Diffusion and intermetallics formation between Pd/Ag metallization and Sn/Pb/Ag solder in surface mount solder joints

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Abstract

Interdiffusion and intermetallics formation between metallization conductor Pd–Ag and solder 62Sn-36Pb-2Ag have been studied. Silver and palladium dot mapping images of solder joints demonstrate that the Pd–Ag metallization layer gradually disappears after 11 days of ageing. It is observed that silver-rich areas exist in the bulk of the 62Sn-36Pb-2Ag solder after ageing but palladium-rich areas are not evident. The diffusion coefficient of the silver in the solder joints for this material system was measured. The activation energy and pre-exponential factor for the silver diffusion were found to be about 0.475 eV and $0.56 \times 10^{-10}$ m$^2$ s$^{-1}$, respectively for the configuration of surface mount thick film solder joints studied. X-ray diffraction results reveal the formation of the intermetallic compounds Ag$_5$Sn, Ag$_3$Sn, Pd$_3$Sn$_2$, Pd$_5$Sn$_2$, Pd$_4$Sn, PbPd$_3$, and Pb$_3$Pd$_5$.

Keywords: Interdiffusion; Intermetallics; Joint; Metallization; Solder

1. Introduction

Thick film hybrid circuit technology is widely used in hybrid microelectronics. In this technology, a metallization pattern is printed on the ceramic substrate to form the circuit pattern. Ag/Pd-based conductors are probably the most commonly used alloy systems in thick film hybrid circuits [1]. The screen printing process is used to apply the material for conductors, resistors, and solder onto the ceramic substrate. The conductor material is held within an organic binder which contains a glass frit to bond the metallic conductor to the ceramic substrate during the sintering process. A similar process applies for the resistors. The solder, which is in the form of a paste consisting of solder particles and a flux binder, is screen-printed over selected conductor pads.

Components to be soldered to the assembly are then placed on the solder-coated conductor pads. A reflow-soldering process is then used utilising condensation (vapour phase) or infra-red techniques. The conductor material should be wetted satisfactorily by the solder:flux combination, but should not be leached away (dissolved) into the solder.

One of the main factors that affects reliability of a thick film solder joint is the interaction of the Pd/Ag conductor metallization with Pb/Sn solder. Some investigations of element diffusion, intermetallics formation, and the effects of temperature cycling tests on solder joint adhesion strength have been done previously [2–6]. The results show that swelling in the conductor film due to the volume change associated with element interdiffusion between the solder and the conductor and formation of intermetallics during soldering and service life, decreases the adhesion strength between the solder and the conductor. However, the interface reactions between the conductor metallization layer and the solder and especially the effects of thermal ageing at an
elevated temperature for real industrial assemblies are not yet well understood. Further understanding of the kinetics of the solid-state diffusion in the solder joints is very important for the electronics industry. This investigation aims at observing the interfacial reactions between the solder and metallisation layer and especially the effect of thermal ageing at an elevated temperature on the solid-state diffusion between a Pd–Ag metallised layer and 62Sn-36Pb-2Ag solder alloy. The data may find useful application in industry.

2. Experimental procedure

Commercial DuPont Pd/Ag (weight ratio: 1:3) conductor 6120 was printed on a 96% Al2O3 substrate (Kyocera, Japan) to form the electric circuit using thick film printing technology. After drying at 150°C for 10 min, the samples were air fired in a belt furnace. The total firing cycle time was 30 min with 10 min of peak firing at a temperature of 850°C. Surface mount passive components were then assembled on the substrates by means of standard infrared reflow using solder paste 62Sn-36Pb-2Ag (Electro-Science Laboratories, USA).

Separate test samples were aged isothermally in an oven at 70, 100, and 150°C for periods of 0, 2, 5, 11, 20, 32, and 47 days. The metallographic preparation of the solder joints was done according to the method described in our previous work [7]. The microstructure of the solder joints of the specimens was investigated with...
a scanning electron microscope (SEM JSM-820). X-ray element dot mapping was used to characterize the element interdiffusion at the interface of the conductor metallization and solder. Element diffusion depth measurements were taken from the samples, the mean of 10 readings taken at different locations on each sample being recorded. An X-ray diffractometer (XRD Siemens D500) was employed to investigate the composition of the intermetallics.

