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Inhibiting the consumption of Cu during multiple reflows of Pb-free solder on Cu

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An effective approach to inhibiting the consumption of Cu during multiple reflows of SnAg2.3 solder on Cu is reported. By depositing a very thin layer of solder on Cu, followed by a 10-min reflow, the scallop-type morphology of interfacial Cu_6Sn_5 intermetallic compounds (IMC) became flat, and the channels between them closed up. When additional solder was deposited on the sample and reflowed again, the consumption of Cu as well as the growth the IMC was retarded.

Keywords: Intermetallic compound; Soldering; Diffusion; 3D-IC packaging

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Molten tin wets copper at a very high rate, and they even continue to react and form Cu–Sn intermetallic compounds (IMC) at room temperature after solidification [1–10]. Because of the high wetting rate, SnPb as well as Sn-based Pb-free solders have been widely used in electronic packaging technology for chip-to-substrate joints. For the same reason, copper serves as the most popular under-bump-metallization (UBM) in the microelectronic packaging industry. This is because there are now thousands of solder joints on a piece of Si chip, which must all be wetted and joined simultaneously in a single reflow in which the temperature is slightly above the melting point of the solder. In device manufacturing, several reflows are required, so the solder joints are remelted several times to form more and more IMC. However, IMC induce brittleness in the solder joint, so the fewer the better. Also, since the thickness of thin film Cu UBM is limited, it can be completely consumed in a few reflows. When a thick Cu UBM is used, the preferential dissolution of Cu, due to anisotropic diffusivity of Sn in Cu, has caused early failure in devices. Thus, from the point of view of yield of solder joints, a quick wetting reaction is required. But from the point of view of reliability of solder joints, no more solder reaction is required after the first reflow. There is therefore a conflict of interest. An ideal solder joint process is one which joins easily and quickly during the first reflow, but the solder reaction should stop or become very slow in subsequent reflows. This means that it will be very beneficial to inhibit the Cu–Sn reaction after chip-join in the first reflow. Indeed, several approaches to inhibiting the growth of the IMC have been proposed, including altering the solder composition and incorporating Ni into the Cu UBM [11,12]. Yet, none of them is effective. Currently, the microelectronics industry is moving towards three-dimensional (3D) integrated circuit (IC) packaging in which the chip technology and packaging technology are merged together [13]. In 3D IC, the consumption and dissolution of the Cu column in through-Si via by solder reaction is a critical issue. An effective approach to retarding the consumption of Cu is reported here, and the mechanism is discussed.

SnAg2.3 solder and electroplated copper were used to demonstrate this approach. A 100-nm-thick Ti layer was deposited on a Si wafer first, followed by sputtering of a Cu seed layer 500 nm thick. Then lithography was employed to pattern cylindrical holes 100 μm in diameter in photo-resist for electroplating of Cu UBM and the solder. Two types of structure of solder/UBM were fabricated: the first was 19-μm-thick solder on 20-μm-thick Cu UBM, and the second was 2-μm-thick solder on 20-μm-thick Cu UBM. These samples were reflowed at 260 °C for 1 min straight after the electroplating of the solder layer. Figure 1a and b shows cross-sectional scanning electron microscopy (SEM) images for the 19-μm-thick solder and 2-μm-thick solder on 20-μm-thick Cu UBM, respectively. The solder in the

