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Elimination of voids in reactions between Ni and Sn: A novel effect of silver

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Interfacial reaction under in a confined space is becoming an increasingly important issue, due to its applications for wafer bonding in three-dimensional integrated circuits. This study aims to uncover the space confinement effects on Ni/Sn and Ni/SnAg reactions. Space confinement causes the formation of voids near the center of Ni/Sn/Ni sandwiches. Adding Ag effectively eliminates these voids, which, if present, would undoubtedly degrade the reliability of wafer bonding joints. The mechanism for the formation of these voids is proposed and verified.

Keywords: Soldering; Intermetallic compounds; Interface diffusion; Coarsening; Aging

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Current state-of-the-art solder joints in flip-chip microelectronic packages have their diameters in the 100 μm range. In three-dimensional integrated circuits (3-D ICs) under development today, the diameter of a typical microsolder joint is only about 10 μm. In this transition between generations from flip-chip to 3-D ICs, the volume of a solder joint shrinks by a factor of 1000. Many new issues arise due to such a large miniaturization of the solder volume. One such issue is the interfacial reactions between the solder and the substrate in a confined space several micrometers in size. In this study, the interfacial reaction between Ni and solders under such space confinement are investigated. The Ni–solder system is chosen because, first of all, this system is one of the most important material systems for microelectronic packaging, and secondly there are plenty of data on bulk-scale Ni–solder reactions [1–9] available in the literature for comparison. According to the literature, in the reactions between Ni and Sn or SnAg solders on the bulk scale [2–9], Ni_3Sn_4 is the only reaction product formed at temperature below 260 °C, which is near the highest temperature solder joints are expected to experience during assembly. It was reported that the Ag atoms did not become incorporated into Ni_3Sn_4 but simply formed Ag_3Sn, which was dispersed within the solder as round particles of thin plates [7,8].

Experimentally, Ni/Sn/Ni or Ni/Sn2.4Ag/Ni sandwiches were prepared by sequentially electroplating Ni and Sn or Sn2.4Ag (wt.%) layers onto silicon wafers. The thickness of the solder layers was 5, 7 or 10 μm for Sn and 7 μm for Sn2.4Ag, and the thickness of the Ni layers was kept constant at 12 μm. At such Ni to solder ratios, the first reactant to be completely consumed is the solder. The lateral dimensions of each sandwich were 3 mm × 3 mm. Under this configuration, the space was confined along the vertical direction; along the lateral directions, the space could be considered as infinite. Ignoring the edge regions, the direction of the interdiffusion fluxes can be considered limited to the vertical direction, i.e. the space-confined direction. After plating, the sandwiches were aged at 150, 180 or 200 °C for periods of up to 528 h. It should be noted that no reflow was needed or carried out during the assembly of the sandwiches.

Figure 1(a)–(c) shows the Ni/Sn(7 μm)/Ni sandwiches aged at 180 °C for 28, 48 and 120 h, respectively. During aging, two layers of Ni_3Sn_4 grew towards each other from the opposite interfaces, as shown in Figure 1(a). At 28 h, Ni_3Sn_4 grains growing from the opposite directions started to impinge on each other at certain locations. When aging time reached 48 h, as showed in Figure 1(b), both Ni_3Sn_4 layers became thicker, and more Ni_3Sn_4 grains touched those grains growing from

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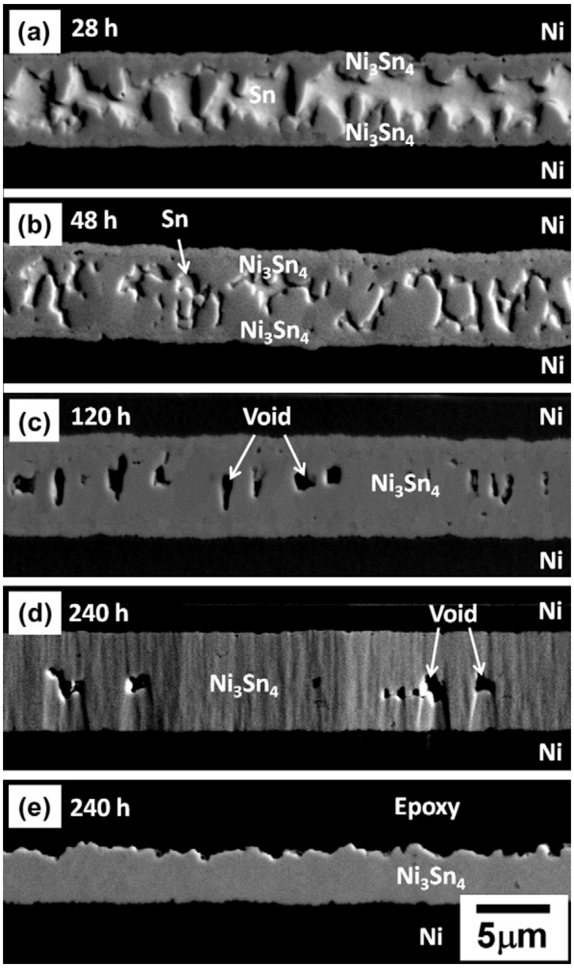

