Microstructural Evolution in Sn/Pb Solder and Pd/Ag Thick Film Conductor Metallization

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Abstract—Intermetallic compound formation between thick film mixed bonded conductor and Sn/Pb solder is investigated. Microstructural evolution of the interfacial morphology, elemental, and phase distribution are probed with the aid of electron microscopy and X-ray diffraction. A decrease in adhesion strength occurs when the sample is aged at 130°C for long periods of time. Microstructural analysis reveals the formation of intermetallic compounds Pd$_3$Sn, Pd$_5$Sn, Pd$_3$Sn$_2$, PdSn, Pd$_2$Pb, Ag$_3$Sn, and Ag$_2$Sn. A possible mechanism of adhesion loss for the conductor is described. In the initial stage, the fracture interface is located where the Pd$_2$Pb exists, which is near the solder. However, the fracture takes place within the solder after aging. It is argued that volume change of the conductor film resulting from the intermetallic formation and incoherency between the compounds due to grain growth are major factors in the degradation of the peel strength.

I. INTRODUCTION

The soldered joint is widely applied on all electronic products for practical applications, such as computers, radios, TV sets, etc. [1]. However, the soldered joint will degrade after extensive use and the mechanical strength will decrease. As a result, the electrical resistance will increase or the fillet's volume will shrink [2], [3]. The degradation is believed to be accompanied by the interfacial interaction between the base metal and the solder which will produce the intermetallic compound at the interface [2]. To prevent the joint degradation, the mechanism must be probed and understood.

Thick films are widely used in hybrid microelectronics. As the device becomes miniaturized and condensed, the solder joint reliability is more crucial. In this paper, a series of aging tests at 130°C is performed to investigate the degradation of the soldered joints between the Pd/Ag thick film conductor and the Sn/Pb solder. The interfacial interaction and failure mode of the joint will be studied with the aid of electron microscopy and X-ray diffraction to reveal the morphological development and phase distribution.

II. EXPERIMENTAL PROCEDURES

In the solder–conductor interaction experiment, a Pd/Ag conductor paste, Dupont 6134, was used as the base metal. The major constituents of the conductor are Pd, Ag, and Bi, with the Pd/Ag ratio around 1/8.65 [4]. The leads were 0.8-mm diameter tinned copper wire, and were soldered with a 63 Sn/37 Pb eutectic alloy at 230°C, along with a RMA-type flux.

The conductor paste was printed through a 325 mesh stainless steel screen with a pattern [4] on a 96% Al$_2$O$_3$ substrate, then leveled in air for 10–15 min, dried at 150°C for 15 min, and fired in a belt furnace with a 32-min cycle including a dwell time of 850°C peak temperature between 7–9 min.

Crooks were carefully formed at one end of each wire lead as shown in Fig. 1(a)–(c), then the leads were slipped onto a test pattern with the wire centered over test pads. Each lead grips the substrate edge firmly at its crooked end and in contact with the underlying pads. A fixture which made the specimen easy to handle during soldering was applied on the other end of the substrate to keep the correct alignment.

Specimens were degreased in a solvent using an ultrasonic cleaner for at least 15 min, allowed to dry, and then dipped into the RMA-type flux from the crooked end about two thirds of the substrate in length. The molten solder bath was held at 230°C, and the surface was free of flux residues and dross. Substrates were vertically dipped into the bath until adhesion test pads were fully immersed after the flux was wicked up. The dwell time was 5 s. Soldered specimens were cleaned in three solvent-containing beakers using an ultrasonic cleaner, and the total cleaning time was about 20 min.

After a 12-h room temperature storage, specimens were placed in a 130 ± 5°C oven to be aged. The wires were bent into a 90° configuration, as shown in Fig. 1(d) and (e), after aging. Tests were conducted in a universal material test machine with a crosshead speed of 26.2 or 2.28 mm/minute, respectively. The adhesion strength was measured at the maximum breaking force divided by the test pad area, 2 mm by 2 mm. The fracture surfaces of test pads were evaluated by scanning electron microscopy (SEM) and electron probe microanalysis (EPMA). The phases were identified with a X-ray diffractometer (XRD). Several specimens were cut transversely with a diamond saw, and the cross-sectional view and the elemental distribution were inspected by EPMA.