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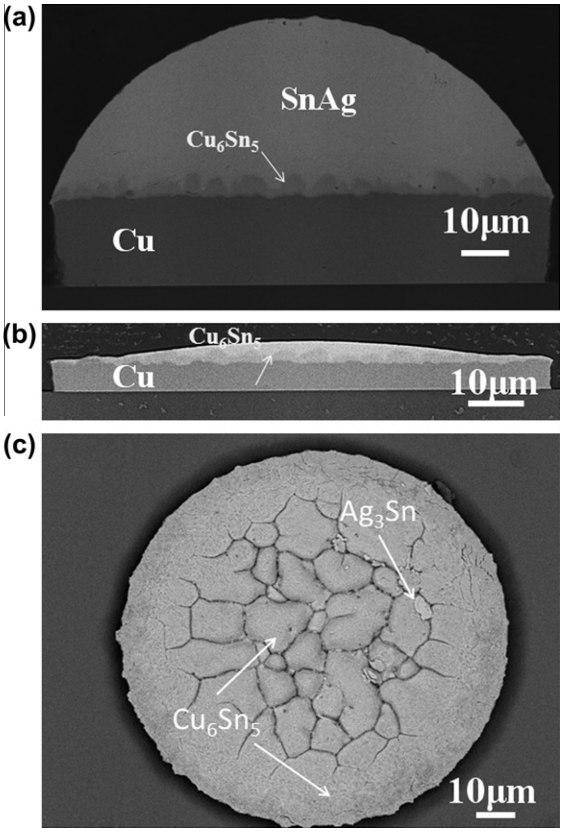

Figure 1. (a) Cross-sectional SEM images for the as-fabricated 19-μm-thick solder sample and (b) cross-sectional SEM images for the as-fabricated 2-μm-thick solder sample. (c) Plan-view SEM images for the as-fabricated 2-μm-thick solder sample. The remaining solder was etched away selectively.

2-μm-thick solder sample is consumed almost completely to form Cu–Sn IMC, except the central part. Yet, for the 19-μm-thick solder sample, there is plenty of unreacted solder on the Cu UBM, and the morphology of the interfacial Cu_6Sn_5 IMC appears to be scallop-type. Between two neighboring IMC scallops, there is a channel which connects the molten solder and the Cu during reflow. The channel is the fast diffusion and dissolution path of Cu to the molten solder. To reduce the consumption of Cu, the channel has to be closed.

To close up the channels between Cu_6Sn_5 IMC, the 2-μm-thick solder samples were reflowed at 260 °C for 10 min. After the heat treatment, the solder was completely consumed and transformed into Cu–Sn IMC. Then, additional SnAg solder was deposited on these samples, and another reflow of ~1–3 min was needed to stabilize the deposited solder. The total amount of the deposited solder was close to that of the 19-μm-thick solder samples, so that a direct comparison can be made between these two types of samples: one is the 2-μm-thick solder with heat treatment at 260 °C for 10 min, followed by the addition of a thick solder layer, and the other is the 19-μm-thick solder samples without heat treatment. Then, interfacial reactions were investigated for additional reflows at 260 °C for 1–10 min of these two types of samples for comparison. The change in microstructure was examined by SEM. Focused ion beam (FIB) was employed to observe the cross-sectional morphology of the Cu–Sn IMC.

Heat treatment at 260 °C for 10 min can alter the morphology of the Cu–Sn IMC in the 2-μm-thick solder samples. Figure 1c shows the plan-view SEM image for the 2-μm-thick solder sample reflowed at 260 °C for 10 min. The Cu_6Sn_5 IMC in the periphery of the circular pad merged together and became flat; thus there were no obvious channels between neighboring Cu–Sn grains. In addition, the Cu_6Sn_5 grains near the center of the pad grew bigger, resulting in fewer channels in this sample. When additional solder was deposited onto this sample and additional reflow processes were conducted, it was found that the growth of the Cu–Sn IMC was significantly inhibited in the Cu/IMC interface of the 2-μm-thick solder sample. Figure 2a–c shows the cross-sectional SEM image for the 2-μm-thick-solder sample after the additional solder was deposited, reflowed for 5 min and reflowed for 10 min, respectively. The interfacial IMC were identified to be Cu_6Sn_5 by SEM energy dispersive X-ray. However, the morphology of the Cu–Sn IMC appears very different from the scallop-type in the 19-μm-thick solder sample shown in Figure 1a. The shape of the Cu_6Sn_5 IMC is not a semi-circular scallop, but a cylinder. In the cylinder, the height of the IMC is approximately only one-third to one-quarter of its width, as shown in Figure 2b and c, which suggests that the channels closed up and the dissolution Cu flux was reduced.

