Dissolution kinetics of BGA Sn–Pb and Sn–Ag solders with Cu substrates during reflow

Ahmed Sharif, Y.C. Chan*

Department of Electronic Engineering, City University of Hong Kong, 83 Tat Chee Avenue, Kowloon Tong, Hong Kong

Received 23 April 2003; accepted 2 September 2003

Abstract

An investigation has been carried out to compare the dissolution kinetics of the Cu pad of the ball grid array (BGA) substrate into the molten conventional Sn–Pb solder and Sn–3.5Ag solder. A fixed volume of the BGA solder ball (760 μm diameter) was used on the 15–18 μm thick Cu pad having a circular area with a diameter of 650 μm. The dissolution measurement was carried out by measuring the change of Cu pad thickness as a function of time and temperature. A scanning electron microscope (SEM) was used to observe the microstructure of the solder joint and to measure the consumed thickness of Cu. A fast dissolution of the substrate occurred in the beginning for the molten solder/solid Cu reaction couple. But the dissolution in Sn–Ag was much more higher than that in Sn–Pb solder. The rates of Cu dissolution were measured for different soldering temperatures ranging from 225 to 240 °C and activation energies of 54 and 116 kJ/mol were found for the dissolution reaction in Sn–Ag and Sn–Pb solder, respectively.

© 2003 Published by Elsevier B.V.

Keywords: Sn–3.5Ag solder; Cu substrate; Dissolution; Cu₆Sn₅ phase; Activation energy

1. Introduction

Lead–tin solders still play an important role in electronic packaging, such as flip-chip, solder-ball connections in ball grid array (BGA), and integrated circuit assembly to a printed circuit board [1]. The ban of lead in electronic products will occur in most industrialized countries before the end of this decade. Latest reports from the legislation parliament of the European Community indicate that, for the EU members, lead has to be replaced by July 2006 [2]. Hence, how to cut down the use of Pb in soldering and how to develop Pb-free solders are urgent materials issues in advanced microelectronics technology. Although some Pb-free solders have been in use for years, there are no obvious replacements for the Sn–Pb alloys that are most common in microelectronics industry. Also many of the fundamental phenomena that determine solder behavior are yet to be understood. The successful introduction of lead-free solder joints in the electronic industry must be based on the past experience in the use of Sn–Pb solders. Because of the lack of the information regarding reliability in practice, reliability tests are needed before lead-free solder can replace traditional tin–lead solder.

As a consequence of the announced lead ban, lead-free solders are subject to numerous investigations worldwide. All alternatives to the standard eutectic tin–lead solder investigated so far are based on tin alloys with a tin content significantly over 90 wt.% in combination with copper, silver, antimony, bismuth, or zinc. A key issue affecting the integrity and reliability of solder joints for such Sn-based alloys is the fast interfacial reactions between the molten solder and the under bump metallization (UBM). Among the binary alloys, Sn0.5–0.8%Cu and Sn3–4%Ag play a dominant role. The Sn/Ag solders exhibit melting points in the range of 220–221 °C, which is more than 30 °C beyond the melting point of the standard eutectic tin–lead solder. A previous study [3] demonstrated a fair wettability of the solder to Cu substrates.

It is well known that soldering involves a reaction between molten solder and substrate, which forms some sort of intermetallic layer and which dissolves some of the substrate [4]. The interfacial chemical reactions enhance the
wettability between the solder and the substrate. Intermetallic growth kinetics for solid–liquid couples is significantly faster compared to growth kinetics for solid–solid couples. Many investigators have studied the intermetallic formation at liquid solder/solid substrates interfaces [5–13]. Very little information is available for the substrate dissolution behavior [12,14,15].

Copper is widely used in the under bump metallurgy and substrate metallization for flip-chip and BGA application. At the liquid solder/Cu substrate interface, the formation and growth of intermetallic compounds occur by the dissolution of Cu into the molten solder. The previous studies have shown that the amount of dissolved Cu influences the solution of Cu into the molten solder. Very little is known about the dissolution kinetics of Cu into molten solder joints on a Si chip; the typical thickness of Cu is about 1 μm. Since the amount of Cu is limited and some of the Cu must remain intact through all the reflows and subsequent reworks to avoid dewetting of the solder, the understanding of the consumption rate of Cu is very important. This was a strong motivation for us, to have a closer look at the consumption rate of Cu in the soldering reaction with Sn–Pb and Sn–Ag solders.

2. Experimental

Flexible substrates with 15–18 μm thick 99.9 wt.% Cu pad with a diameter of 650 μm, surrounded by solder mask were used to attach the solder ball. All substrates were cleaned in a dilute solution of hydrochloric acid and then rinsed in water prior to soldering to remove surface oxidation. The commercial name of the flux used in this work was CLEANLINETM LR721H2 BGW no-clean flux. Eutectic 63Pb–37Sn solder balls with a diameter of 0.76 mm were placed on the prefluxed Cu substrate as shown in Fig. 1 and then soldered at four different temperatures: 225, 230, 235, and 240 °C for times (t) of 1, 2, 5, and 10 min in a convection reflow oven (BTU VIP-70N).

