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Rate of consumption of Cu in soldering accompanied by ripening

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What is the rate of consumption of Cu in soldering reactions has been a critical question in electronic packaging technology. The Cu films are consumed by Cu–Sn compound formation. Because the Cu thickness is limited and the rework of a solder joint requires a layer of unreacted Cu, the loss of Cu in soldering must be under control. At the solder interface, Cu–Sn intermetallic compounds do not form layered structures. Rather, the Cu₆Sn₅ phase grows as scalloplike grains into the molten solder and ripening occurs between the grains. Therefore, it has been difficult to determine the compound growth rate, and in turn the Cu consumption rate. Using cross-sectional and top-polished samples, we have measured the total volume of Cu–Sn intermetallic compounds formed between eutectic SnPb alloy and Cu substrate as a function of reflow time and temperature. We have deduced that after 1 min reflow, for example, the thickness of Cu consumed was about 0.36, 0.47, and 0.69 μ m at 200, 220, and 240 °C, respectively. © *1995 American Institute of Physics*.

The advance in very large scale integrated (VLSI) technology has increased the demand on functionality and reliability of input/output (I/O) connections.¹ The need of a greater number of I/O connections has caused the redistribution of wiring from boards, cards, and modules to the Si chip itself. To accommodate a large number of I/O counts, area arrays of solder bumps are being used in the controlled collapsed chip connection (C4) configuration for chip joints and ball grid array (BGA) for lower level joints.^{1–3} For these applications and, in particular, for a direct chip-to-board electronic packaging, there is a renewed interest in solder technology.¹ The reaction kinetics at the solder interface becomes an important issue.

At the liquid solder/Cu substrate interface, the formation and growth of intermetallic compounds occur by the dissolution of Cu into the molten solder. Although a number of studies have been performed on the dissolution of metals,^{4–7} very little is known about the dissolution kinetics of Cu into a molten solder accompanied by compound formation. In the case of thin-film metallization for making solder joints on a Si chip, the typical thickness of Cu is about 1 μ m. 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. In this letter, we report the consumption rate of Cu in the soldering reaction with eutectic SnPb alloy.

The eutectic SnPb/Cu samples were prepared by reflowing eutectic (63Sn37Pb, wt %) SnPb alloy on Cu plates in the mildly activated rosin flux (RMA) at three different temperatures; 200, 220, and 240 °C. The electropolished-Cu (99.95% purity) plate was immersed in the heated flux at one of the reflow temperatures with ± 3 °C control, and a small (~2.0 mg) solder ball was placed on the plate. The wetted ball spread out as a cap and it was solidified by cooling after a given reflow time. Due to the selective Cu–Sn reaction in which Pb does not react with Cu,⁸ a very rough scalloplike compound structure was developed. The growth of the scalloplike grains is accompanied by ripening,⁹ so it was difficult to measure the Cu consumption rate directly.

In order to determine the rate of Cu consumption, we assume that the total loss of Cu from the substrate is equal to the sum of Cu in the Cu–Sn compounds and in the liquid solder. From the mass balance of Cu, the consumed thickness of Cu is

$$\Delta h = \frac{1}{\rho_{\rm Cu}A} \left(\frac{nV}{100} \rho_L + f_{\rm Cu} \rho_c V_c \right),\tag{1}$$

where A is the total interfacial area between solder and Cu, n is the wt % of Cu in liquid solder, V is the total volume of liquid solder, f_{Cu} is the weight fraction of Cu in the Cu–Sn compound, V_c is the total volume of the Cu–Sn compound, and ρ_{Cu} , ρ_L , and ρ_c are the density of the Cu, liquid solder, and Cu–Sn compound, respectively. After the saturation of Cu in the molten solder, the consumption rate of Cu depends only on the change of volume of Cu–Sn compounds, and the rate equation is given by

$$\frac{dh}{dt} = \frac{f_{\rm Cu}}{A} \frac{\rho_c}{\rho_{\rm Cu}} \frac{dV_c}{dt}.$$
(2)

Since the solubility of Cu in the liquid SnPb solder is very low^{10-12} and the amount of the liquid solder used is small, the entire liquid solder cap will be saturated with Cu very quickly. Therefore, during the reflow, we can calculate the consumption rate of Cu by the rate of change of the total volume of Cu–Sn compounds.

