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Effect of Ni–P thickness on solid-state interfacial reactions between Sn–3.5Ag solder and electroless Ni–P metallization on Cu substrate

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Abstract

Solid-state interfacial reactions between Sn–3.5Ag solder and electroless Ni–P metallization on Cu substrate were investigated for three different Ni–P thicknesses. It was found that during interfacial reactions, Ni_3Sn_4 intermetallic grows at the Sn–3.5Ag/Ni–P interface along with the crystallization of electroless Ni–P layer into Ni_3P compound. Additional interfacial compounds (IFCs) such as Ni–Sn–P, Cu_3Sn, Cu_6Sn_5, $(Ni_{1-x}Cu_x)_3Sn_4$, and $(Ni_{1-x}Cu_x)_6Sn_5$ were also found to grow at the Sn–3.5Ag/Ni–P/Cu interfaces depending upon the Ni--P thickness. In the sample with thin Ni–P layer, formation of these IFCs appeared at lower aging temperature and within shorter aging duration than in the samples with thicker Ni–P. The complete dissolution of electroless Ni–P layer into Ni_3P and Ni–Sn–P layers was found to be the main cause for the growth of additional IFCs. Across the Ni_3P and Ni–Sn–P layers, diffusion of Cu and Sn takes place resulting in the formation of Cu–Sn and Ni–Cu–Sn intermetallics. It is shown in this paper that multi-layered IFC growth at the Sn–3.5Ag/Ni–P/Cu interfaces can be avoided by the selection of proper Ni–P thickness.

Keywords: Electroless nickel; Solder; Interfacial reaction; Intermetallic compound

1. Introduction

Under bump metallization (UBM) is a combination of thin metallic layers which not only provides good solderable surface but also protects the underlying IC metallization from reacting with solder. During soldering process, UBM reacts with solder and forms a thin layer of interfacial compound (IFC). Formation of the thin layer is desirable to achieve good metallurgical bond. However, excess growth of the IFC affects the mechanical reliability of the solder joint which is a generic reliability problem in flip-chip solder joints [1–3].

Cu is a promising UBM material for Sn–Pb solder because of its good wettability with solder. However, Cu reacts rapidly with Sn of the solder forming thick layers of Cu–Sn intermetallics. This IFC over-growth problem is exacerbated in the case of Pb-free solders, used due to the legislation and environmental concerns, as the Pb-free solders are Sn-rich alloys constituting one or two more elements such as Ag, Cu, and Bi. The IFC growth has been found to be reduced in the case of Ni UBM, as the reaction between Ni and Sn is much slower than between Cu and Sn [4]. The Ni UBM can be deposited by various chemical and physical deposition techniques. Among them, electroless nickel with a thin layer of immersion gold has been considered as a promising UBM due to its easy processing and low cost.

Electroless nickel is a Ni–P alloy, where P comes from hypophosphite-reducing agent during the reduction of Ni from an ionic Ni solution. The presence of P in the electroless Ni–P UBM causes its complicated interfacial reactions with solder. The interfacial reactions include formation of Ni_3Sn_4 intermetallic and Ni_3P compound at the solder/Ni–P interface [2–12]. Other reaction products such as Ni_3Sn_2 and $Ni_{12}P_5$ were also reported [5,7], although Ni_3Sn_4 and Ni_3P were the major phases. Further, a ternary Ni–Sn–P compound was also reported to form at the solder/Ni–P interface [8], which grew during liquid-state aging [9,10]. Recently, it was found [12] that this Ni–Sn–P compound can grow even during solid-state aging. Although numerous studies have been done on the interfacial reactions between solder and electroless Ni–P

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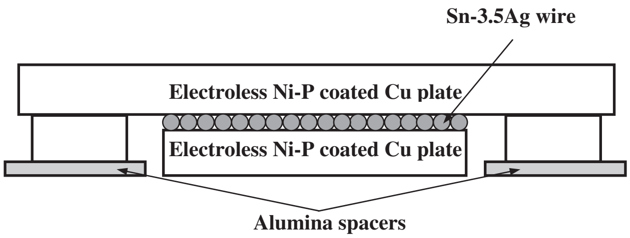

Fig. 1. Schematic illustration for joining the electroless Ni–P coated Cu plates.

UBM, the understanding made so far on the influence of Ni–P UBM thickness on the interfacial reactions is incomplete. Accordingly, in this work, solid-state interfacial reactions between solder and electroless Ni–P UBM on Cu substrate were studied for different thicknesses of Ni–P UBM.

