Interfacial microstructures and kinetics of Au/SnAgCu

Teck Kheng Leea,⁎, Sam Zhanga,1, C.C. Wonsb,2, A.C. Tanc,3, Davin Hadikusumab

a School of Mechanical and Aerospace Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore, 639798, Singapore
b School of Materials Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore, 639798, Singapore
c Micron Semiconductor Asia Pte Ltd., 990 Bendemeer Road, Singapore, 339942, Singapore

Available online 19 October 2005

Abstract

The gold/lead-free solder system, or Au/SnAgCu is a potential flip chip interconnect solutions for fine-pitch applications. This paper studies the interfacial microstructures and initial isothermal solid–liquid interdiffusion kinetics during the first 3 s of bonding at 230–290 °C. As revealed by Scanning Electron Microscopy (SEM), different morphologies of AuSn, AuSn2 and AuSn4 are observed under different bonding conditions. The initial Au–Sn solid/liquid interdiffusion kinetics is discussed with respect to its microstructures. The rate of Au consumption is used as a measure of the rate of intermetallic compound (IMC) formation. The fitted power law relationship reveals kinetically that Au consumption follows the Arrhenius relationship with a time exponent of 0.5. Isothermal aging at temperatures between 125 °C and 165 °C gives rise to activation energies and the rate of Au consumption in solid–liquid interdiffusion to be two orders of magnitude faster than solid interdiffusion.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Solid–liquid interdiffusion; Interfacial microstructures; Kinetics; Au; SnAgCu

1. Introduction

Lead-free soldering has become a global trend in micro-electronic packaging due to the registration and implementation of tax for lead containing solders for electronic, automotive, and aircraft industries by 2006 [1,2]. Recent studies have shown that SnAgCu (SAC) solder is a promising Pb-free solder as it possesses excellent wettability, superior mechanical strength and good compatibility with existing assembly processes. Being a tin dominant lead free solder, SAC suffers poor reliability with Au due to its rapid formation of brittle Sn–Au intermetallics [3,4]. This dampens the prospect of SAC as the bonding material with Au studs for low-cost, fine-pitch, flip chip interconnect systems with the underbump metallization removed [5,6].

Both dissolution and reaction play important roles in the early stage of bonding [7]. The total chemical driving force arises from the dissolution of Au in molten solder and the interfacial reaction leads to the formation of intermetallics compounds [8] that are detrimental to joint reliability. Au dissolves and diffuses throughout the molten solder. Shin et al. reported that dissolution of Au wire in molten SnAg solder, forming pure AuSn₄ compounds with a diffusivity of \(4 \times 10^{-5} \text{cm}^2 \text{s}^{-1}\) at 230 °C for 10 s. Base on plot in Zribi [12,13], the dissolution rate of Au wire in molten eutectic solder is estimated to be 1.3 μm/s at 209 °C. Both studies showed that Au has a fast dissolution rate with molten Sn base solder. In solid diffusion, researchers found that solutes

* Corresponding author. Micron Semiconductor Asia Pte Ltd., 990 Bendemeer Road, Singapore, 339942, Singapore. Tel.: +65 62903357; fax: +65 62903184.
E-mail addresses: leetk@micron.com (T.K. Lee), msyzhang@ntu.edu.sg (S. Zhang), wongcc@ntu.edu.sg (C.C. Wong), drtan@micron.com (A.C. Tan), davin@pmail.ntu.edu.sg (D. Hadikusuma).

1 Tel.: +65 67904400; fax: +65 67911859.
2 Tel.: +65 67904595; fax: +65 67909081.
3 Tel.: +65 62903193; fax: +65 62903439.

0040-6090/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
in noble metals, such as Au, diffuse rapidly in Sn [14] with a parabolic growth rate. The high Sn content in SAC promotes excessive reaction and growth of IMC [15] than eutectic solder.

2. Experimental procedure

The gold studs with a tip diameter of 25 um were mechanically bumped on aluminium metallized dies using a thermosonic wire bonder. The Au-bumped die was then bond into a corresponding via containing SAC [6]. The height of 50 studs was measured using a high magnification 2D-microscope for analysis. The interaction of Au with molten SAC was investigated at temperatures of 230 °C, 260 °C and 290 °C for durations of 0.3 s, 1 s and 3 s. For the thermal aging growth study, the bond samples were heated at 125 °C, 150 °C, and 165 °C for durations of 100 h, 200 h, 300 h, and 500 h. All bonded samples were directly encapsulated in epoxy and sectioned using a diamond cut-off wheel for metallographic analysis. All microstructure characterizations were carried out in scanning electron microscope (SEM) with an energy dispersive X-ray detector (EDX). Each intermetallic layer was identified by EDX and its thickness measured at different locations across the interface using a digitized SEM micrograph. After bonding and aging, the remaining height of Au stud was measured using a high magnification scope and then subtracted from the average height of the stud as an estimate of the amount of Au consumed.