After reflowing the samples were mounted in epoxy molding compound. For interfacial microstructure examination, the samples were ground and polished very carefully. The chemical and microstructural analysis of the gold-coated samples were obtained by using a Philips XL 40 FEG scanning electron microscope (SEM) equipped with an energy dispersive X-ray (EDX) spectrometer.

3. Results and discussion

Fig. 2 represents the backscattered electron micrographs for the interfaces of Sn–Pb and Sn–Ag solder balls on Cu substrate after reflow at 240 °C for various times. By measuring the remaining Cu thickness and by subtracting it from the initial thickness, the consumed Cu thickness is deduced. In the flexible substrate, there is a portion of Cu pad under the solder mask that remained unaffected after the reflow. From this unreacted part, the initial thickness of the Cu pad is measured. Only the Cu6 Sn5 intermetallics were observed in the interfaces using the SEM and no Cu3Sn was observed. According to EDX analysis also no Ag or Pb was detected in the interfacial layer, so Ag and Pb were not directly involved in the interfacial reactions. The dissolution thickness increases with time. In this figure, the consumed thickness difference would be more pronounced for the two solders for various time fractions if there was no variation in the initial thickness of Cu pad of the substrate. However, from this figure it is apparent that the dissolution is much higher in the case of Sn–Ag solder. Since there are channels between the IMCs, the dissolution of Cu into the liquid solder occurs simultaneously with the ripening of IMCs. These channels remain more or less open for the dissolution in Sn–Ag solder. But in the case of Sn-Pb alloy, these channels between the IMCs are closed after a certain period. The dissolution rate in Sn–Pb solder reaches a steady state after a certain time. In the early period, diffusion of Cu for the dissolution reaction in the Sn–Pb alloy occurs by volume diffusion, but in the later stage is mainly by grain boundary diffusion. For the Sn–Ag solder, the dissolution rate is very high even at 10 min and the ripening action of the IMCs reduces the channels for volume diffusion of Cu, so that the dissolution rate decreases gradually.

At the solder interface, Cu6Sn5 grows as scallop-like grains and results in a rough interfacial morphology between the IMCs and the solder [12]. By examining the growth of scallops during constant temperature reflowing, it has been found that they increase in size but decrease in number. According to Kim and Tu [12], the flux of the ripening is much larger than that of the interfacial reaction by almost a factor of 10 in the liquid–solid reaction because of the larger solubility and diffusivity in the liquid state. From Fig. 2 it is also observed that the ripening action for Sn–Ag solder is much more pronounced. The size of each scallop grain after reflow at 240 °C for 10 min for Sn–Ag solder is much larger than that of Sn–Pb sol-
So it may be concluded that the interfacial energy per unit area between Cu₆Sn₅ and molten Sn-Ag solder is higher than that between Cu₆Sn₅ and molten Sn-Pb solder. For this reason, Cu₆Sn₅ that forms in the interface between the liquid Sn-Ag solder and Cu substrate, coalesces more quickly to possess less free energy thermodynamically.

The dissolution of Cu during reflow at the four different temperatures is plotted in Fig. 3. For the Sn-Ag alloy, dissolution curves are much steeper in the early stage of reflow. So the consumption rate is relatively high during initial reflow and becomes lower with time. Other researchers [11,16] also observed that a fast dissolution of the substrate occurred in the beginning for the molten Sn/solid Cu

reaction couple. From this graph, it is also evident that the initial consumption rate is higher for the highest temperature. At high temperature, the diffusion rate is much higher so that Cu atoms can move faster into the liquid solder. A large flux flowed into the unsaturated liquid phase in the beginning of the reaction, and the dissolution effect reduced when a less unsaturated liquid phase is used. The consumption occurs by dissolution through the channels between the scallop grains. With time these channel areas reduces and the dissolution of Cu also reduces.

Here for Sn–Pb solder, the dissolution rate is also high at the initial stage but not as high as for Sn–Ag solder alloy. The melting temperatures of Sn–Pb and Sn–Ag solder are around 183 and 221 °C, respectively. So the working temperatures for Sn–Pb solders are more than 40 °C than its melting point. However, the dissolution rate of Sn–Pb solder alloy is much smaller in each condition than that of Sn–Ag solder. In the later stage of reflow, the channels between the IMC grains become closed. So the consumption rate becomes much slower.

