Journal of Alloys and Compounds 579 (2013) 75–81

Contents lists available at SciVerse ScienceDirect

Journal of Alloys and Compounds

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

Effects of Ni_3Sn_4 and $(Cu,Ni)_6Sn_5$ intermetallic layers on cross-interaction between Pd and Ni in solder joints

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ARTICLE INFO

Article history:
Received 23 February 2013
Received in revised form 3 May 2013
Accepted 3 May 2013
Available online 16 May 2013

Keywords:
Ni(P)/Pd/Au surface finish
Pb-free solder
Pd resettlement
Cross-interaction
Diffusion barrier

ABSTRACT

We examined the effects of layers of intermetallic compound (IMC) Ni_3Sn_4 and $(Cu,Ni)_6Sn_5$ formed at the solder/Ni interface, on the cross-interactions between Pd and Ni during solid-state aging and reflow soldering. Two types of diffusion couples, Pd/Sn/Ni and Pd/Sn–Cu/Ni, were aged at 150 °C to study the solid-state interactions. In contrast to the Pd/Sn/Ni couples in which a Ni_3Sn_4 layer formed at the Ni interface, the Pd/Sn–Cu/Ni couple where a $(Cu,Ni)_6Sn_5$ layer formed at the Ni interface exhibited no significant interaction between Pd and Ni. The $(Cu,Ni)_6Sn_5$ layer acted as an effective barrier against Ni diffusion and thus inhibited the resettlement of $(Pd,Ni)Sn_4$ onto the Ni interface. For the interaction during reflow, Sn–3.5Ag and Sn–3.0Ag–0.5Cu solder balls were isothermally reflowed on an electroless Ni(P)/electroless Pd/immersion Au (ENEPIG) surface finish at 250 °C, and the dissolution kinetics of the $(Pd,Ni)Sn_4$ particles converted from the 0.2-μm-thick Pd-finish layer were examined. The spalled $(Pd,Ni)Sn_4$ particles very quickly dissolved into the molten solder when the IMC layer formed on the Ni substrate was $(Cu,Ni)_6Sn_5$ rather than Ni_3Sn_4. The dependence of the dissolution kinetics of the spalled $(Pd,Ni)Sn_4$ particles on the IMC layers was rationalized on the basis of a Sn–Ni–Pd isotherm at 250 °C. The present study suggests that the formation of a dense $(Cu,Ni)_6Sn_5$ layer at the solder/Ni interface can effectively alleviate the $(Pd,Ni)Sn_4$-related degradation of solder joint reliability.

1. Introduction

The electroless Ni/electroless Pd/immersion Au (ENEPIG) surface finish has recently been widely used as a superior alternative to the conventional electroless Ni/immersion Au (ENIG) finish in the microelectronic packaging industry. This is partly because the electroless Pd (EP) layer inserted between the Au and Ni(P) layers acts as a barrier against the diffusion of Ni atoms and, thus, improves the solder wettability as well as the wire bondability with a thinner Au layer [1–3]. In addition, the EP layer prevents galvanic hyper-corrosion of the Ni(P) layer surface during immersion in the Au plating solution, thereby mitigating the “black pad” problem associated with the ENIG surface finish [3–7]. Although the thickness of the EP layer in the ENEPIG surface finish is typically in the 0.04–0.2 μm range, its use in emerging packaging applications such as package-on-package (PoP) and flip-chip technologies can result in poor solder joint reliability due to the formation of $(Pd,Ni)Sn_4$ intermetallic compound (IMC) near the solder/Ni(P) interface [8–10]. The solder balls used in PoP technology interconnect on both sides of the ENEPIG surface finishes. The solder joints used in flip-chip technology have a low ratio of the solder volume to the pad area. Therefore, when the EP layer dissolves into the solder in such solder joints, the resultant Pd concentration in the solder can be high enough for the $(Pd,Ni)Sn_4$ phase to form near the solder/Ni(P) interface, thereby deteriorating joint reliability.

When Sn-based solders are reflowed on the ENEPIG surface finish, the EP layer quickly transforms into a $PdSn_4$ layer after the top Au layer dissolves into the molten solder. The $PdSn_4$ layer then spalls off from the Ni(P) layer and gradually dissolves into the molten solder until the solder becomes saturated with Pd [10–13]. After the detachment of the $PdSn_4$ layer, the underlying Ni(P) layer is exposed to the molten solder and starts to react with the solder. It is well known that the IMC layer formed at the solder/Ni(P) interface during reflow can be either Ni_3Sn_4 or $(Cu,Ni)_6Sn_5$ depending on the Cu content in the Sn-based solder [14–17]. Therefore, it is of practical and fundamental interest to identify the effects of the IMC at the solder/Ni(P) interface on the dissolution kinetics of the spalled $PdSn_4$ into the molten solder. Although many studies have been reported on the interfacial reactions between Pb-free solders and ENEPIG surface finish during reflow [7–13,18,19], the

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http://dx.doi.org/10.1016/j.jallcom.2013.05.055

dissolution kinetics of the spalled (Pd,Ni)Sn_4 particles into the molten solder has not been addressed yet.

