Short communication

Asymmetrical growth of Cu₆Sn₅ intermetallic compounds due to rapid thermomigration of Cu in molten SnAg solder joints

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Abstract

We observed asymmetrical growth of Cu₆Sn₅ intermetallic compounds (IMCs) on the two interfaces of Cu/SnAg/Cu solder joints during reflow at 260°C on a hot plate. The IMCs grew to 12.3 μm on the cold end and 3.5 μm on the hot end after reflow for 40 min. However, the consumption of Cu on the cold end is less than that on the hot end. We propose that rapid thermomigration of Cu is responsible for the asymmetrical growth of the IMCs. With the simulated thermal gradient of 51°C/14°C/cm across the liquid solder, the heat of transport of Cu is calculated as 20 kJ/mol.

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1. Introduction

As the microelectronic industry approaching the end of Moore’s law of Very-Large-Scale Integration (VLSI) in silicon chip technology, three dimensional integration circuit (3D IC) emerges to be a promising solution to scaling limit in VLSI circuits [1,2]. In 3DIC, a Si chip is stacked on another Si chip, and through-silicon-vias (TSV) of Cu and microbumps of solder are employed to provide interconnection between the chips. The thickness or height of the solder layer ranges from few microns to 20 microns. Interfacial reaction between TSV of Cu and solder takes place in both the upper and lower chips. Because of the low microbump height, the cross interaction across the two ends of a microbump becomes very serious.

On thermomigration, many studies reported that it occurs during accelerated electromigration tests in flip chip solder joints and it may cause damage in the neighboring joints which carried no current [2–10]. Huang et al. calculated that a thermal gradient of 1000 °C/cm is needed to observe thermomigration of Sn and Pb atoms during electromigration tests [4]. For thermomigration of Cu atoms, Chen et al. reported a thermal gradient over 400 °C/cm is required [10]. The above thermomigration takes place in a solid state. In liquid state reactions, diffusion rate is much faster than that in solid state, then the thermal gradient needed may be much lower. Whether Cu thermomigration occurs in liquid-state reaction during reflow is of interest, however, up to now no studies report it. In addition, asymmetrical growth of Cu–Ni–Sn intermetallic compound (IMC) has been reported in Cu/solder/Ni structures during reflow [11–13]. However, no asymmetrical growth of Cu₆Sn₅ IMCs is reported on the two interfaces of Cu/SnAg/Cu solder joints during reflow.

Here, we investigated the Cu thermomigration in Cu/30 μm SnAg/Cu joints at 260 °C on a hot plate as well as in an oven. Asymmetrical reactions due to thermomigration of Cu atoms was observed in the samples reflowed on a hot plate after 5 min, but symmetrical reaction, without thermomigration of Cu, occurred in samples reflowed in the oven. Finite element simulation and theoretic calculation were performed to verify the experimental results.

2. Experimental

Sandwich structures of Cu/SnAg/Cu were fabricated. First, a 20 nm Ti and 200 nm Cu seed layer were sputtered on a Si wafer, followed by electroplating of an array of patterned Cu under-bump-metalization (UBM), 100 μm in diameter and 20 μm in thickness. Second, 19 μm thick Sn2.5Ag solder were electroplated on all the patterned Cu UBMs. The wafer was reflowed at 260 °C for 1 min to form solder cap on the Cu UBM. Then, the wafer was cut into 1 × 2 cm² pieces. To fabricate the test samples, a Si die was flipped...
over to align with another die and reflowed at 260 °C for 3 min. In order to investigate the Cu thermomigration in liquid state, the flip-chip samples underwent additional reflow of 5, 10, 20, 40 min on a hot plate or in an oven maintained at 260 °C. Then the samples were cooled in air and the cooling rate was about 5 °C/cm.

After the reflow, the samples were cross-sectioned and polished for interfacial microstructure examination by scanning electron microscopy (SEM). Finite element analysis was carried out to simulate the temperature gradient across the solder joints. The die size was 2308 μm × 2308 μm, which is the same size with the real sample. The thickness of the Si chip was 700 μm. For the boundary conditions, the temperature on the surface of the bottom die was set to be 260 °C. All the free surfaces of the samples contact with the air and the convention coefficient was set to be 15 w/m²k.

3. Results and discussion

Fig. 1(a) shows the cross-sectional SEM image for the as-fabricated sample. The bump height was approximately 30 μm. The sample in Fig. 1(a) experienced 3 min reflow on a hot plate, where the bottom die contacted the hot plate and the top die was exposed to the air. Therefore, the bottom die was the hot end and the top die was the cold end, as labeled in the figure. IMC of Cu₆Sn₅ was formed at both Cu/solder interfaces. The measured thickness for the interfacial IMCs was 2.3 μm and 2.9 μm on the hot end and cold end, respectively.

Fig. 1(b) presents the cross-sectional SEM image for the sample after additional 10 min reflow at 260 °C. The Cu₆Sn₅ IMC on the cold end is measured to be 5.2 μm, whereas it is only 3.5 μm on the hot end. As reflow time increased to 20 min, Fig. 1(c) shows that the IMCs on cold end continue to grow thicker, about 6.7 μm. Yet the IMCs on the hot end did not grow at all, remaining about 3.4 μm. When the reflow time increased to 40 min, Fig. 1(d) shows that the asymmetrical growth appears more significantly. The IMCs on the cold end was 12.3 μm, yet it is still 3.5 μm on the hot end.