Even after 10 min of reflow at 240 °C for Sn–3.5Ag solder, there is still some Cu substrate that remains unreacted when the substrate thickness is more than 17 μm (Fig. 2a (iv)). But if the thickness of the substrate is less than 17 μm, after 10 min of reflow, the substrate is fully consumed from the interface and the IMCs appear in the bulk of the solder (Fig. 4). Both solder balls, with a volume of 2.29 × 10³ μm³, can consume much Cu from the substrate. From the Cu–Pb binary diagram, it can be seen that the solubility of Cu in Pb is extremely low. The eutectic point in the Cu–Pb system is at 0.06 wt.% Cu. The solid solubility (at T < 327 °C) of Cu in Pb is less than 0.007 wt.%. However, the solubility of Cu in liquid Pb is a fraction greater than 0.06 wt.%, though not appreciably. Also from the Cu–Sn binary diagram, it can be seen that the concentration of Cu in Cu–Sn eutectic at 227 °C is 0.7 wt.% and the solid solubility of Cu in Sn is practically close to zero. So the Cu pick up by Sn–Pb and Sn–Ag can therefore be attributed to the Sn content in the solders. At 240 °C the maximum solubility of Cu in Sn is around 1.1 wt.%. For Sn–Ag solder after reflowing at 240 °C for 10 min, about 15 μm of Cu substrate is consumed by the solder and it is observed that the solder dissolves around 2.7 wt.% of Cu. So it is interesting how the Sn–Ag solder dissolves more than 1.1 wt.% of Cu at 240 °C. Intermetallic compound formation by Cu/Sn reaction is not fast enough to consume all the Cu atoms that have entered the liquid solder. The unreacted portion will diffuse out to enter the bulk of the molten solder. When the percentage of Cu reaches the threshold limit of Cu₆Sn₅ compound formation, Cu–Sn IMC also nucleates in the bulk solder. As a result the Cu content in liquid solder also decreases, and for that the liquid solder can dissolve more Cu from the substrate. By this process, Sn–Ag solder can absorb such a large amount of Cu in the liquid state. During solidification, as the solubility of Cu in the bulk solder decreases, Cu and Sn react to form Cu₆Sn₅ IMC that will deposit on the existing IMCs in the bulk solder.

![Fig. 4. SEM micrograph showing no Cu at the interface in the Sn–Ag solder after soldering for 10 min at 240 °C.](image)
Fig. 5 shows such kind of IMC in the bulk of the Sn–Ag solder. Sn–Pb solder also exhibits IMCs in the bulk (Fig. 6), but the amount is not as much as in the case of Sn–Ag solder.

A thermally activated parabolic model was used to calculate the dissolution rate constants at each temperature using $x = (kt)^{1/2}$, where $x$ is the dissoluted thickness (µm), $k$ is the dissolution rate constant (µm²/min), and $t$ is the reflow time (min). A simple Arrhenius relationship was used to determine the activation energy for the dissolution of the Cu substrate:

$$k = A e^{-E/RT}$$  
(1)

or, logarithmically

$$\ln k = \ln A - \frac{E}{R} \left(\frac{1}{T}\right).$$  
(2)

where $k$ is the rate constant, $A$ is the pre-exponential factor, $E$ is the activation energy, $R$ is the universal gas constant, and $T$ is the temperature in Kelvin (K).

Fig. 6. SEM micrograph illustrating Cu–Sn IMCS in the Sn–Ag bulk solder after soldering for 2 min at 240°C.

A plot of the square of the consumed thickness versus time is shown in Fig. 7. The slope of these lines gives the rate constant, $k$. An Arrhenius plot of the natural logarithm of $k$ versus $1/T$, shown in Fig. 8, gives the activation energy for diffusion. From this plot, $E$ was found to be 116 and 54 kJ/mol for Sn–Pb and Sn–Ag, respectively for the above condition. The dissolution of Cu in Sn–Pb solder is much less than Sn–Ag solder. For that reason, activation energy for Cu dissolution into Sn–Pb solder is higher than that of Sn–Ag solder. As mentioned previously, published liquid state diffusion data are very limited. Activation energy for the diffusion of Cu in liquid Sn is 17.56 kJ/mol [17], which is very low compared to the both 116 and 54 kJ/mol. The higher activation energy observed in this work may be due to the lower tendency to absorb Cu as compared to that of pure tin.

Fig. 7. Plot of $x^2$ vs. $t$ for the consumption of Cu substrate with (a) Sn–Ag solder and (b) Sn–Pb solder.
4. Conclusions

The effects of reflow at four different temperatures (225, 230, 235, and 240°C) on the dissolution of Cu substrate in Sn–Ag and Sn–Pb BGA solder ball are presented in this paper. A very fast dissolution of the substrate is observed in the early stages of the molten solder/solid Cu reaction for both the solder alloys. The dissolution in Sn–Ag is much higher than that in Sn–Pb solder. The consumption occurs by dissolution through the channels between the scallop grains. For Sn–Ag solders, these channels remain open more or less, but for Sn–Pb solder, they become closed in the later stage of the dissolution. Many Cu–Sn IMCs are observed in the bulk of the Sn–Ag solder. Sn–Pb solder also exhibits IMCs in the bulk, but the amount is not as much as in the case of Sn–Ag solder. The apparent activation energy calculated for the dissolution of Cu in the Sn–Pb and Sn–Ag solder alloy are found to be 116 and 54 kJ/mol, respectively.

Acknowledgements

The authors would like to acknowledge the financial support provided by CERG project no. CityU 1187/01E (City U Project no. 9040621) of the Research Grant Council of Hong Kong and the research studentship of City University of Hong Kong. The technical support from Mr. M.O. Alam is gratefully acknowledged.

References