Figure 1. Micrographs showing Ni/Sn(7 μm)/Ni sandwiches after aging at 180 °C for (a) 28, (b) 48, (c) 120 and (d) 240 h. The cross-sections in (a)–(c) were prepared by mechanical polishing, and that in (d) was prepared by using an ion beam cross-section polisher. (e) Micrograph from an Ni/Sn(5 μm) bilayer structure from which the Sn has been completely been consumed. No void is observed because the volume shrinkage due to reaction is completely compensated for by the decrease in thickness.

the opposite direction, isolating Sn into many small pockets in the cross-sectional view. When the aging time reached 120 h, as showed in Figure 1(c), all Sn had been converted into Ni_3Sn_4. One key observation of this study was the existence of many voids within the Ni_3Sn_4. To avoid the possibility that these voids were artifacts due to mechanical polishing, a sample that had been aged for 240 h, shown in Figure 1(d), was cross-sectioned by using an ion beam polisher, which is known to have the capability of producing a relatively high quality and artifact-free surface. The fact that voids still existed in Figure 1(d) suggested that these voids were an intrinsic feature of such reaction under space confinement. In fact, these voids consistently showed up in all of the Ni/Sn/Ni samples aged at all temperatures as long as all the Sn had been consumed. The existence of these voids raises serious reliability concerns, as such voids would no doubt weaken the solder joints.

To understand the mechanism responsible for void formation, it needs to be noted that there is a net volume shrinkage when Ni and Sn react to form Ni_3Sn_4. The molar volumes for Ni, Sn and Ni_3Sn_4 are 6.59, 16.26 and 75.25 $cm^3\,mol^{-1}$, respectively [10,11]. The volume shrinkage is calculated to be $\{75.25 - [3(6.59) + 4(16.26)]\}/[3(6.59) + 4(16.26)] = -0.113$, or -11.3%. With this information, the mechanism of void formation can be understood with the help of the illustration shown in Figure 2. Before the Ni_3Sn_4 grains from opposite directions start to impinge on each other, as is the case shown in Figure 1(a), the volume shrinkage could freely be accommodated by the thickness decrease in the sandwiches. However, when enough of the Ni_3Sn_4 grains impinged on each other, as are the cases shown in Figure 1(c) and (d), the decrease in vertical thickness became difficult to accommodate without plastic deformation of the Ni_3Sn_4 grains. As plastic deformation of the hard Ni_3Sn_4 was very difficult, the volume shrinkage had to be dissipated through other means. Because Sn was the main diffusion species through Ni_3Sn_4 [8,12], more Sn atoms diffused out of the Sn pocket shown in Figure 2 than Ni atoms that reached the pocket. As the reaction continued, a void gradually formed and grew within each Sn pocket.

The proposed mechanism suggests that no void will form if there is no Ni_3Sn_4 impingement and trapped Sn pockets. This is indeed what we observe in Figure 1(e). Here, a Ni/Sn(5 μm) bilayer structure was plated and then left to react until the Sn had completely disappeared. Because now all the volume shrinkage could be accommodated by the decrease in vertical thickness, no void was observed at all.

Although the literature indicates that Ag atoms do not become incorporated into Ni_3Sn_4 but simply become Ag_3Sn [7,8], the present study shows that the addition of Ag completely eliminate these voids. Figure 3(a)–(d) shows the Ni/Sn2.4Ag(7 μm)/Ni sandwiches aged at 180 °C for 12, 72, 378 and 528 h, respectively. As shown in Figure 3(a), two layers of Ni_3Sn_4 grew toward each other from the opposite interfaces, and Ag_3Sn at this stage existed as small round particles. These small Ag_3Sn particles had coarsened into larger ones by the time the aging had reached 72 h, as shown in Figure 3(b). At 378 h, Ni_3Sn_4 grains growing from opposite directions started to impinge on each other, and there was a small amount of Sn left, as shown in Figure 3(c). Very surprisingly, the Ag_3Sn particles were flattened somewhat and located between the two Ni_3Sn_4 layers. It should be emphasized that nearly all the Ag_3Sn ended up located between the two Ni_3Sn_4 layers. When the aging time reached 528 h, as showed in Figure 3(d), all the Sn had

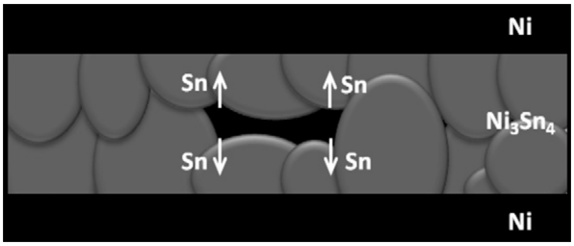

Figure 2. Schematic drawing showing the mechanism responsible for void formation.