Study on interface of Sn-Ag-Zn lead free solder with low silver content

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Abstract. The interface reaction between Sn-1Ag-1Zn low silver alloy solder and different substrates was studied. After aging at 200 ℃, a double-layer IMC structure is formed at the interface. Cu5Zn8 and Ag3Sn are formed from Cu substrate to solder in turn. The morphology of interface Cu5Zn8 has no change with aging. After aging for 100 h, the thickness of Ag3Sn is only about 4 μm, and the IMC of bilayer structure blocks and suppresses each other. After Sn-1Ag-1Zn solder is welded to Cu substrate with Ni barrier layer, Ni3Sn4 layer is formed on the surface, and its thickness increases slowly with aging time at 200 ℃. After aging for 1000 h, the thickness of Ni3Sn4 layer is only about 1 μm, and the morphology is smooth. There is no aggregation of other alloying elements near the interface and IMC which destroys the reliability of the interface is formed. The Ni barrier layer has a good barrier effect.

1. Introduction

Due to the highly integrated development of environmental protection and microelectronics technology, lead-free solder has become a research hotspot. Sn-Ag solder is widely used and is the most ideal lead-free solder. However, high melting point and high cost can not meet the development requirements of packaging technology. In order to reduce the melting point of Sn-Ag solder and improve its comprehensive properties, researchers at home and abroad obtain a wide range of lead-free solders by adding the third component. Among them, Sn-Ag-Cu and Sn-Ag-Zn alloy solders are recognized as the most promising lead-free solders. At present, Sn-Ag-Cu eutectic solder is the mainstream lead-free solder, but there are some main problems, such as high melting point, high cost, coarse intermetallic compounds greatly reduce the reliability and so on. K. S. Kim[1] studied Sn-Ag Cu ternary alloy solder. The strength of the alloy increases with the increase of Ag content, but the elongation decreases obviously, which is due to the formation of Ag3Sn phase. Ag3Sn particles increase with aging process. If these particles are formed in the stress concentration area, cracks will form along the particle interface. Howes studied the solubility of Cu in Sn-Pb alloy. It is found that the solubility of Cu decreases with the decrease of Sn content. When Sn-Ag-Cu solder is used in reflow soldering and wave soldering, the comprehensive properties of Sn-Ag-Cu solder are improved, but the wettability and interface reliability are still lower than those of Sn-Pb solder[2]. Adding Zn element into lead-free solder can improve the reliability of solder joint[1, 3]. J. M. Song and others studied the microstructure change of Sn-9Zn solder after adding a small amount of Ag, which improved the toughness of the solder alloy[4]. Y. L. Tsai [5] found that the melting point and melting range of Sn-9Zn solder increase with the increase of Ag content. Zn combines with anti-corrosion element Ag to form intermetallic compound to improve corrosion resistance. There are few researches on adding Zn as the third component in Sn-Ag solder at home and abroad, especially in Sn-Ag-Zn solder with low silver component[6, 7]. The addition of Zn
can inhibit the growth of intermetallic compounds and improve the reliability of solder joint interface[8,9,10]. There are few reports on its interface research, so it has a great development prospect.

2. Experiment
Pure tin, zinc ingot and pure silver were added into the crucible in proportion to melt at 600 °C for 30 minutes. The molten metal surface was covered with KCl LiCl and fully stirred to obtain uniform snagzn alloy. Weigh 1g Sn-1Ag-1Zn solder, put it into rosin solution and heat it to melt. Set the melting temperature at 260 °C. When the solder is melted into a ball, it is quenched in quenching oil, and the prepared alloy ball is cleaned with acetone and stored dry.

Put 1g small balls on a 100 mm * 100 mm copper plate, place them on the electric heating plate for 120 s, and set the temperature of the electric heating plate at 250 °C. After cooling, the spreading area of solder was measured, and the average value of three times of experimental data for each alloy solder was taken. Before the experiment, the copper plate was degreased with acetone, washed with deionized water, corroded in 10% HCl for 10s, the oxide film was removed, washed with deionized water and dried.

