Solid-state growth kinetics of Ni$_3$Sn$_4$ at the Sn–3.5Ag solder/Ni interface

M. O. Alam and Y. C. Chan

Department of Electronic Engineering, City University of Hong Kong, Tat Chee Avenue, Kowloon Tong, Hong Kong

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Systematic experimental work was carried out to understand the growth kinetics of Ni$_3$Sn$_4$ at the Sn–3.5Ag solder/Ni interface. Sn–3.5%Ag solder was reflowed over Ni metallization at 240 °C for 0.5 min and solid-state aging was carried out at 150–200 °C, for different times ranging from 0 to 400 h. Cross-sectional studies of interfaces have been conducted by scanning electron microscopy and energy dispersive x ray. The growth exponent $n$ for Ni$_3$Sn$_4$ was found to be about 0.5, which indicates that it grows by a diffusion-controlled process even at a very high temperature near to the melting point of the SnAg solder. The activation energy for the growth of Ni$_3$Sn$_4$ was determined to be 16 kJ/mol. © 2005 American Institute of Physics. [DOI: 10.1063/1.2149487]

I. INTRODUCTION

Solders made of tin (Sn) and lead (Pb) have been used for nearly 5000 years.1 In the immense electronic material world, solder plays a crucial role in the assembly and interconnection of the silicon chip. As a joining material, solder provides electrical, thermal, and mechanical continuities in electronic assemblies. The performance and quality of the solder are crucial to the integrity of a solder joint, which in turn is vital to the overall functioning of the assembly.

Because of the strong drive towards the miniaturization of electronic products, the volume of solder joints is decreasing and the solderable pad metallization is becoming thinner. During the soldering process, along with the dissolution of the pad metallization, the formation of intermetallic compounds (IMCs) between the Sn-containing solder and the substrate is inevitable.2–5 The initial formation of these IMCs at the interface during soldering ensures a good metallurgical bond. However, during the service life the IMC layer usually grows thicker, which might affect the subsequent reliability of mechanical joints, especially for these tiny solder joints.

Although some Pb-free solders have been in use for many years, there is currently no obvious “drop-in” replacement for Sn–Pb alloys, which are still the most commonly used solders in the microelectronics industry. However, among many types of Pb-free solder proposed to date, Sn–3.5Ag is one of the base binary Pb-free alloys while considering to replace the eutectic Sn–Pb solder in modern electronic packaging applications.3–7

Copper is an excellent surface for soldering but it oxidizes easily in air, and copper oxides resist wetting with solder. To prevent nonwettable copper oxides at the solder pad, either gold or organic surface protector (OSP) is now used to cover the copper. Unfortunately, Au and Cu diffuse into each other very rapidly.8 Any exposed Cu quickly forms unsolderable copper oxides on the solder pad surface. Again, during a reflow soldering process, the dissolution rate of Cu into the Sn-based solder is very high.4 The solution to these problems is the use of a “barrier layer” of Ni. Ni prevents Au and Cu from interdiffusing and provides a durable, wettable, and conductive surface for component assembly.9,10 Also compared to Cu, the rate of dissolution of Ni in the Sn-based solder is much lower at the soldering or reflow temperature because its diffusivity and solubility are very low in the solder.11–17 Even during solid-state aging the rate of IMC formation at the solder/Ni interface is slower than that of the solder/Cu interface.2,11,14

Because of the lower melting temperature of the solder alloys, most of the previous works on the solid-state aging of solder joints were conducted up to 150 °C. On the other hand, most of the interfacial reaction studies so far reported between Sn–Ag solder and Ni metallization were conducted above the melting temperature of the solder to simulate reflow soldering phenomena.3–5,12,13,15–18 However, in this study we were interested in investigating solid-state reactions at very high homologous temperatures (such as 0.95$T_m$) to establish the growth kinetics of the interfacial products at the Sn–3.5Ag solder interface with the Ni metallization.