3. Result and discussion

3.1. Microstructures at different bonding conditions

At bonding temperature of 230 °C for 0.3 s (Fig. 1), intermetallic layer of AuSn2 and AuSn4 are formed at the interface with needle-like AuSn4 phases projected from the interface into the solder. Upon contact, the Au dissolved and diffused throughout the molten SAC while reacting with Sn to form a diffusion layer of AuSn2, AuSn4 or their combination. The formation of this diffusion layer retarded the dissolution rate of Au into molten SAC. During cooling, the saturated Au solution precipitated as AuSn4 phases, in accordance with the Au–Sn binary phase diagram. Thus, needle-like AuSn4 phases were seen throughout the SAC. No traces of Ag3Sn or Cu contained intermetallic were observed, similar to Kim et al.’s finding [11]. Similar microstructures were observed for 1 s and 3 s sample with thickening IMC layers and growth of needle-like AuSn4 precipitates due to more Au dissolved into molten SAC.

Fig. 2(a) shows the microstructures at 260 °C for 0.3 s. The Au tip was no longer apparent with layers of AuSn, AuSn2 and AuSn4 sequentially laying out from Au into SAC. At 0.3 s, the AuSn4 phase appeared to radiate from the bond interface into SAC. As the bonding time increased to 1 s (Fig. 2(b)), the AuSn and AuSn2 layers thickened with growing AuSn2 dendrites into the SAC. In bulk solder, AuSn4 precipitates were observed with few needle-like AuSn2 precipitates. As time increases to 3 s (Fig. 2(c)), chunks of AuSn2 were surrounded with AuSn4 phases in SAC.

The IMC layers formed were similar to the IMC layers for Au with SnAg [5]. This is a result of thermodynamic constraints. The AuSn4 phases throughout the SAC were likely due to the precipitation of the saturated solution as Au dissolved and diffused throughout SAC. As the bonding time increased, more Au dissolved and generated a thickening of AuSn and AuSn2 layers. Dendritic AuSn2 was seen to grow from the interface and eventually formed spherical chunks of AuSn2 in the middle of the bond interface. This was likely due to the shape of the Au stud which accelerated interaction at the tip. The spheroid structure minimized the adhesion and with its brittleness, self-weight and stresses, the chunks of AuSn2 phases spalled off from the interface into the bulk SAC during cooling. During solidification, non-equilibrium cooling existed.
and thus promoted segregation. This resulted in precipitation of high-melting AuSn₂ phases followed by low-melting AuSn₄ phases during cooling as seen in Figs. 2 and 3.

A similar phenomenon was observed for all bonding occurring at a temperature of 290 °C. Thickening AuSn and AuSn₂ layers with more chunks of AuSn₂ were observed in the SAC (Fig. 3). This was a result of higher diffusivity of Au into molten SAC with the increase in bonding temperature. A similar segregation phenomenon was also observed.

### 3.2. Kinetics of solid liquid interdiffusion

A generic power law in Eq. (1) was used to estimate the rate of IMC growth for Au with SAC. A regression power law curve was then fitted over the individual growth of Au–Sn intermetallic layers and the rate of Au thickness consumed over time. The aim was to estimate the time exponent of the interactions. In Eq. (1), \( x \) is the intermetallic thickness, \( k \) is the rate constant at temperature \( T \), \( t \) is the time of bonding and \( n \) is the time exponent. Fig. 4(a) shows the growth of individual Au–Sn layers and the consumption of Au at 230 °C. The Au consumption, layer thickness of AuSn₂ and AuSn₄ all increased with a positive time exponent varying from 0.68 to 0.71. Positive growths were also observed for AuSn and AuSn₂ intermetallic layers (Fig. 4(b)) at a bonding of 260 °C. A faster Au consumption was observed with no change of AuSn₄ thickness for the different bonding duration, suggesting precipitation of AuSn₄. Similar observations were also seen at a bonding temperature of 290 °C.

\[
x = k t^n.
\]