The size of the substrate is 30mm * 100mm. There are two kinds of substrates, one is the bare copper substrate, the other is the substrate plated with Ni barrier layer. The welding experiment was carried out with Rhesca ptr-1101 bonding tester with heating plate. Fix the base plate on the heating plate, heat it to 200 ℃, dip the prepared alloy solder ball with flux and place it on the base plate, and set the welding time for 20 seconds to make the solder fully spread. After welding, the substrate is cooled at room temperature. The solder joints welded on different substrate surfaces were aged for 10h, 100h and 1000h respectively in a 200 ℃ heating furnace. The microstructure of reflow soldering and aging solder joints was characterized by SEM and EDS.

3. Results and discussion
The microstructure of Sn-1Ag-1Zn alloy solder welded with bare copper substrate at 200 ℃ for 20s is shown in Fig. 1. It can be seen from the figure that a uniform intermetallic compound with a thickness of about 4um is formed between Sn-1Ag-1Zn and bare copper substrate after welding. The content of Zn and Ag is higher than that of Cu and Sn by eds. the intermetallic compounds at the interface are Ag3Sn, AgZn3 and Cu5Zn8. Among them, Ag3Sn and AgZn3 compounds are close to the solder side and push towards the solder.

The solder joints were aged at 200 ℃ for 10h, 100h and 1000h at 200 ℃ for 20s. After 10 h aging, the cross-section morphology of the interface is shown in Fig. 2. Compared with the interface morphology in Fig. 1 just completed welding, obvious delamination phenomenon appears in the welding interface after 10 h aging. According to the analysis of EDS, Ag3Sn extends into the solder and the
contrast is deep. Cu5Zn8 is on the side of copper substrate, and the contrast is shallow. The layered structure is evolved from the single layer structure after welding. In addition, there is no enrichment of other elements and no other types of intermetallic compounds near the interface.

When aging time is extended to 100h and 1000h respectively, the interface morphology is shown in Fig. 3. It can be found that with the aging time increasing, the interface morphology tends to be stable before 1000h and evolves on the double-layer structure, and the number of Ag3Sn with shallow contrast increases continuously. After 100h, Cu5Zn8 has been completely covered by it. However, the increasing trend of Ag3Sn thickness was not obvious, and kept about 4um. The morphology of Cu5Zn8 does not change with aging. The compounds on the interface surface were calibrated by XRD. The main intermetallic compounds are Ag3Sn, AgZn3 and Cu5Zn8. This is consistent with the result of the element content analysis in energy dispersive spectrometer.

When the aging time reaches 1000 h, the morphology of intermetallic compounds is obviously different. Ag3Sn continued to extend into the solder, and separated from Cu5Zn8. The density decreased obviously. Cu5Zn8 decomposed and new intermetallic compounds were produced. The thickness of Cu6Sn5 is 6um. The separation of Ag3Sn and Cu5Zn8 and the formation of new copper tin compounds are obvious. After aging for 1000 h, the interface morphology is shown in Fig. 4. On the interface between the solder and the copper substrate, Ag3Sn is island like and Cu6Sn5 is dispersed near Ag3Sn. In the lower part of the interface, tin in solder reacts with copper substrate to form Cu-Sn intermetallic compound.
Sn-1Ag-1Zn alloy solder was welded on Cu substrate with 3um thickness at 200 ℃ for 20s. The morphology and microstructure of the interface are shown in Fig. 5. The dark layer with a thickness of about 3um in the middle is a nickel barrier layer, the upper part is alloy solder and the lower part is copper substrate. There is no obvious intermetallic compound formation. The diffusion of Cu and Sn atoms is well prevented by Ni layer, and Sn, Ag and Zn are not accumulated at the interface between solder and Ni layer.