II. EXPERIMENTAL PROCEDURES

The area-array solder mask-defined copper bond pads on the flexible substrate of the ball grid array (BGA) package were used as the base for electrodeposition of Ni and Au. The average thicknesses of Ni and Au were 4 and 0.5 μm, respectively. Commercially available BGA solder balls of eutectic Sn–3.5%Ag (mp=221 °C) were used for this study. The solder mask-opening diameter was 600 μm and the diameter of the BGA solder ball before melting was 760 μm. After having been dipped into the flux, solder balls were placed on the Au/Ni/Cu bond pads and reflowed in a N$_2$ atmosphere reflow oven. A schematic diagram of the soldering process on a BGA substrate is shown in Ref. 4. The peak reflow temperature was 240 °C and the time over the melting point of the solders was about 0.5 min. Immediately after the reflow, the substrates were subjected to high-temperature aging at 150, 175, and 200 °C for time up to 400 h. After aging the samples were sectioned carefully using a slow speed diamond saw and mounted in epoxy. The cross-

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|}
\hline
Temperature & Time & Description \\
\hline
150 °C & 0.5 min & Solid-state aging \n175 °C & 0.5–400 h & Solid-state aging \n200 °C & 0.5–400 h & Solid-state aging \\
\hline
\end{tabular}
\caption{Experimental conditions for solid-state aging.}
\end{table}

Systematic experimental work was carried out to understand the growth kinetics of Ni$_3$Sn$_4$ at the Sn–3.5Ag solder/Ni interface. Sn–3.5%Ag solder was reflowed over Ni metallization at 240 °C for 0.5 min and solid-state aging was carried out at 150–200 °C, for different times ranging from 0 to 400 h. Cross-sectional studies of interfaces have been conducted by scanning electron microscopy and energy dispersive x ray. The growth exponent $n$ for Ni$_3$Sn$_4$ was found to be about 0.5, which indicates that...
sectioned samples were ground and polished with a deal of great care for studying interfacial microstructure. To reveal the fine details of the interface, mild etching was carried out by dilute HCl solution (2 vol % in water) for 10 s. The prepared samples were investigated with a Philips XL 40 field-emission gun (FEG) scanning electron microscope (SEM) equipped for energy dispersive x-ray (EDX) analysis. The backscattered electron (BSE) mode of SEM was used to examine the morphology of cross-sectioned samples and to measure IMC thickness. Average thickness of IMC layer was determined by measuring the layer thickness at 20 equally spaced points for each solder joint. At least five solder joints were used for final average value.

III. RESULTS AND DISCUSSION

The microstructure of the as-reflowed interface of Sn–3.5%Ag solder on the Au/Ni/Cu bond pads is shown in Fig. 1. From the EDX results along with previous experiences of this research group,\textsuperscript{3,5,9,19} as well as the existing literature survey,\textsuperscript{11–16} the IMC formed is confirmed to be Ni\textsubscript{3}Sn\textsubscript{4}. During reflow, Sn in the solder reacts very quickly with Au layer—dissolving all the Au from the bond pad to the solder. Then, grains of Ni\textsubscript{3}Sn\textsubscript{4} nucleate at the solder-electrolytic Ni interface. However, these Ni\textsubscript{3}Sn\textsubscript{4} grains grow rapidly at the liquid solder/Ni interface until a continuous layer is formed. The scallop morphology of the interface in Fig. 1 indicates that grains grew in a repining process with a rough surface of IMC towards the liquid solder.\textsuperscript{12} The average thickness of the IMC layer just after reflow (i.e., before solid-state aging) was 0.6 μm.

Microstructures of the solder interface after aging at each temperature for different times were carefully investigated. Figure 2 shows the most representative BSE-SEM micrographs of the solder interfaces after aging at 150, 175, and 200 °C for 200 h. It is clear from the microstructures that the thickness of the IMC layer is increasing with increasing temperature. It is also interesting to see the decrease of roughness at the IMC/solder interface after aging. This is an obvious phenomenon, as surface energy of the IMC grains to the solid solder is higher than that of the IMC grains to the liquid solder.\textsuperscript{18,19}

EDX analysis here again confirmed that only one IMC layer of Ni–Sn, i.e., Ni\textsubscript{3}Sn\textsubscript{4}, was formed at the solder inter-

face. There was no Au-containing IMC layer noticed at the Sn–3.5Ag solder interface, although a Au-containing IMC such as (Au,Ni)Sn\textsubscript{4} was reported to be formed as a continuous layer at the Sn–Pb solder interface during solid-state aging.\textsuperscript{3,19}

With time, the thickness of the IMC layer was also increased. The average thickness of the IMC was determined as described in the Experimental section. Figure 3 shows plots of the IMC thickness against the aging time at the different temperatures. The curves seem to be parabolic over the temperature range studied. However, from the trend of the curves at three different temperatures, it is clear that at higher temperature, the IMC growth rate is higher.