However, the 19-μm-thick solder sample exhibits a different growth rate and morphology of Cu_6Sn_5. Figure 3a–c shows the cross-sectional SEM image on

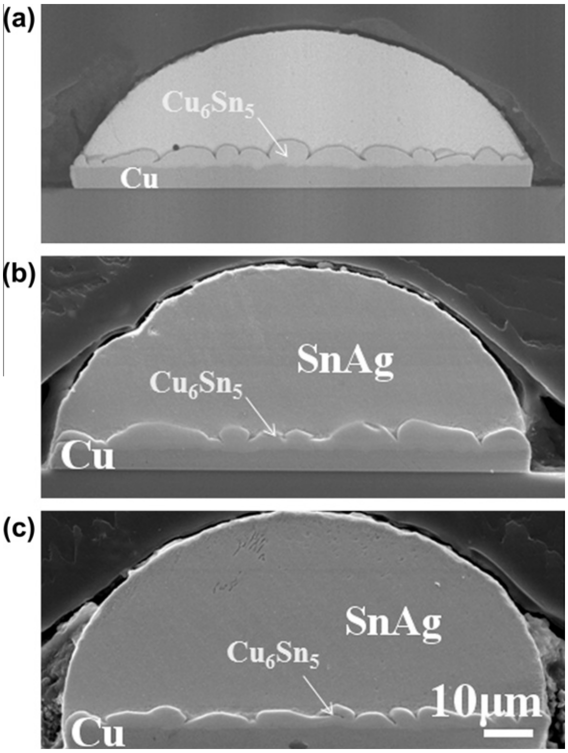

Figure 2. Cross-sectional SEM images for the 2-μm-thick solder sample after (a) additional solder was deposited, (b) reflow for 5 min and (c) reflow for 10 min.

the interfacial IMC for the 19-μm-thick solder sample after reflow for 0, 5 and 10 min, respectively. The morphology of the Cu_6Sn_5 grains is close to semi-circular (scallop-type). In addition, the total IMC thickness is measured to be 4.38 μm, which is thicker than 3.11 μm for the 2-μm-thick solder sample. Figure 4 shows the total Cu–Sn IMC thickness as a function of reflow time. Each thickness value was obtained by averaging at least four samples. As described in the experimental section, it took 3 min at 260 °C to reflow the additional solder on the 2-μm-thick solder sample. Therefore, the measured thickness value starts from 3 min.

The inhibition mechanism was investigated. It was found that the channels between the Cu_6Sn_5 scallops play a critical role in the growth of the Cu–Sn IMC. To observe the top-view morphology of the Cu_6Sn_5 IMC, selective etching to remove the unreacted solder was conducted using a solution of one part glycerol, one part acetic acid and one part nitric acid at 25 °C. Figure 5a shows the top-view or plan-view SEM images of the Cu_6Sn_5 IMC after etching away the unreacted solder in the 19-μm-thick solder sample after 10 min reflow at 260 °C. The shape of the Cu_6Sn_5 IMC appears scallop-like, and there are channels between the scallop-like IMC. It is reported that the channels serve as

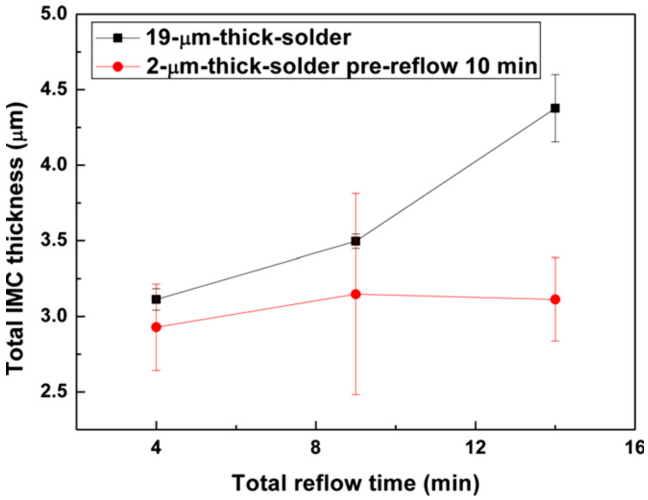

Figure 4. Plot of the total Cu–Sn IMC thickness as a function of reflow time for the two sets of samples.