After the residual solder on the interface surface was corroded, the compounds on the interface surface were calibrated by X-ray diffraction. The calibration results show that the intermetallic compounds at the interface are Ag₃Sn, Cu₆Sn₅ and Cu₅Zn₈, which are consistent with the results obtained by EDS. Sn-1Ag-1Zn alloy solder ball was welded on Cu substrate with Ni layer barrier. After aging at 200 ℃ for 10 h, the morphology and microstructure of the welding joint are shown in Fig. 6(a). It is found that with aging, the thickness of Ni₃Sn₄ of Ni barrier layer and alloy solder increases slightly, and the thickness of barrier layer decreases, but the blocking effect is good. Ni atoms did not diffuse to both sides, Sn, Ag, Zn in solder and Cu atoms in substrate did not diffuse into the barrier layer. When the aging time was prolonged to 1000h, the microstructure of the interface was observed after 240h, 480h and 1000h, as shown in Fig. 6(b)(c)(d). It is found that the thickness of Ni₃Sn₄ compound between solder ball and barrier layer increases with the increase of aging time. However, the growth rate is relatively slow, and the thickness of the barrier layer becomes smaller, which can be understood as the reaction at the interface consumes the barrier layer. After aging at 200 ℃ for 1000 h, the thickness of the barrier layer is still about 60%, and the morphology is basically stable, and the blocking effect is stable. No other intermetallic compounds were formed. It can be further speculated that after further aging, there will be no aggregation of alloying elements and no other intermetallic compounds will be formed near the side barrier layer. The distribution of alloying elements in the solder joint is relatively stable, and the interfacial reaction between alloy elements and substrate is well prevented, and the microstructure near the interface is relatively stable.
After the solder was corroded, the intermetallic compounds at the interface were observed by scanning electron microscope. When the aging time is 1000 h, the morphology of the interface is shown in Fig. 9. It is found that the intermetallic compounds at the interface are granular. There are more granular compounds on the interface of bare copper substrate and less granular compound above the interface of copper plate with barrier layer. The content of elements in the interface was analyzed by energy dispersive spectrometer (EDS). It was found that the granular metal compounds at the interface were mainly Ag and Sn. Combined with the atomic number ratio, it is speculated to be Ag3Sn. At the bottom of the interface, the main elements are Sn and Ni. Combined with the atomic number ratio, the smoother structure is Ni3Sn4. Ag3Sn should be a metal compound formed by internal element diffusion in solder during aging. The results show that the amount of Ag3Sn at the interface of the substrate coated with Ni barrier layer is relatively small. It may be that Ni3Sn4 formed above the barrier layer consumes the Sn atoms from the interface, thus inhibiting the formation of Ag3Sn.

The phenomenon of lamellar exfoliation was found in some parts of the observed interface after solder removal, as shown in Fig. 7. Through the measurement of element distribution and content, it is found that the area covered by lamellar structure is mainly Sn and Ni. The spalling area of lamellar structure is mainly Ni, while the distribution of Cu is more uniform. It can be inferred from the above that the lamellar structure should be ni3sn4 above Ni and the Ni barrier layer below. The barrier layer effectively prevents the diffusion of atoms between the alloy solder and copper matrix. It is found that the atomic number ratio of Sn and Ni in lamellar structure is close to Ni3Sn4, and the content of other metal elements is very small. The results show that Ni and Cu are the main elements in the area after delamination, which further verifies the good blocking effect of Ni barrier layer.
4. Summary

In this paper, the wettability of multi-component Sn Ag Zn was studied, and Sn-1Ag-1Zn was selected as solder. The stability and reliability of the interface were studied by welding the alloy solder to bare copper substrate and Electroplated Ni barrier layer copper substrate and aging treatment at 200 °C. Sn-1Ag-1Zn has good wettability and forms complex metal compounds after being welded to bare copper substrate. From 200 °C aging, there are multi-layer intermetallic compounds at the interface, which form Cu5Zn8 and Ag3Sn in turn along the solder direction. After aging for 100 h, a double-layer structure is separated from each other to produce the effect similar to the barrier layer. After Sn-1Ag-1Zn solder was welded on the substrate of nickel plated barrier layer, Ni3Sn4 metal compound was formed on the surface, and its thickness increased slowly with the extension of 200 °C. The results show that the aging time is more than 1000h, the thickness of Ni3Sn4 is about 1um and relatively smooth, and the effect of nickel barrier layer is good. In the long aging process, the loss result is ideal, the heat aging resistance is good, the quality of solder joint is good, the reliability is high, and the environmental pollution is less. The low silver content of Sn-1Ag-1Zn solder reduces the cost and improves the properties. It is a promising alloy solder.

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