Moreover, Pd atoms dissolved into the molten solder may precipitate as $PdSn_4$ particles during the solidification stage after the reflow soldering. During subsequent aging, $PdSn_4$ particles dispersed throughout the solder can decompose and then re-precipitate as a ternary (Pd,Ni)Sn_4 phase enriched with Ni at the solder/IMC interface over the Ni(P) layer, especially when the IMC formed on the Ni(P) layer is Ni_3Sn_4 [20,21]. This is analogous to the phenomenon known as "Au resettlement" during solid-state aging [22–24], in which the $AuSn_4$ particles in the solder matrix migrate toward the Ni substrate to form a ternary (Au,Ni)Sn_4 layer over the Ni substrate. Similar to the $AuSn_4$ phase during Au resettlement, the binary $PdSn_4$ phase tends to change into a ternary (Pd,Ni)Sn_4 phase by incorporating Ni atoms so as to reduce its free energy [8,9,25]. Au resettlement strongly depends on the kind of IMC formed on the Ni substrate; that is, it readily occurs when the IMC layer is Ni_3Sn_4 [22–24], but it is inhibited when the IMC layer is $(Cu,Ni)_6Sn_5$ [26]. To the best of our knowledge, there has been no reported direct comparison of the effects of the Ni_3Sn_4 and $(Cu,Ni)_6Sn_5$ layers on Pd resettlement over the Ni or Ni(P) substrate during solid-state aging.

The aim of this paper is two-fold. First, the dependence of Pd resettlement over the Ni substrate on the IMC layers (Ni_3Sn_4 and $(Cu,Ni)_6Sn_5$) formed at the solder/Ni interface is to be examined. For this purpose, two types of diffusion couples, Pd/Sn/Ni and Pd/Sn–Cu/Ni, were aged at 150 °C to study the cross-interaction between Pd and Ni layers. Lu et al. [25] recently compared the cross-interactions in Pd/Sn/Ni and Pd/Sn/Cu couples during reflow at 250 °C. However, the present study deals with how the solid-state cross-interactions between Pd and Ni depend on the IMC layers formed over the Ni layer. Further, the present study is different from the recent report by Lin et al. [27] who employed the Ni/Pd/Sn/Cu and Ni/Sn/Pd/Cu diffusion couples to study the solid-state cross-interaction between Ni and Cu layers in the presence of a (Pd,Ni)Sn_4 or $PdSn_4$ IMC layer in between them. The second objective is to compare how the dissolution behaviors of the spalled $PdSn_4$ or (Pd,Ni)Sn_4 particles during reflow depend on the IMC layers formed at the solder/Ni interface. For this purpose, two kinds of solder balls, Sn–3.5Ag and Sn–3Ag–0.5Cu, were reflowed on an ENEPIG surface finish at 250 °C.

2. Experimental details

Two types of diffusion couples, Pd/Sn/Ni and Pd/Sn–Cu/Ni, were prepared for the solid-state cross-interaction between Pd and Ni by first electroplating either a Sn or Sn-1.0 wt.% Cu layer (60 ± 5 μm thick) and then a Pd layer (0.75 ± 0.1 μm thick) on a Ni foil substrate. The only difference between the two diffusion couples was the intermediate layer (Fig. 1). The as-prepared diffusion couples were cut into 10 × 10 mm^2 samples and were then isothermally aged at 150 °C for various durations of up to 1225 h. The samples were aged by immersing them in silicone oil preset at 150 ± 1 °C, to prevent them from oxidizing.

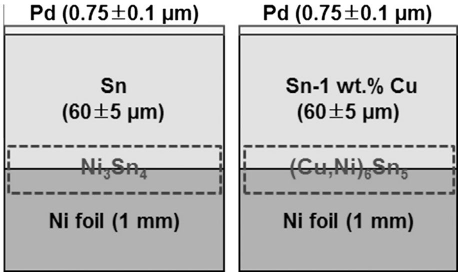

Fig. 1. Schematic diagrams of the Pd/Sn/Ni and Pd/Sn–Cu/Ni diffusion couples used for solid-state aging at 150 °C. The only difference between the two couples is the intermediate layer: one is pure Sn used to form a Ni_3Sn_4 layer at the Ni interface and the other is Sn-1 wt.% Cu used to form a $(Cu,Ni)_6Sn_5$ layer at the Ni interface.

