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Ripening-assisted asymmetric spalling of Cu-Sn compound spheroids in solder joints on Si wafers

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In reacting eutectic SnPb solder with Ti/Cu and Cr/Cu/Au thin film metallization on Si wafers, we have observed spalling of Cu_6Sn_5 spheroids when the solder consumes the Cu. The formation of the spheroids is assisted by the ripening reaction among the compound grains. In addition we have observed an asymmetric spalling phenomenon using a sandwich structure, in which two wafers were soldered face-to-face. The spalling occurs predominantly at the interface at the bottom of the solder joint. It suggests that gravity plays a role. © *1996 American Institute of Physics*. [S0003-6951(96)02316-9]

To synchronize with the advance in very large scale integration (VLSI) of Si technology, a high density of input/ output (I/O) connections is required in packaging the Si chip.^{1–3} The trend in low power electronic packaging is to shift from peripheral wire bonds to area array solder bumps, especially in the flip-chip technology.^{4–6} In this technology, small solder bumps are arrayed in a grid pattern on the face of a chip. The chip is flipped and aligned to a module substrate having a matching footprint of wettable I/O terminals. Then, the solder bumps are reflowed to achieve the controlled collapse chip connection (C4).

During the solder reflow process, intermetallic compounds are formed at the solder/Cu interface. Since the amount of Cu is limited in thin film metallization, spalling of the intermetallic compounds occurs after the Cu is consumed.⁷ The spalling tends to dewet and weaken the solder joint. However, the phenomenon and mechanism of spalling are unclear. In this letter, we report that the spalling is assisted by the ripening reaction among the compound grains. The grains become spheroids before they detach from the substrate.

Since the C4 solder joints have two interfaces; chip-tosolder and solder-to-substrate, the spalling at these two interfaces may be different. In this letter, we report the use of a sandwich structure to study them. We found that the spalling seems to depend on whether the compounds form above or below the solder. The asymmetric phenomenon suggests that gravity may play a role in the spalling.

Two kinds of Cu film samples were used in this study; Ti/Cu and Cr/Cu/Au evaporated on oxidized Si wafers. The Ti/Cu films were prepared by a consecutive deposition of 2500 Å of Ti by *e*-gun and 8500 Å of Cu by thermal evaporation. The Cr/Cu/Au films were prepared at IBM East Fishkill by *e*-gun evaporation, having thicknesses of 2500 Å Cr/ 5000 Å Cu / 1100 Å Au. For the solder, we have used the eutectic (63Sn37Pb, wt %) SnPb solder. Although high-Pb (e.g., 5Sn95Pb, wt %) solders are being used in chip-level interconnection, we chose the eutectic solder for a comparison to earlier soldering studies on Cu sheet.^{8,9} also because the low melting solder/Cu film system is of interest in the direct chip-on-card technology, for example, smart cards in the future.

In our study, a small (~0.5 mg) solder ball was reflowed on the Ti/Cu film in the mildly activated rosin flux (RMA) at 200 °C with ± 3 °C control. To remove the Cu-oxide, the Cu film samples were etched using a 50% ammonium hydroxide solution diluted with water before reflowed.¹⁰ Figures 1(a) and 1(b) show the cross-sectioned views in scanning electron microscope (SEM) of interface between the solder and Cu film after reflowed for 90 and 600 s, respectively. Using energy dispersive x-ray (EDX) analysis, the scallop-like grains at the interface in Fig. 1(a) were determined to be Cu₆Sn₅. We found that there is a ripening reaction among them; they grow bigger but fewer with annealing time. Even after all Cu has been consumed by the Cu-Sn reaction, the ripening continues but the morphology of the Cu₆Sn₅ scal-



FIG. 1. Backscattered electron SEM images of the cross-section of interface between the eutectic SnPb solder and Ti/Cu film reflowed at 200 $^{\circ}$ C (a) for 90 s, (b) for 600 s.



FIG. 2. (a) Schematic of sandwich structure, (b) cross-section of the sample reflowed at 200 °C for 600 s using eutectic SnPb solder on Cr/Cu/Au film.

lops begins to change into spheroids. The change is accompanied by decreasing the contact area between the grains and bottom metallization. This is because there is no more Cu; the ripening becomes conservative. The smaller grains will be dissolved into the bigger grains. The contact area decreases and it exposes the Ti or Cr surface to the liquid solder, in turn, spalling will lead to more exposed surface as shown in Fig. 1(b). If the Ti and Cr surfaces are oxidized, they can not be wetted by the solder. It can present a serious dewetting problem and the interface will be vulnerable to mechanical failure. In the earlier report on solution-assisted spalling by Berry et al.⁷ no ripening reaction among the Cu₆Sn₅ grains was mentioned. We show that it is the conservative ripening which dissolves the smaller grains and results in spalling. We have observed the same type of spalling in the reflow of solder on the Cr/Cu/Au films.

In the face-to-face samples of two wafers with a solder joint in between them, the schematic in Fig. 2(a) shows the sandwiched structure while the micrograph in Fig. 2(b) shows the cross-section of a reacted sample. The small (~ 0.5 mg) solder disk with a thickness of about 120 μ m was sandwiched by two wafers and the wafers were supported by spacers with the same thickness to maintain the spacing. The cross-section of the sandwich was polished using SiC paper and alumina powder, and a light etching was performed using a mixture of 5% HCl in methanol to delineate the interfacial structure of the solder joint.¹⁰ Figures 3(a) and 3(b) are the enlarged micrographs of the top and bottom interfaces of the joints. They clearly show an asymmetric spalling behavior of the two solder interfaces. After 10 min reflow at 200 °C, although a severe spalling has already occurred at the bottom interface, the Cu-Sn compounds at the top interface do not show any spalling. Because of the selective reaction of Cu with Sn, the composition of solder next to the Cu-Sn compounds will be enriched in Pb. Therefore, there is a concentration gradient of Pb in the molten solder to mix the solder. However, when the molten solder flows to the ex-



FIG. 3. Enlarged SEM images of interface shown in Fig. 2(b) (a) top interface, (b) bottom interface.

posed Ti or Cr surface, it exerts a lifting force to the Cu_6Sn_5 grains due to gravity or density difference. When the grains transform to spheroids which have a nonwetting contact angle (180°) to the Ti or Cr surfaces, they may be lift up from the bottom interface by the gravity force. Although the detailed mechanism of spalling such as shape change of the Cu_6Sn_5 grains and their wetting behavior on Ti or Cr surfaces remains to be studied, the gravity effect seems in agreement with the observed asymmetric behavior.

On the wetting behavior of Cu_6Sn_5 on Ti or Cr surfaces, we expect some adhesion between them since they are all metals. Nevertheless, the dewetting of the intermetallic from the metal surface is due to the total surface energy changes in the shape change from a scallop to a spheroid. It includes their interfaces with the molten solder.

The avoidance of ripening assisted spalling in product may be achieved by locking the intermetallic compounds with a "phased" region between Cr and Cu.¹¹ In phasing Cr and Cu, the crystallites of Cr and Cu become intermixed and the intermetallics of Cu become locked into the Cr so that they will not separate easily. Follow-on studies are planned to examine intermetallic ripening on phased structures.

In summary, the spalling of the Cu-Sn compounds at the solder interface on thin film metallization is an important reliability issue of flip-chip technology. We have found that the ripening among the Cu_6Sn_5 grains assisted the spalling. Under the influence of gravity, the spalling tends to occur predominantly at the bottom interface of a solder joint.

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