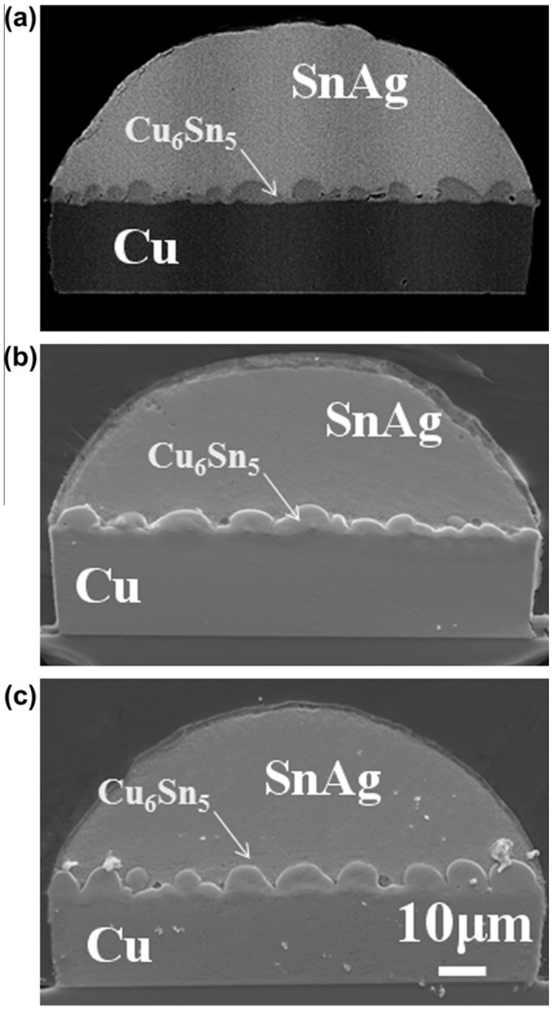

Figure 3. Cross-sectional SEM images for the 19-μm-thick-solder sample. (a) as-fabricated sample; (b) reflow for 5 min; and (c) reflow for 10 min.