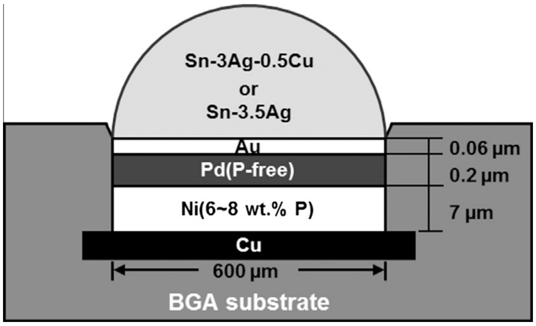

Fig. 2. Schematic diagram of the solder joint configuration used to examine the dissolution of spalled (Pd,Ni)Sn_5 particles during reflow at 250 °C. Either a Sn–3.5Ag or a Sn–3.0Ag–0.5Cu solder ball was reflowed on the ENEPIG-finished pad.

Fig. 2 illustrates the solder joint configuration used to compare the dissolution kinetics of the $PdSn_4$ or (Pd,Ni)Sn_4 particles during reflow soldering on ENEPIG-finished bonding pads. Two kinds of 450-μm-diameter solder balls, Sn–3.5 wt.%Ag (SA35) and Sn–3 wt.%Ag–0.5 wt.%Cu (SAC305), were reflowed on 600-μm-diameter bonding pads with an ENEPIG surface finish at 250 °C for various time lengths up to 900 s. The ENEPIG finish was fabricated over the Cu pads of a ball-grid array (BGA) substrate with thicknesses of 7.0 μm Ni(P), 0.2 μm Pd, and 0.06 μm Au by using the chemicals provided by KPM TECH. Although the Ni(P) layer contained 7 ± 1 wt.% P, the Pd layer was P free, as analyzed using a calibrated X-ray fluorescence (XRF) spectrometer. Before the ENEPIG-finished pads were soldered, they were first coated with rosin mildly activated (RMA) flux, and the solder balls were then manually placed on the flux-coated pads. The solder balls on the ENEPIG-finished pads were reflowed by immersing them in silicone oil preset to 250 ± 2 °C.

After the samples were either aged or reflowed for predetermined durations, they were quenched in water and cleaned with acetone to remove any residual silicone oil from the surface. The samples were then mounted in epoxy and were metallographically polished to reveal their cross-sectional microstructure. The polished samples were lightly etched for a few seconds in a solution consisting of CH_3OH + 10% HCl to differentiate the various phases. The cross-sectional microstructure of the diffusion couples was examined using scanning electron microscopy (SEM) in backscattered electron (BSE) imaging mode. The phase compositions were analyzed using an energy-dispersive X-ray spectrometer (EDX) operated at 20 keV. Each of the composition data reported herein was obtained by averaging at least three measurements made at different locations. The IMC thickness was determined from the cross-sectional SEM micrographs by dividing the area of the IMC layer by the length of the linear interface. The thickness data reported herein are the average values of the thicknesses determined from three different SEM micrographs.

3. Results and discussion

3.1. Solid-state cross-interaction in Pd/Sn/Ni

Fig. 3 shows the microstructural evolution of the Pd/Sn/Ni diffusion couple during aging at 150 °C for 1225 h; the micrographs in the upper row correspond to the Pd/Sn side and those in the lower row correspond to the Sn/Ni side. After the diffusion couple was aged for 9 h (Fig. 3a), the top 0.75-μm-thick Pd layer had entirely transformed into a $PdSn_4$ layer. No meaningful EDX signals of Ni were detected from the $PdSn_4$ layer at this stage. On the other hand, a continuous layer of Ni_3Sn_4 was formed at the Sn/Ni interface. Moreover, there were scattered particles on the Ni_3Sn_4 layer and the particles were identified by EDX to be the (Pd,Ni)Sn_4 phase containing approximately 0.9 at.% Pd, indicating that measurable Pd diffusion had already occurred across the Sn layer.

The top $PdSn_4$ layer grew thicker with prolonged aging, even though Pd atoms continuously diffused out of the layer. EDX further revealed that the binary $PdSn_4$ layer became ternary (Pd,Ni)Sn_4 containing ~1.4 at.% Ni after 100 h of aging (Fig. 3b) and that the Ni content in the (Pd,Ni)Sn_4 layer increased with increasing aging time. Therefore, as denoted in Fig. 3, the top (Pd,Ni)Sn_4 layer is hereafter represented as $(Pd_{1-x}Ni_x)Sn_4$, whereas the (Pd,Ni)Sn_4 phase formed on the Sn/Ni side is denoted as $(Pd_{1-y}Ni_y)Sn_4$. The increase in the thickness of the $(Pd_{1-x}Ni_x)Sn_4$ layer with increasing aging time implies that the flux of Ni atoms into the layer from the Sn/