Two kinds of eutectic SnPb/Cu samples were prepared for measuring the total volume of Cu–Sn compounds; crosssectional samples and top-polished samples. To see why these samples are needed, a selective Pb etching was performed to reveal the morphology of the compounds, as shown in Fig. 1. Figures 1(a) and 1(b) show the crosssectioned and top-polished views of the compounds, respectively. In a previous work,⁹ we have reported the growth of the scalloplike Cu₆Sn₅ compound grains through combined kinetic processes of ripening and interfacial reaction. Be-

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FIG. 1. Backscattered electron images of the eutectic SnPb/Cu interface after a reflow at 220 °C for 1 min, (a) cross-sectioned view, (b) top-polished view of Cu_6Sn_5 .

tween the Cu₆Sn₅ and Cu, a thin layer of the Cu₃Sn compound grows. However, the thickness of the layer is much smaller than the size of the scalloplike Cu₆Sn₅ grain. The thickness of the Cu₃Sn layer is 0.29 and 0.57 μ m after 10 and 40 min reflow at 200 °C as compared to the size of 5.59 and 10.27 μ m of Cu₆Sn₅, respectively. Therefore, we assume that the dominant interfacial compound growth is Cu₆Sn₅. From Fig. 1, we measured the height, diameter, and number of scalloplike Cu₆Sn₅ grains. Figure 2 shows how the num-



FIG. 2. Interfacial Cu–Sn compounds (a) number of Cu–Sn compound grains per $\rm cm^2$ of the interface, (b) total volume of grains of the interface.



FIG. 3. The consumed average thickness of Cu, Δh , and consumption rate of Cu, dh/dt, vs reflow time at three different temperatures.

ber and volume of the grains evolve as a function of reflow time at the three temperatures. The number of grains per unit area decreases with time and temperature while the total volume of grains increases with time and temperature. Since there are always channels between the compound grains, the ripening of grains occurs simultaneously with the dissolution of Cu into liquid solder through the channels. Therefore, the ripening is not a constant volume process due to the accompanying interfacial reaction; the total volume of the Cu₆Sn₅ compound increases with time at a given temperature as shown in Fig. 2(b). The kinetic analysis of the soldering reaction will be reported elsewhere.¹³

The consumed thickness of Cu during the reflow at the three different temperatures is plotted in Fig. 3. From the slopes of the curves, we calculated the consumption rate of Cu, dh/dt (μ m/s), of each temperature. The consumption rate of Cu is relatively high at the initial reflow and becomes lower with time. After 1 min reflow, the consumed thickness of Cu was about 0.36, 0.47, and 0.69 μ m at 200, 220, and 240 °C, respectively. The consumed thickness and the consumption rate are summarized in Table I. Due to the low interdiffusion coefficient of Cu in the solid η' phase (Cu₆Sn₅),^{14,15} the consumption mainly occurs by dissolution through the channels between the grains. Therefore, the reduction of the channel area by ripening might control the consumption rate of Cu during the reflow; it decreases with the time of reflow. The rate might be effected by the spalling of Cu-Sn compounds during reflow which was reported to occur on Cu thin films.¹⁶ However, we have not detected any spalling on our Cu sheets.

In conclusion, we have studied the interfacial morphology and reaction rate in the soldering reaction between the

TABLE I. Copper consumption data during reflow with eutectic SnPb solder.

	200 °C		220 °C		240 °C	
Time (s)	Δh (μ m)	$dh/dt \times 10^3$ (μ m/s)	$\Delta h \ (\mu m)$	$dh/dt \times 10^3$ (μ m/s)	Δh (µm)	$dh/dt \times 10^3$ (μ m/s)
10	0.18	7.85	0.24	9.75	0.32	12.04
60	0.36	2.97	0.47	3.41	0.69	3.84
300	0.83	1.24	0.97	1.33	1.12	1.38
600	1.14	0.85	1.30	0.89	1.47	0.89

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eutectic SnPb solder and Cu. We found that a very rough scalloplike Cu–Sn compound was developed and the growth of the compound was accompanied by ripening. We measured the total volume of the interfacial Cu–Sn compound as a function of time and temperature, and by assuming the mass balance of Cu, we deduced the consumption rate of Cu in the soldering reaction. The rate determines the processing parameters and their limits of solder joints on thin-film metallization in electronic packaging.

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