To study growth kinetics of any reaction layer with time at a particular temperature, it is appropriate to use the following empirical power-law relationship:

\[ x - x_0 = kt^n, \]

where \(x\) is the total thickness of the reaction layer at time \(t\), \(x_0\) is the initial thickness (i.e., at the aging time of \(t = 0\)), \(k\) is the growth rate constant, and \(n\) is the time exponent. The values of \(k\) and \(n\) for a particular temperature can be obtained
by means of multivariable linear regression analysis. From the value obtained for \( n \), it is possible to deduce the types of solid-state growth kinetics at a solder interface and can realize associated growth mechanisms.\(^{20}\)

A linear regression analysis of total IMC thickness as a function of aging time was conducted to determine the best-fit \( n \) values for all aging temperatures. For a better representation, Eq. (1) is rewritten into the following logarithmic expression:

\[
\log(x - x_0) = \log k + n \log t,
\]

where the time exponent \( n \) actually equals the slope of \( \log(x - x_0) \) vs \( \log t \) for each temperature. Figure 4 shows the log plot of Fig. 3, however, after adopting the values of \( n \) and \( k \) that were determined from the linear regression analysis by using Eq. (1). Three lines obtained from three aging temperatures are nearly parallel to each other which reveal that similar mechanism of \( \text{Ni}_3\text{Sn}_4 \) IMC growth is operative between 150 and 200 °C. The \( n \) values always remain near 0.5.

From the \( n \) values of the growth kinetics of \( \text{Ni}_3\text{Sn}_4 \) studied here, it is believed that it obeys a parabolic growth law. This was also confirmed by others at temperatures up to 175 °C.\(^{21,22}\) Because of the high homologous temperature of the solder alloy, not much work has been done elsewhere beyond 175 °C in understanding the mechanism of the IMC growth.

In this study to understand the growth kinetics of \( \text{Ni}_3\text{Sn}_4 \) at the Sn–3.5%Ag solder interface, along with aging at 150 and 175 °C, a much higher temperature (200 °C) was studied, which was near to the melting temperature (221 °C) of this alloy. Even at this higher temperature, the growth rate of \( \text{Ni}_3\text{Sn}_4 \) was found to follow parabolic kinetics, which confirms that the formation of \( \text{Ni}_3\text{Sn}_4 \) is a diffusion-controlled process at all temperatures up to the melting point of the solder alloy. The thicker the IMC layer, the longer the time needed for either Sn or Ni to diffuse through the IMC layer—thus the diffusion rate becomes slower and results in a slower rate of IMC growth. As the same mechanism is operative for all the temperatures during solid-state reactions, it is easy to calculate the activation energy for the growth of \( \text{Ni}_3\text{Sn}_4 \) from the following Arrhenius relationship of the growth rate constant \( (k) \):

\[
k = k_0 e^{-Q/RT},
\]

where \( Q \) denotes the activation energy for the growth process, \( R \) is the gas constant (8.314 J mol\(^{-1}\) K\(^{-1}\)), \( T \) is the aging temperature (K), and \( k_0 \) is the preexponential coefficient. The activation energy was calculated from the slope of the Arrhenius plot using a linear regression model.

Figure 5 shows the Arrhenius plot of \( \ln k' \) vs \( 1/T \) for the solid-state growth kinetics of \( \text{Ni}_3\text{Sn}_4 \) IMC.

IV. CONCLUSIONS

Interfacial reactions between the eutectic Sn–3.5%Ag solder and the Ni metallization result in the growth of only \( \text{Ni}_3\text{Sn}_4 \) both in the liquid-state and solid-state reactions. It was found that \( \text{Ni}_3\text{Sn}_4 \) grows parabolically even during high-temperature aging. The value of the solid-state growth exponent of \( \text{Ni}_3\text{Sn}_4 \) at the Sn–3.5%Ag solder interface has been found to be about 0.5. It proves that \( \text{Ni}_3\text{Sn}_4 \) grows through a
bulk diffusion-controlled growth mechanism even at a very high temperature near to the melting point of the SnAg solder. The activation energy for the growth of Ni₃Sn₄ was found to be 16 kJ/mol.

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