III. RESULTS AND DISCUSSION

The specimens aged at 130°C were taken out after 40, 100, 210, 400, and 600 h to test adhesion strength and to evaluate the phases and microstructure. The adhesion strength...
of the conductor 6134 decreases with increasing aging time [4]. The strength loss is relatively abrupt at the first 100 h of aging for the 6134 conductor. After this initial period, the loss in strength is rather slow. Identical trends are observed for both the faster crosshead speed at 26.2 mm/min and the lower one at 2.28 mm/min. Phases at the fracture surface of the specimen are Ag$_2$Sn, Pb, and Pb$_2$Sn for 6134 at the beginning of aging, as shown in Fig. 2. After longer aging time, phases of Ag$_2$Sn, Ag$_3$Sn, Pb, Sn, Pb$_2$Sn, and Pb$_3$Sn occur in the conductor as shown in Fig. 2(b) and (c). Figs. 3-5 show the cross-sectional view of aged specimens. The results are summarized as follows.

1) Tin diffuses into the conductor film after soldering. It takes about 100 h to diffuse to the conductor/substrate interface.

2) The lead in the solder segregates above the silver-rich layer. This phenomenon is evident for the high silver content conductor 6134.

3) The palladium layer always has a greater thickness than silver. It covers the Pb layer, as palladium could form intermetallic compounds with lead on the basis of the Pd–Pb phase diagram. Pb$_3$Pb is the one found in the X-ray spectrum in this paper. It appears that Pb$_3$Pb segregates above the silver-rich compounds, Ag$_2$Sn and Ag$_3$Sn, while there is random distribution for the palladium–tin compounds.

4) After a period of aging, the intermetallic compounds exhibit the grain growth process and show a definite Pd-rich and Ag-rich separated region. For the high silver content conductor 6134, it takes about 600 h to reveal the separated region.
To characterize the interface where the fracture occurs, the fracture mode of the adhesion test is categorized as two types. They are: 1) A mode: the conductor/substrate interface loses their adhesion, and 2) B mode: the conductor/solder interface fracture occurs. Different types of fracture modes indicate different interfaces where the fracture could occur.

The fracture surface at the conductor/solder interface is shown in Fig. 6(a)-(f). The surface morphologies vary with the aging time. For specimens prior to the aging test, there are lots of bubbles and extruders on the fracture surface. The extruders are associated with the surface roughness of the conductor film. For the aged specimens, the chisel edge resulting from the ductile fracture forms a dimple structure, which tends to be more complete as the aging time is increased. Fig. 7 shows the fracture surface in the conduc-
The adhesion loss in thick film conductor at the initial time is abrupt, which is caused by the volume change accompanied with the compound formation. However, it tends to be slow for longer periods of time. The reason for this slow loss is not well understood. Although the redox reaction, indicated in (1), was proposed [7], the enhanced incoherency between the compounds seems to be the major factor in this study. Even for a conductor with a different Pd/Ag ratio [4], [9], this effect is evident. The only difference is the variation in transition time for the incoherency to be observed.

In real applications, the solder joint acts as an electric path between the chips and the printed circuit boards (PCB’s). The resistivity increases after aging. For example, the power dissipation resulting in waste of energy is uneconomical, and the heat evolved makes the joint degradation faster. The resistivities of the intermetallic compounds formed in this paper and of the raw metals can be found in the literature [10]. The intermetallic compound has a higher resistivity, which is two or three orders of magnitude higher than those of the raw metals. The Pd$_3$Pb compound, the Pb-rich layer formed across the electric path, especially increases the resistivity drastically.

IV. CONCLUSION

In a simulated microelectronic hybrid circuit, because there is interaction between the conductor and the substrate, the silver and palladium powders carried by the glass binder flow into the grain boundaries of the substrate where sintering occurs. This enhances the mechanical interlock and increases the adhesion strength. The decrease in adhesion strength occurs when samples are aged at 130°C for longer than 100 h. Investigation of the microstructure of the Sn/Pb alloy by SEM and EPMA reveals the segregation of Pb-rich and Sn-rich phases in the aged samples. X-ray diffraction results suggest the formation of the intermetallic compounds Pd$_3$Sn, Pd$_3$Sn, Pd$_3$Sn, Pd$_3$Sn, and Ag$_3$Sn. It is argued that volume change caused by the intermetallic formation and phase transformation in conductors with expanded lattice structures are attributed to the degradation of the peel strength.

REFERENCES