It is difficult to quantify the growth of the Au–Sn IMC layers in solid–liquid interdiffusion by examining the growth of an individual IMC layers. The individual IMC layers grew at different rates due to changes in atomic volume of diffusing species [8], different IMC layers formation [8], different layers formed by precipitation etc. Lumping all of the Au–Sn intermetallics into as a single IMC layer (Fig. 5) did not appear to be a good representation of IMC growth for solid–liquid interdiffusion. For example, the total IMC layer formed at 260 °C appeared to be slower than the layer formed at 230 °C as time increased. This was associated with the formation of additional AuSn (26.8 cm³/mol [16]) layer which was denser than AuSn₂ (42.8 cm³/mol) and AuSn₄ layer (75.0 cm³/mol) [5]. In addition, the quantifying of intermetallic growth did not account for the amount of Au dissolving in molten SAC. As the solid–liquid interdiffusion is 4 orders of magnitude faster than solid diffusion [19], the rate of Au consumed dominates the interaction and thus, appears to be a better representative variable in estimating the IMC growth.

The \( n \) and \( k \) of the Au consumption for temperatures 230 °C, 260 °C and 290 °C are computed and summarized in Table 1. It is noted that the time exponent varied from 0.41 to 0.68,
ranging around a time exponent of 0.5. A good correlation factor of at least 0.97 was observed in Fig. 6 for different bonding temperatures, suggesting that the rate of Au consumed in SAC follows a parabolic behavior with time. This has similar expression as Eq. (2), which represents the intermetallic layer growth in solid diffusion [17,18]. The rate constant \( k \) in Eq. (3) accounts for the rate of Au reacting and dissolving into SAC and the IMC growth. As Au consumption dominates the interaction, \( k \) represents the net effect of reaction and dissolution of Au with molten SAC. Assuming the reaction is rate-limited by diffusion process, constant \( k \) takes the form of diffusion coefficient (i.e., Arrhenius relationship) as shown in Eq. (3):

\[
x = \sqrt{D t}
\]

\[
k = k_0 \exp \left( -\frac{Q}{RT} \right)
\]

where \( Q \) is the apparent activation energy and \( k_0 \) as a rate constant.

By applying the natural logarithm in Eq. (3), a regression line can be plotted to estimate \( k_0 \) and \( Q \). The rate constant \( k_0 \) and activation energy \( Q \) for Au consumed in molten SAC were thus estimated to be 15.4 cm s\(^{-0.5}\) and 42.65 kJ/mol, respectively. The dissolution rate of Au with SAC was estimated to dissolve 4.38 \( \mu \)m for the initial 1 s at 217 \( ^\circ \)C and then decelerated with the formation of the intermetallic layer by reaction. This has a higher dissolution rate of Au in SAC than in eutectic solder [12,13]. This is likely due to higher dissolution and reaction rate as a result of richer Sn in SAC.

### 3.3. Kinetics at thermal aging

The microstructure under thermal aging appeared to be similar to the microstructures in solid–liquid interdiffusion except it developed thickening intermetallic layers. As a result of the complex growth of IMC layers in solid–liquid diffusion, the growth of individual intermetallic layers was different (Fig. 7). With similar treatment as solid–liquid diffusion, the rate of Au consumption was used to estimate the growth of IMC layers at aging. Fig. 8 shows the rate at which Au is consumed at 125 \( ^\circ \)C, 150 \( ^\circ \)C and 165 \( ^\circ \)C. The kinetics of Au consumed by SAC for thermal aging was computed to have a rate constant of 9.71 \( \times \) 10\(^{-1}\) cm s\(^{-0.5}\) with an activation energy of 23.25 kJ mol\(^{-1}\). The rate at which Au was consumed in solid diffusion was at least two orders of magnitude slower than the Au consumption rate in solid–liquid interdiffusion near the melting point of SAC (217 \( ^\circ \)C). Similar results have been reported by Tu et al. [19] for Au with near-eutectic PbSn. This suggests a change in its kinetics and mechanism as it moves from a solid–liquid interdiffusion to a solid diffusion during aging.
4. Conclusion

Study of the interface reaction between Au and SnAgCu lead free solder reveal that

1. At 230 °C, the AuSn$_2$ forms at the interface while AuSn$_4$ forms at both the interface and precipitates in the bulk of SnAgCu. At 260 °C and 290 °C, AuSn phase appears at the interface with AuSn$_2$ phase spalling off from the interface into solder. During non-equilibrium cooling, segregation of AuSn$_2$ and AuSn$_4$ occurs.

2. The Au consumption is successfully used to estimate the rate of IMC formation. It is found that the Au consumption has similar relationship as Arrhenius relationship with regard to activation energy and temperature, and follows a parabolic relationship with time.

3. The activation energy and diffusion constant of Au diffusion in molten SAC at least two orders of magnitude faster than solid–solid interaction.

References