zn, Ag, Au, Pt, Nb, Ce, and La, have been added to Sn–58Bi solder to manipulate the interface properties of joints [17,20–22]. Among these additives, only rare-earth additives slightly reduce IMC growth, with other types of additive either failing to form an appropriate barrier or unable to slow down IMC growth. Zn addition and Al addition under vacuum can change the interfacial reaction products; however, massive spalling of IMC occurs between the solders and Cu substrates [23,24]. Ga has been used as an additive for Pb-free solders. Up to 0.5 wt.% Ga addition to Sn–8.55Zn–0.5Ag–0.1Al–xGa solders has been examined [25]. Minor Ga addition improved the wettability of the solders but it did not affect the interfacial reactions with Cu [13,25]. Nevertheless, there is very limited information on the effect of Ga addition on interfacial reactions between Pb-free solders and Cu substrates. In the present study, 0.25, 0.5, 1.0, 2.0, and 3.0 wt.% Ga was added to Sn–58Bi solders, creating Sn–57.86 wt.% Bi–0.25 wt.% Ga (Sn–57.86Bi–0.25Ga), Sn–57.71 wt.% Bi–0.5 wt.% Ga (Sn–57.71Bi–0.5Ga), Sn–57.42 wt.% Bi–1.0 wt.% Ga (Sn–57.42Bi–1.0Ga), Sn–56.84 wt.% Bi–2.0 wt.% Ga (Sn–56.84 Bi–2.0Ga), and Sn–56.26 wt.% Bi–3.0 wt.% Ga (Sn–56.26Bi–3.0Ga) alloys, respectively. The interfacial reactions between the Ga-doped Sn–58Bi solders and Cu substrates at 200 °C were investigated and

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the reaction phase formation was identified. Reaction mechanisms are proposed and the thermodynamic foundation is elaborated.

2. Materials and methods

2.1. Alloy and reaction couple preparation

Sn–57.86Bi–0.25Ga, Sn–57.71Bi–0.5Ga, Sn–57.42Bi–1.0Ga, Sn–56.84Bi–2.0Ga, and Sn–56.26Bi–3.0Ga alloys were prepared with a commercially available Sn–58Bi alloy (99.95%, Alfa Aesar, USA) and pure Ga (99.9%, Alfa Aesar, USA). Proper amounts of the source materials were weighted and sealed together in quartz tubes under a vacuum of 10^{-5} Pa. The capsules were annealed at 850 °C for 24 h to ensure the homogeneity of the mixtures and then quenched in icy water. A 500-μm-thick pure Cu foil (99.98%, Sigma Aldrich, USA) was sawed into 5 mm × 3 mm pieces, and then metallographically ground and polished with alumina powders down to 1 μm. Subsequently, Cu substrates were gently etched with a 5% HCl solution, rinsed with deionized water, and dried with N_2 gas. The fresh Cu substrates and Sn–*x*Bi–*y*Ga solders (x = 57.86, 57.71, 57.42, 56.84, 56.26, and y = 0.25, 0.5, 1.0, 2.0, 3.0) were placed in quartz tubes and encapsulated together under a vacuum of 10^{-5} Pa. The Sn–*x*Bi–*y*Ga/Cu couples were then annealed at 200 °C for various predetermined lengths of reaction time and then quenched in icy water immediately at the end of the reactions. In addition, for examining the effect of cooling rate, several cooling conditions, namely quenching in liquid nitrogen, quenching in icy water, cooling down naturally under ambient conditions at room temperature, and cooling down slowly in a furnace, were also examined for the Sn–56.84Bi–2.0Ga/Cu couples reacted at 200 °C for 24 h.

2.2. Microstructural and compositional characterizations

The resulting couples were mounted in epoxy and metallographically examined with an optical microscope (OM, BX-51, Olympus, Japan) and a scanning electron microscope (SEM, TM-1000, Hitachi, Japan) with a backscattered electron detector. The composition of each phase region was analyzed using electron probe micro-analysis (EPMA, JXA-8900R, JEOL, Japan). The thickness of the interfacial layers in the micrographs was measured using image processing software (EM1000, Zhone Zhun Technology Inc., Taiwan) according to the following equation:

$$d = A/l \quad (1)$$

where d is the thickness of the IMC layer, and A and l are the selected area and width of the IMC layer, respectively. The average thicknesses as well as the corresponding error bars were calculated from at least three independent measurements.

2.3. CALPHAD thermodynamic modeling

The phase equilibria of the Bi–Cu–Ga–Sn quaternary system were calculated using the calculation of phase diagram (CALPHAD) method with the PanPhaseDiagram module of PANDAT software [26]. The thermodynamic models of Bi–Cu, Bi–Ga, Bi–Sn, Cu–Ga, Cu–Sn, and Ga–Sn binary systems and Bi–Cu–Sn and Bi–Ga–Sn ternary systems were taken from the literature [27–35]. The preliminary thermodynamic models for the Bi–Cu–Ga and Cu–Ga–Sn ternary systems and the Bi–Cu–Ga–Sn quaternary system were constructed based on the constituent binary and ternary systems without incorporating additional high-order interacting parameters into the Gibbs free energy models.