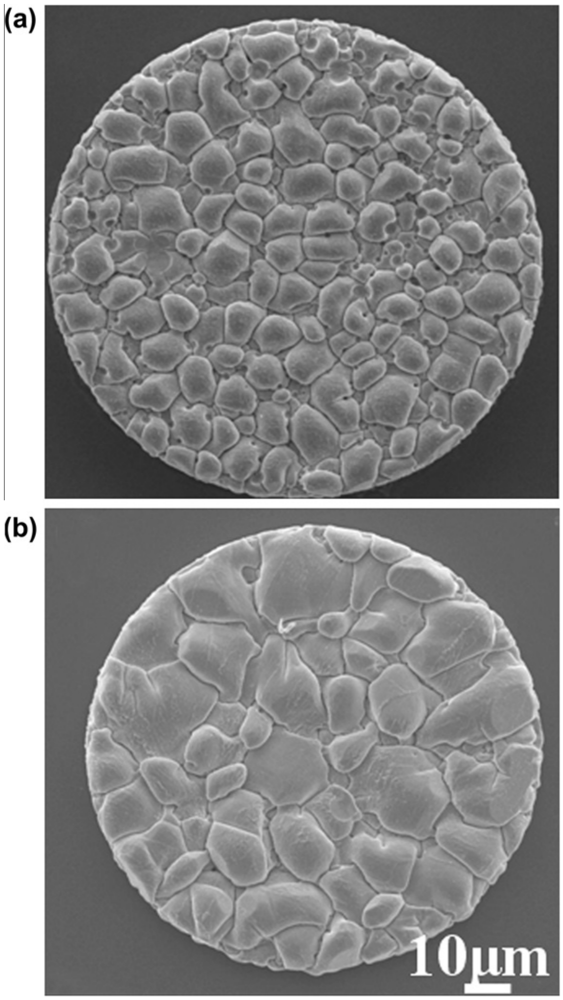

Figure 5. Plan-view SEM images of the Cu_6Sn_5 IMC after etching away of the unreacted solder after 10 min reflow at 260 °C: (a) for the 19-μm-thick solder sample; (b) for the 2-μm-thick solder sample.

rapid diffusion and dissolution paths of Cu into molten solder to facilitate the growth of the Cu–Sn IMC [5].

However, the morphology for the 2-μm-thick solder sample appears different. Figure 5b presents the plan-view SEM image for the Cu_6Sn_5 IMC after selective etching. The average grain size of the IMC appears much bigger than that in Figure 5a. In addition, the channel area appears much less than that in Figure 5a. Comparing Figure 1c and Figure 5b, it is observed that some of the Cu–Sn IMC with closed channels on the periphery of the pad became open again after reflow for 10 min. However, the grain size of the Cu_6Sn_5 remained very large. The total channel area did not increase much. Therefore, the 19-μm-thick solder sample still has more channels between the Cu_6Sn_5 IMC than the 2-μm-thick solder sample after reflow for an additional 10 min. Therefore, the 2-μm-thick solder sample possesses a slower growth rate of the Cu–Sn IMC.

An effective way to slow down the growth of the Cu–Sn IMC in reflow was demonstrated. By depositing a 2-μm-thick solder on Cu and reflowing at 260 °C for 10 min, the channels between the Cu_6Sn_5 scallops can be closed up. When the sample is jointed to a thick solder later, this layer-type Cu_6Sn_5 IMC becomes a diffusion barrier for Cu/solder reaction during additional reflows. Although some of the channels may reopen, the total channel area is much less than the sample without the heat treatment.

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[1] B.F. Dyson, T.R. Anthony, D. Turnbull, J. Appl. Phys. 38 (1967) 3408.
[2] K.N. Tu, Acta Met. 21 (1973) 347.
[3] K.N. Tu, R.D. Thompson, Acta Met. 30 (1982) 947.
[4] S. Bader, W. Gust, H. Hieber, Acta Met. Mater. 43 (1995) 329.
[5] H.K. Kim, K.N. Tu, Phys. Rev. B53 (1996) 16027.
[6] J.Y. Song, J. Yu, T.Y. Lee, Scripta Mater. 51 (2004) 167.
[7] H.F. Zou, H.J. Yang, Z.F. Zhang, Acta Mater. 56 (2008) 2649.
[8] T. Laurila, V. Vuorinen, J.K. Kivilahti, Mater. Sci. Eng., R 49 (2005) 1.
[9] J. Gong, C. Liu, P.P. Conway, V.V. Silberschmidt, Scripta Mater. 60 (2009) 333.
[10] L. Jiang, N. Chawla, Scripta Mater. 63 (5) (2010) 480.
[11] S.-H. Kim, J.-Y. Kim, J. Yu, And T.Y. Lee, J. Elec. Materi. 33 (9) (2004) 948.
[12] W.T. Chen, C.E. Ho, C.R. Kao, J. Mater. Res. 17 (2002) 263.
[13] J.C. Lin, W.C. Chiou, K.F. Yang, H.B. Chang, Y.C. Lin, E.B. Liao, J.P. Hung, Y.L. Lin, P.H. Tsai, Y.C. Shih, T.J. Wu, W.J. Wu, F.W. Tsai, Y.H. Huang, T.Y. Wang, C.L. Yu, C.H. Chang, M.F. Chen, S.Y. Hou, C.H. Tung, S.O. Jeng, D.C.H. Yu, IEEE Int. Elect. Dev. Meeting (2010) 25.