Intermixing reactions in electrodeposited Cu/Sn and Cu/Ni/Sn multilayer interconnects during room temperature and high temperature aging

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Abstract Current push for miniaturization and 3D packaging makes it important to understand reactions in interconnects with ultra small volume. In order to reduce processing time and to have more homogeneous interconnects, solder can be designed in a multilayer form with components layer thickness in the sub-micron or even nanometer range. In this work, reaction kinetics in multilayer interconnects consisting stacks of Cu/Sn/Cu and Cu/Ni/Sn/Ni/Sn deposited by electrodeposition were investigated at room temperature and 150 °C. The progress of the reaction in the multilayers was monitored by using XRD, SEM and EDX. Results show that by inserting a 70 nm thick nickel layer between copper and tin, premature reaction between Cu and Sn at room temperature can be avoided. The addition of the nickel layers also allows the selective formation of Cu_6Sn_5 which is considered to have better properties compared to Cu_3Sn. Details of the reaction sequence and mechanisms are discussed.

1 Introduction

Transient liquid phase (TLP) bonding or soldering has attracted a great deal of attention of researchers in recent years [1–6]. In this process of soldering, a low melting point component in the solder joint melts during reflow and reacts with the solid components to produce typically an intermetallic compound (IMC) whose melting point is higher than the reflow temperature. The new phase is therefore stable at high operating temperatures and has the potential to improve the reliability of solder joint. The TLP soldering process thus combines the dual advantage of low processing temperature and better stability of the joint at high operating temperatures.

A number of researchers reported on TLP soldering in the copper/tin (Cu/Sn) system which is considered to be a good candidate for small and 3D microelectronic packages, MEMS etc. [4–8]. These studies used the low melting tin layer with thickness in the range of a few tens of μm [4]. With the rapid progression towards smaller interconnects, e.g., in 3D packages, it is thus important to investigate TLP soldering process with component thickness in the range of sub-micrometers and even nanometers.

One practical and economical way to deposit solder of small volume is electrodeposition. However, it has been observed that even during room temperature deposition a thin layer of Cu_6Sn_5 can form between tin based solder and copper [5, 7–9]. Such premature intermixing reaction can reduce the shelf life of yet-to-join components and can eventually cause difficulties in producing sound solder joints. This problem is anticipated to be more acute when the thickness of component layers in TLP solders decreases. It is therefore highly important to understand the spontaneous intermixing reaction between Cu and Sn during room temperature aging and to find way to limit such premature mixing.

In this paper, we study the intermixing of 1.3 μm Cu/1.1 μm Sn multi-layered samples at room temperature and at 150 °C. Another set of samples were also prepared by inserting a thin, 70 nm nickel (Ni) in between Cu and Sn and their intermixing behavior investigated. Growth of reaction products and their nature are discussed.

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2 Methodology

In this study, the multilayers interconnect system were prepared on commercially pure copper substrates by electrodeposition. Two types of baths were used for copper deposition in this study, namely the acidic copper bath ($CuSO_4 \cdot 5H_2O$, 90 g/L; H_2SO_4, 200 g/L) [10] and alkaline pyrophosphate copper bath ($CuSO_4 \cdot 5H_2O$, 30 g/L; $Na_4PO_2O_7$, 120 g/L; NH_3, 1 ml/L). Watts bath is used for the deposition of nickel and methanesulfonic acid (MSA) based bath ($SnSO_4$, 30 g/L; gelatin, 1 g/L; hydroquinone, 5 g/L; MSA, 120 ml/L) is used for the deposition of tin [11]. The bath pH was adjusted to 8.5 by using sulphuric acid for the pyrophosphate copper bath. Stirring condition was set at 80 rpm for all baths. Deposition current density was 10 mA/cm^2 for the pyrophosphate copper bath and 20 mA/cm^2 for the MSA-based tin bath and Watts bath. The deposition time required to achieve required thickness was estimated using the Faraday's law. Copper was plated to achieve a thickness of 1,300 nm while tin was plated to a thickness of 1,100 nm. Nickel was plated to a thickness of 70 nm. Sequential deposition was carried out to prepare both Cu/Sn and Cu/Ni/Sn multilayers interconnect. Cu/Sn multilayers were prepared in the sequence of Cu/Sn/Cu/Sn/Cu while Cu/Ni/Sn multilayers were prepared in the sequence of Cu/Ni/Sn/Ni/Cu/Ni/Sn/Ni/Cu.