3. Results

3.1. Phase equilibria of Bi–Ga–Sn ternary alloys

Fig. 1(a) shows the calculated Sn58Bi–Ga isoplethal section of the Bi–Ga–Sn ternary system. The liquidus points of Sn–57.86Bi–0.25Ga, Sn–57.71Bi–0.5Ga, Sn–57.42Bi–1.0Ga, Sn–56.84Bi–2.0Ga, and Sn–56.26Bi–3.0Ga alloys are very close to each other (around 150 °C), as labeled in Fig. 1(b). Therefore, the reactions at 200 °C in the Sn–*x*Bi–*y*Ga/Cu couples (x = 57.86, 57.71, 57.42, 56.84, 56.26, and y = 0.25, 0.5, 1.0, 2.0, 3.0) are all liquid/solid (L/S) reactions. As shown in Fig. 1(b), the 0.25, 0.5, and 1.0 wt.% Ga-doped Sn–*x*Bi–*y*Ga alloys are in the (Bi) + (Sn) two-phase region at room temperature and typical electronic device operation temperatures; however, for the alloys with higher Ga content, e.g., 2.0 and 3.0 wt.% Ga-doped Sn–*x*Bi–*y*Ga alloys, a small amount of the Ga-rich liquid phase remains at low temperatures until the Class I reaction (ternary eutectic reaction): L = (Bi) + (Sn) + (Ga) at 20.5 °C.

When the molten solders are in contact with solid substrate, nominal compositions of the molten solders are changed by both

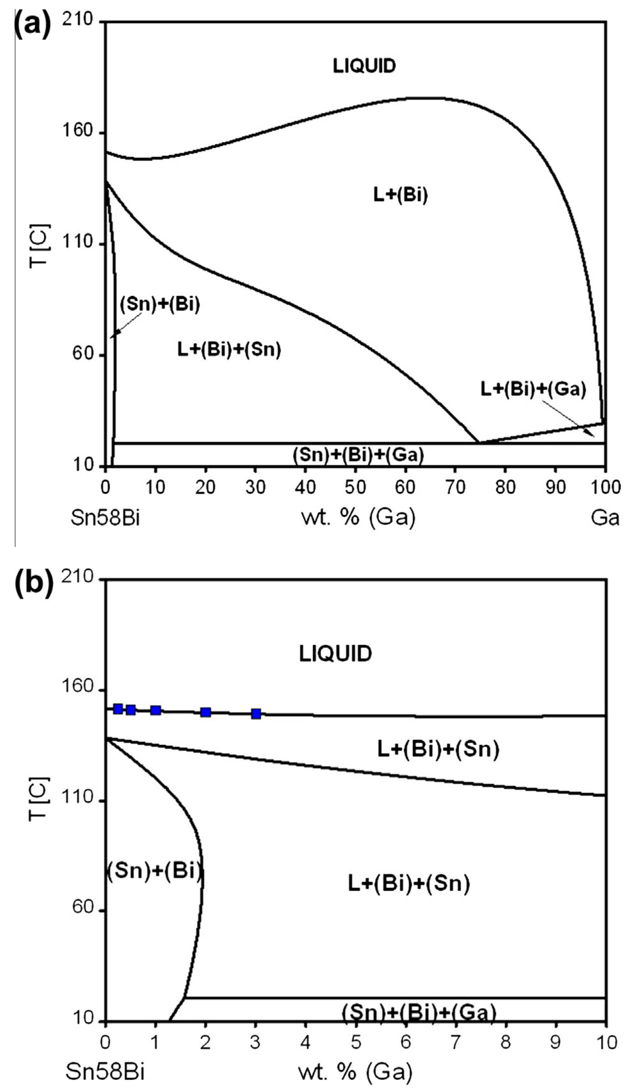

Fig. 1. (a) Sn58Bi–Ga isoplethal section of Bi–Ga–Sn ternary system and (b) Sn58Bi-rich region of Sn58Bi–Ga isoplethal section.

the dissolution of substrate materials into the liquid phase and the consumption of active elements in the liquid phase through interfacial reactions with the substrates. In the following sections, the interfacial reactions in the Sn–*x*Bi–*y*Ga/Cu couples at 200 °C are presented. In particular, 2.0 and 0.25 wt.% Ga-doped Sn–*x*Bi–*y*Ga/Cu couples, i.e., Sn–56.84Bi–2.0 Ga/Cu and Sn–57.86Bi–0.25 Ga/Cu couples, were examined in detail for understanding the general trend of the effect of Ga content on the interfacial reactions in Sn–*x*Bi–*y*Ga/Cu couples at 200 °C.

3.2. Interfacial reactions in Sn–56.84Bi–2.0Ga/Cu couples at 200 °C

3.2.1. Reaction phase identification and transformation

Fig. 2(a)–(c) shows backscattered electron images (BEIs) of Sn–56.84Bi–2.0Ga/Cu couples reacted at 200 °C for 12, 48, and 240 h, respectively. At the end of the L/S reactions, the couples were quenched in icy water immediately. As shown in Fig. 2(a), only two distinct phase regions can be observed in the area of the solder matrix. The bright and light grey phase regions in the solder matrix are presumed to be (Bi) and (Sn) phases, respectively; the (Ga) phase was not found after a 12-h reaction at 200 °C. In addition, two interfacial layers were found: a thin light grey layer on the top of the Cu substrate and a dark grey layer with