2. Experimental procedure

Cu (99.99%) plate of size of 70 mm × 25 mm × 6 mm was used to fabricate the multi-layered reaction samples Cu/Ni–P/Sn–3.5Ag/Ni–P/Cu. The Cu plate was surface cleaned, first by polishing down to 1 μm finish, then by ultrasonically cleaning with acetone for 10 min, then by etching with 20 vol.% HNO_3 solution for a few seconds, and finally by cleaning with de-ionized water. Electroless Ni–P was plated on the surface cleaned Cu plate in two steps. In the first step, Cu surface was activated using the ruthenium-based commercial pre-initiator. Then, electroless Ni–P was plated on the activated Cu surface using commercial electroless nickel solution. Electroless Ni–P metallization, of three different thicknesses, was plated on the Cu plate by selecting the three different deposition times but at the same process conditions. Thin layer (~500 Å) of non-cyanide immersion gold was also deposited on the electroless Ni–P surface to protect the surface from oxidation.

The electroless Ni–P coated Cu plate was cut into two pieces of size of 40 mm × 25 mm × 6 mm and 30 mm × 25 mm × 6 mm, and then joined with each other using Sn–3.5Ag solder. Fig. 1 illustrates the set-up used to join the plates. The joint was formed during the reflow process by placing a number of small pieces of solder wires on the small electroless Ni–P coated Cu plate and pressing them by the big plate. No-clean paste flux was applied on both the plates before placing the Sn–3.5Ag wires. The reflow process was carried out in IR reflow oven (ESSEMTEC RO-06E) which involved preheating at 150 °C for 100 sec, then reflowing at 250 °C for 60 sec, and finally cooling down to 160 °C in the oven. Alumina spacers of thickness of around 650 μm were used to maintain the uniform thickness of solder in between the plates. The joined plates were cut into a number of small samples with the help of diamond saw. Fig. 2 shows the schematic diagram of reaction sample.

As-prepared reaction samples were isothermally aged in the oven (Lenton WHT4/30) at 160, 180, and 200 °C for 48, 100, 225, and 400 h. After aging, the samples were removed from the oven and cooled in air to room temperature. JEOL JSM-6360A scanning electron microscope (SEM) was used for microstructure analysis. For the cross-sectional SEM, the samples were cold mounted in epoxy and polished down to 1 μm finish. After polishing, solder etching was carried out to reveal the microstructure. Etching was done with 4 vol.% hydrochloric acid for a few seconds. Energy dispersive X-ray (EDX) spectroscopy was performed in the SEM to analyze the chemical composition of IFCs.

3. Results

The thicknesses of three as-plated electroless Ni–P layers were measured to be around 3.9, 7.3, and 9.9 μm while the P content was found to be around 16 at.%. According to their thicknesses, the electroless Ni–P layers are termed as thin, medium, and thick Ni–P.

3.1. As-prepared reaction samples

Fig. 3 shows the IFCs formed at the Sn–3.5Ag/Ni–P interface in the as-prepared samples having electroless Ni–P layers of different thicknesses. Regardless of Ni–P thickness, all the samples have similar interfacial microstructure and chemistry. Needle-type and chunky-type Ni_3Sn_4 intermetallic formed at the Sn–3.5Ag/Ni–P interface during the reflow, some of which spalled off into the molten solder. Underneath the Ni_3Sn_4, Ni–Sn–P layer formed whose composition was difficult to measure by EDX in the SEM owing to its submicron thickness. Underneath the Ni–Sn–P layer, a dark thin Ni_3P layer having large number of voids formed within the electroless Ni–P layer.

3.2. Aged reaction samples

Solid-state aging at 150 °C for 1000 h is a required reliability test for solder/UBM joint [4]. In this work, solid-state aging was carried out at higher temperatures (160 to 200 °C) to shorten the aging duration to 400 h. Fig. 4 shows the back-scattered SEM images of Sn–3.5Ag/Ni–P/Cu interfaces in the samples aged at 160 °C for 225 h showing the growth of Ni_3Sn_4 intermetallic and Ni_3P layer. It can be observed that in the sample with thin Ni–P, the electroless Ni–P layer completely transformed into Ni_3P, whereas in other samples,

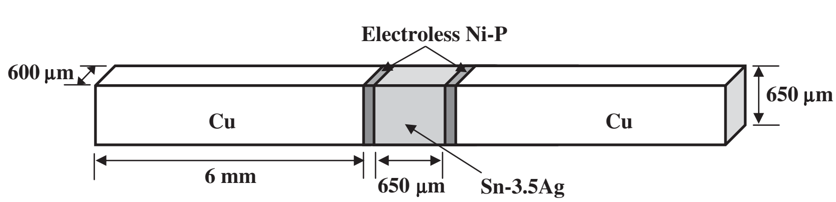

Fig. 2. Schematic diagram of reaction sample.