Electrochemical polarization studies were performed on deposition baths with a potentio/galvanostat, PC14/300 (Gamry Instruments) in a three-compartment cell using platinum as the counter electrode. An Ag/AgCl electrode was used as the reference electrode which was placed in a Luggin capillary to minimize errors due to iR drop across the electrodeposition bath. Studies are done to investigate the suitability of each bath on different electrodeposits. Room temperature aging studies were done at a temperature of 25 °C with humidity of about 50 %. High temperature aging studies were done using a Memmert oven. FEI Quanta 450 field-emission scanning electron microscope (FESEM) was used to examine the cross-section of the electrodeposits. Line scans using energy dispersive X-ray spectroscopy (EDX) was used to determine the composition of the multilayers system. The phases of the multilayers sample after aging were investigated by X-ray diffraction method using PanAnalytical diffractometer with Cu Kα radiation which has a wavelength, λ of 1.5418 Å. After that, the peaks shown in the XRD pattern was identified by using the Powder Diffraction File card (JCPDS).

Table 1 Combinations of component layers and deposition bath

System	Electrodeposits in deposition baths
Cu/Sn multilayers system	Sn deposition on Cu
	Cu deposition on Sn
Cu/Ni/Sn multilayers system	Ni deposition on Cu
	Cu deposition on Ni
	Ni deposition on Sn
	Sn deposition on Ni

3 Results and discussion

3.1 Electrodeposition: polarization studies

Electrochemical polarization studies were done to investigate the suitability of each electrodeposition bath to different components in the multilayer. It is crucial to check whether the deposited layers were compatible in the next deposition bath. All combinations of component layers and deposition baths encountered in this study are listed in Table 1.

Polarization studies for all combinations mentioned in Table 1 were carried out. Figure 1 shows polarization curves for all combinations which falls into three main groups. Ni deposition occurs at the most cathodic potential, followed by Sn deposition which happens at intermediate potential while Cu deposition happens at the least cathodic potential. It is seen from the figure that Ni deposition on Cu as well as on Sn shows a similar behaviour. From visual examination, it was observed that Ni electrodeposits could form readily on Cu and on Sn. Sn deposition on Cu and on Ni also shows similar behaviour (Fig. 1). Cu deposition on

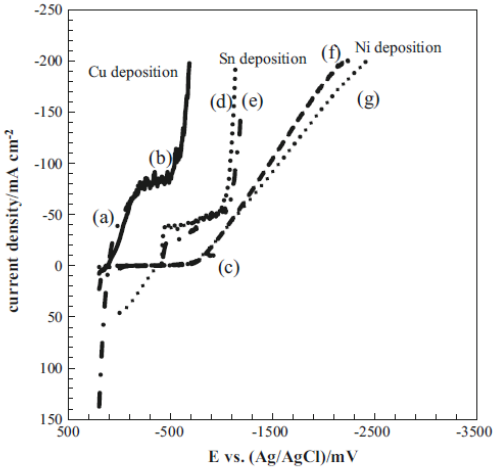

Fig. 1 Polarization curves showing *a* acidic Cu deposited on Sn, *b* acidic Cu deposited on Ni, *c* pyrophosphate Cu deposited on Sn, *d* Sn deposition on Ni, *e* Sn deposition on Cu, *f* Ni deposition on Cu and *g* Ni deposition on Sn

Sn using acidic bath shows a similar polarization behaviour as that for Cu deposition on Ni. However, from visual examination, it was found that Sn immediately got discoloured and turned black when it was dipped into the acidic copper bath. This is thought to be due to the severe dissolution reaction of Sn in the sulphuric acid based copper bath. Thus, deposition of Sn layer on Cu was not feasible. The cathodic polarization behaviour of copper deposition in pyrophosphate bath on Sn was therefore studied.

