Suppression of Whisker Growth in Tin-Based Lead-Free Solder Layers by Addition of POSS Particles (Postprint)

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Abstract

Polyhedral oligomeric silsesquioxane (POSS) with nanostructures was incorporated as a reinforcement phase into Sn, Sn-3.0Ag-0.5Cu, and Sn42-Bi58 solder alloys to investigate the effect of the reinforcement on whisker growth behavior in tin-based lead-free solder layers under constant temperature and humidity (85 °C, 85% relative humidity) conditions. The results demonstrate that under constant temperature and humidity conditions, the driving force for whisker growth in tin-based lead-free solder layers is the compressive stress exerted on the surrounding solder layer due to volume expansion caused by the formation of Sn oxides; the addition of POSS can effectively mitigate the oxidation process of metallic Sn, suppress the formation of Sn oxides, and thereby retard whisker growth; among Sn, Sn3.0Ag0.5Cu, and Sn58Bi solder layers, the Sn solder layer exhibits the strongest whisker growth propensity, while the Sn58Bi solder layer exhibits the weakest.

Full Text

Abstract

Whisker growth in Pb-free solder joints is a major reliability concern in the electronic industry. Several theories and models have been developed to explain whisker growth, and many attempts have been made to find solutions to this issue. Micro-alloying, such as introducing Cu, Bi, Ag, etc. into solders, is considered an effective method to mitigate whisker growth. However, when alloying with these metal elements, the structure of solders will be changed, therefore the reliability of solders needs to be reevaluated. The purpose of this research is to explore the possibility of mitigating whisker growth through a reinforcement strategy without altering the structure of solders. In this study, a novel reinforcement, nano-structured cage-type polyhedral oligomeric silsesquioxane (POSS),

was employed and expected to mitigate whisker growth. POSS was added into Sn, Sn3.0Ag0.5Cu, and Sn58Bi solders respectively. Whisker growth behaviors of these modified solders under high humidity and temperature environment (85 ℃, 85% relative humidity) were analyzed and discussed. The results indicated that the driving force of whisker growth was compressive stress generated by the volume expansion of tin oxides. The high humidity and temperature condition facilitated the formation of tin oxides and therefore provided continuous driving force for whisker growth. POSS addition could effectively inhibit the oxidation process of metallic tin and reduce the amount of tin oxide formation; consequently, whisker growth was mitigated. Among Sn, Sn3.0Ag0.5Cu, and Sn58Bi solders, Sn solder was the most prone to whisker growth, while Sn58Bi was the least prone.

Experimental Results

2.1 Effect of POSS on Whisker Growth in Sn Solder Layers

Fig. 1 shows SEM images of surface morphologies of Sn and Sn+POSS aged for different times under 85 ℃ and 85% relative humidity: (a) Sn for 450 h, (b) Sn+POSS for 450 h, (c) Sn for 750 h, and (d) Sn+POSS for 750 h.

Figure 2 shows SEM images of whisker morphologies of Sn and Sn+POSS aged for different times under 85 ℃ and 85% relative humidity. The oxide layer has been arched up, indicating that upward stress exists beneath the solder layer driving whisker growth. When the Sn solder layer was aged for 750 h, the whisker morphology on the solder surface changed. As shown in Fig. 2d [Figure 2: see original paper], the whiskers became short and thick. At this stage, the surface morphology changed significantly, with many raised hillocks appearing in addition to the formed whiskers. Figure 2e is an enlarged view of the local area in Fig. 2d, showing a whisker growing upward and breaking through the surface oxide layer during growth. Notably, the contour of the broken oxide layer at the whisker root matches the cross-sectional shape of the whisker growth, indicating that the whisker growth process extrudes through the broken oxide layer contour as an outlet under the action of stress from beneath the oxide layer. Figure 2f shows the morphology of a whisker breaking through the surface oxide layer to grow outward, with the surface oxide layer still wrapping around the whisker and only the tip exposed. In contrast, as shown in Figs. 2g and h, Sn+POSS exhibited no massive whisker growth on the solder surface after aging for 750 h, with only small-sized whiskers observed at local positions.

Table 1 lists the composition of the whisker surface and the oxide layer wrapping the whisker root.

Table 1 EDS results of positions 1~3 in Fig. 2 (atomic fraction / %)

Figure 3a [Figure 3: see original paper] shows a cross-sectional SEM image of the Sn solder layer aged for 750 h under constant temperature and humidity conditions, where dark blocky oxide SnOx can be observed in the surface region.

In contrast, for the Sn+POSS solder layer shown in Fig. 3b, only a small amount of small blocky oxide SnOx was observed near the surface.

Comparing whisker growth in Sn and Sn+POSS solder layers reveals that in Sn solder layers, the formation of oxide SnOx causes volume expansion, generating compressive stress on the surrounding solder matrix and providing the driving force for whisker growth. When the stress level is sufficient to break through the surface oxide layer, whiskers begin to grow outward. Adding POSS can effectively alleviate oxidation in the depth direction of the solder layer, reducing both the quantity and size of SnOx formation, thereby decreasing the compressive stress caused by oxides and suppressing whisker growth.