However, the consumption of Cu UBM is in the opposite direction on the hot end and on the cold end. The Cu UBM was approximately 20 ± 1.0 μm in the sample before jointing. After the reflow at 260 °C for 40 min, as shown in Fig. 1(d), the Cu UBM decreased to 17.9 ± 0.2 μm on the cold end, but it reduced to 15.1 ± 0.1 μm on the hot end, indicating that the consumption of Cu UBM was faster on the hot end. We recall that the IMC on the hot end grew much slower than that on the cold end.

As a controlled experiment for comparison, samples were reflowed in an oven of uniform temperature for various periods. No obvious difference in IMC thickness on both ends was found. Fig. 2 shows the cross-sectional SEM image for the flip-chip sample reflowed at 260 °C for 40 min. The IMC thickness on bottom and top interface was measured to be 5.7 ± 0.2 μm and 6.3 ± 0.3 μm, respectively. There was no obvious difference in IMC thickness for all the reflow conditions in oven.

Fig. 3 summarizes the thickness of Cu₆Sn₅ IMC as a function of reflow time on the hot end and cold end. In addition, the average IMC thickness for the sample reflowed in the oven was also plotted in the figure. The results indicate that the IMC on the cold end grows the fastest and the IMC on the hot end grows slower than that in the oven.

Since no electrical current was in the tests and since in molten state, stress may not be significant, only thermal gradient may be responsible for the asymmetric IMC growth. A thermal gradient can exist in the sample during reflow on a hot plate, because heat was dissipated through the free surface of the top die. However, it is hard to measure the thermal gradient in the solder joint because the temperature difference may be very small across the molten solder. To find out the thermal gradient across the solder joint, instead, we used finite element analysis to simulate the thermal gradient by using a commercial software analysis. Fig. 4 shows the temperature distribution in the molten solder when convection coefficient was set to 15 W/m²K. The temperature difference was 0.15 °C across the solder layer, resulting in a thermal gradient of 51 °C/cm in the molten solder.
To verify if the simulation results are reasonable, calculation was performed on the basis of the equation below [14].

$$J = \frac{CDQ^*}{kT} \left( \frac{\partial T}{\partial x} \right)$$  \hspace{1cm} (1)

where $J$ is the thermomigration flux, $C$ is concentration, $D$ is diffusivity, $Q^*$ is heat of transport, $k$ is Boltzman constant, $T$ is temperature, and $\partial T/\partial x$ is thermal gradient. The solubility of Cu in liquid SnAg solder is 1.54 wt % at 260 °C [15]. The diffusivity of Cu in molten SnAg solder is taken to be $3.2 \times 10^{-5}$ cm$^2$/s [16]. In our study, we can obtain thermomigration flux from the Cu consumption data in Fig. 1. The thermomigration flux in units of atoms/cm$^2$–sec can be expressed as

$$J = \frac{\text{atoms}}{At} = A \rho \Delta x N_A \frac{\partial T}{\partial x}$$  \hspace{1cm} (2)

where $A$ is cross-sectional area of the solder joint, $t$ is reflow time, $\Delta x$ is the Cu consumption thickness due to thermomigration, $\rho$ is Cu density (7.3 g/cm$^3$), $N_A$ is Avogadro number, $M$ is molecular weight of Cu (63.5 g/mol). In Fig. 1(d), the calculated Cu thermomigration flux is $1.49 \times 10^{16}$ atom/cm$^2$. Therefore

$$Q^* \times \left( \frac{\partial T}{\partial x} \right) = 1 \times 10^3 \text{(kJ·k/mol·cm)}$$  \hspace{1cm} (3)

With the simulated thermal gradient of 51 °C/cm, we obtain the value of $Q^*$ as 20 kJ/mol. This value seems to be reasonable.

Meechan and Lehman studied Cu thermomigration using a pure Cu disc maintaining one end at 1249 °C and the other end at 530 °C. The temperature gradient was 1194 °C/cm. The measured heat of transport is $5 \pm 3.5$ kcal/mol [17]. Furthermore, Stracke and Herzig investigated Cu thermomigration in Pb at the temperature range of 181 °C–303 °C [18]. They reported that Cu migrated to the cold end and obtained the heat of transport to be 5.1 kcal/mol. In the present study, Cu migrates in molten solder and Cu with a very high diffusivity [19]. Therefore we obtained a higher value of $Q^*$, 20 kJ/mol.

Although the thermal gradient is approximately 51 °C/cm across the solder layer, thermomigration of Cu affects significantly the growth of the interfacial IMC. This is because the thickness of the solder layer was only 30 μm. The diffusion length was approximately two orders of magnitude shorter than the specimen adopted by Meechan and Lehman [17], therefore a low thermal gradient is sufficient to cause thermomigration. In the microbumps for 3D IC application, the method of hot pressing may be used to join the microbumps [20], which has a thermal gradient across the solder layer. Hence, Cu thermomigration should play an important role on the interfacial IMC growth in 3D IC.

4. Conclusion

In summary, we observed a significant asymmetrical growth of IMC in molten SnAg solder joints during reflowing on a hot plate at 260 °C. For example, the Cu$_6$Sn$_5$ IMC grew to 12.3 μm on the cold end, yet it was only 3.5 μm on the hot end after the reflow for 40 min. We propose that it is due to thermomigration of Cu. Thermomigration flux can be measured from the asymmetrical consumption of Cu on the two ends; the consumption is more on the hot end. With a simulated thermal gradient of 51 °C/cm across the molten solder, the heat of transport of Cu is calculated to be 20 kJ/mol.

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