Figure 2 compares the polarization curves for the deposition of Cu on Sn using acidic bath as well as pyrophosphate bath. From the inset, it is seen that Cu deposition on Sn from pyrophosphate copper bath starts at a potential of around −510 mV while that from acidic copper bath starts from anodic potential. The open circuit potential of Cu deposition on Sn from pyrophosphate bath is −531.5 mV while that from acidic bath is around +8.629 mV. These data reveals that deposition of Cu on Sn is more feasible when pyrophosphate bath was used as the deposition happens at more cathodic potentials and dissolution of Sn does not happen. Therefore, for the preparation of all samples reported here, electrodeposition of Cu was done in the pyrophosphate bath.

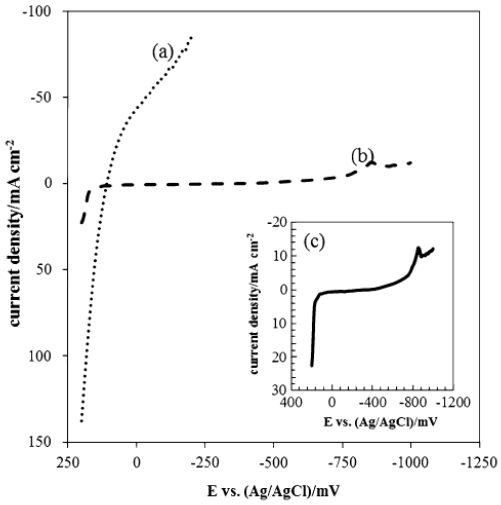

Fig. 2 Cathodic potentiodynamic polarization curves for the deposition of Cu on Sn using *a* acidic sulphuric copper bath, *b* alkaline pyrophosphate copper bath and *c inset curves* for alkaline pyrophosphate copper bath

3.2 Cu/Sn system during room temperature aging

Cu/Sn multilayers sample was subjected to room temperature aging to study the reactions between Cu and Sn in the solid state. Figure 3 shows micrographs of Cu/Sn samples after room temperature aging for 1 and 21 days.

In Fig. 3a, region with darker contrast corresponds to Cu layers while region with lighter contrast corresponds to Sn layers. Within the Sn layers, the dark grey region represents Cu_6Sn_5 IMC phase, with EDX analysis showing 51.42 at.% Cu and 48.58 at.% Sn. It is seen that the Cu_6Sn_5 IMC scallops grow even after 1 day of room temperature aging. The IMC grows in a vertical direction and impingement occurs between the upper IMC and lower IMC scallops. After 21 days, the Cu_6Sn_5 IMC grows to a greater extent as shown in Fig. 3b. The EDX analysis for the Cu_6Sn_5 IMC phase reveals 52.50 at.% Cu and 47.50 at.% Sn. The fast impingement of the Cu_6Sn_5 IMC scallops even after 1 day can be attributed to their small size. Smaller grains are expected to merge faster because of their larger curvatures [12].

Figure 4 shows the XRD patterns for Cu/Sn multi-layered system subjected to room temperature aging for 1, 21, 35 and 70 days. After 1 day aging, the occurrence of the Cu_6Sn_5 IMC phase is revealed by the presence of the peak at 30.179°, which confirms the SEM observations. Sn is consumed as aging time increases. A SnO peak also appears after 21 days, presumably due to the oxidation of Sn under atmospheric conditions.

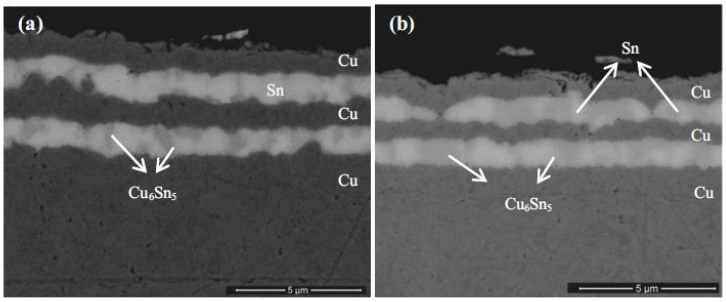

Fig. 3 FESEM micrographs showing cross sectional images of Cu/Sn after **a** 1 day and **b** 21 days of room temperature aging at a magnification of ×4,000

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