2.2 Effect of POSS on Whisker Growth in SAC305 Solder Layers

Figure 4 [Figure 4: see original paper] shows SEM images of surface morphologies of SAC305 and SAC305+POSS aged for different times under 85 ℃ and 85% relative humidity. For the SAC305 sample, after aging for 450 h under constant temperature and humidity conditions, the solder surface exhibited undulations and roughness, as shown in Fig. 4a; this phenomenon became more pronounced after aging for 750 h, as shown in Fig. 4c. The enlarged view in Fig. 4e reveals that these protrusions consist of short, thick whiskers. Notably, cracks were observed in the region near the whiskers shown in Fig. 4e, indicating that internal stress caused cracking in the solder matrix. This phenomenon indirectly demonstrates that the driving force for whisker growth originates from internal stress. After adding POSS, whisker growth was significantly mitigated. As shown in Fig. 4b, the SAC305+POSS sample showed no obvious undulations or roughness on the solder surface after aging for 450 h under constant temperature and humidity conditions; after 750 h, local undulations could be observed from Fig. 4d. Comparing Figs. 4e and f reveals that after POSS addition, short, thick whiskers were only observed at local positions, with less damage to the solder surface, and both whisker size and distribution density were significantly reduced.

Figure 5a [Figure 5: see original paper] shows a cross-sectional SEM image of the undulating region in the SAC305 solder layer aged for 750 h under 85 ℃ and 85% relative humidity. It can be seen that the light-colored structure is the solder matrix, with large dark oxide SnOx formed, and obvious corrosion points observed at the interface between the oxide and solder matrix. Figure 5b shows a cross-sectional SEM image of the SAC305+POSS solder layer under the same conditions, where no blocky oxide formation was observed, but obvious corrosion points could be seen near the surface.

These results indicate that under constant temperature and humidity conditions, Sn in SAC305 samples is highly susceptible to oxidation; the volume expansion during the formation of SnOx generates compressive stress on the solder matrix, thereby promoting whisker growth. After adding POSS, the oxidation of Sn was effectively inhibited, reducing the compressive stress caused by volume expansion from oxide formation within the solder layer, ultimately manifesting as suppressed whisker growth.

2.3 Effect of POSS on Whisker Growth in Sn58Bi Solder Layers

Figure 6 [Figure 6: see original paper] shows SEM images of surface morphologies of Sn58Bi and Sn58Bi+POSS aged for different times under 85 ℃ and 85% relative humidity. It can be seen that both Sn58Bi and Sn58Bi+POSS solder surfaces exhibited varying degrees of undulations and roughness, with the extent expanding as aging time increased. Comparing Sn58Bi (Figs. 6a and c) and Sn58Bi+POSS (Figs. 6b and d) samples after aging for 450 and 750 h, no obvious difference was observed from the surface macro-morphology. However, comparing the enlarged views in Figs. 6e and f reveals that small, short rod-like whiskers appeared on the Sn58Bi solder surface, as shown in the inset of Fig. 6e, while no such whiskers were observed on the Sn58Bi+POSS solder surface.

Figure 7 [Figure 7: see original paper] shows cross-sectional SEM images of Sn58Bi and Sn58Bi+POSS aged for 750 h under 85 ℃ and 85% relative humidity, where the dark phase is the Sn-rich phase and the white phase is the Bi-rich phase. In Fig. 7a, small whiskers can be observed on the surface of the Sn58Bi solder layer, with oxide SnOx formed inside the dark Sn-rich phase at the bottom of the whiskers. Oxide SnOx was also observed in the near-surface region of the Sn58Bi+POSS solder layer, but no whisker growth was observed.

These results indicate that compared with Sn and SAC305 solder layers, Sn58Bi solder layers have a stronger ability to suppress whisker growth, which may be due to the blocking effect of the eutectic lamellar Bi-rich phase on the oxidation process of the Sn-rich phase. The driving force for whisker growth in Sn58Bi solder layers is the internal stress generated by volume expansion during SnOx formation. Adding POSS can effectively slow down the oxidation phenomenon of Sn58Bi solder layers under constant temperature and humidity conditions, prevent the oxidation process from further developing in the depth direction, reduce the compressive stress on the solder surface caused by oxide expansion, and thereby suppress whisker growth.

Conclusions

This study investigated the effect of POSS addition on whisker growth in Sn, Sn3.0Ag0.5Cu, and Sn58Bi solder layers under constant temperature and humidity conditions. Under these conditions, the driving force for whisker growth in Sn-based Pb-free solder layers is the compressive stress generated on the surrounding solder layer by volume expansion from Sn oxide formation. Adding POSS can effectively alleviate the oxidation process of metallic Sn, inhibit Sn oxide formation, and thereby mitigate whisker growth. Among Sn, Sn3.0Ag0.5Cu, and Sn58Bi solder layers, the Sn solder layer has the strongest whisker growth propensity, while the Sn58Bi solder layer has the weakest.

References

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Note: Figure translations are in progress. See original paper for figures.