3. Results and discussions

3.1. Microstructure of solder joints

Backscattered SEM micrographs and X-ray element mapping for lead, tin, silver, and palladium of cross sections of a surface mount solder joint before ageing are shown in Fig. 1. The silver and palladium dot mapping demonstrates that a distinct layer of metallization conductor remains next to the ceramic substrate. The thickness of the metallization layer was approximately 10 μm.

SEM micrographs and X-ray element mapping for surface mount solder joints aged at 150°C for different times are presented in Figs. 2–7. There is evident tin diffusion into the Pd/Ag conductor. It is observed that the diffusing tin reaches the conductor/substrate interface after 120 h of ageing. The silver and palladium X-ray mapping reveals that the longer the ageing time the more serious the silver and palladium diffusion into the solder, with the silver diffusion rate somewhat lower.
than the palladium. Further work is required to understand the diffusion mechanism for this.

The silver and palladium dot mapping images of solder joints after ageing for 11 days at 150°C (Figs. 4–7) demonstrate that no distinct layer structure of metallization conductor remains next to the ceramic substrate, but the distribution of elements is not easy to quantify. The interdiffusion of metallization conductor and solder causing the metallization layer to gradually disappear may be a key factor affecting the adhesion strength of the solder joints.

It is worth noting that silver-rich areas exist in the bulk of the 62Sn-36Pb-2Ag solder. This is identified in the silver dot mapping images shown in Figs. 2–4 and 7. This may be a direct confirmation of the presence of Ag₅Sn primary crystals in the bulk solder, reported in the previous work [2]. However, palladium-rich areas in the bulk of the 62Sn-36Pb-2Ag solder are not evident.

3.2 Kinetics of solid-state diffusion

The diffusion coefficient is a most important parameter for describing the diffusion process. Over a wide range of temperature, experimentally measured diffusion coefficients often fit a relation [8]:

\[ D = D_0 \exp\left(\frac{-Q}{RT}\right) \]

where $D$ is the diffusion coefficient, $D_0$ is the pre-exponential factor, $Q$ is the activation energy, $R$ is the gas constant, and $T$ is the absolute temperature.
D = D_0 \exp(-Q/kT) \quad (1)

where: $k$ is the Boltzmann constant and $T$ is the absolute temperature. Both $Q$ and the pre-exponential factor $D_0$ are independent of temperature. $Q$ and $D_0$ depend on the identity of the diffusing element and the composition of the matrix crystal. External forces and pressure can also affect $Q$ and $D_0$. Eq. (1) is called the Arrhenius equation for diffusion. By definition, the experimental quantity $Q$ is given by

$$Q = -k \frac{\partial \ln D}{\partial(1/T)} \quad (2)$$

and is called the experimental activation energy.

The relationship between the diffusion depth and ageing time for the one-dimensional diffusion is considered to have the usual form [9]:

$$d = \sqrt{2Dt} \quad (3)$$

That is, the diffusion depth $d$ is proportional to square root of time $t$.

To determine the diffusion parameters, the diffusion depth of silver and palladium in all solder joints was measured. The observed diffusional direction is along the direction perpendicular to the substrate. The relationships between mean diffusion depth and square root of ageing time are plotted in Figs. 8 and 9. The
graphs show that the mean diffusion depth of silver and palladium in the surface mounted thick film solder joints increase linearly with the square root of ageing time, and the diffusion rate increases with ageing temperature.

From Eq. (3) and Fig. 9, the diffusion rate of the silver in solder joints can be determined and was found to be 14.16, 7.05, and 3.01 nm s$^{-1/2}$ for the ageing temperatures 150, 100, and 70°C, respectively. The activation energy related to the bulk diffusion for the silver in the thick film solder joints was found to be about 0.475 eV by plotting the Arrhenius curve, $d$ against $1/T$, shown in Fig. 10. The pre-exponential factor, $D_0$, for silver diffusion in the surface mounted thick film solder joint was found to be $0.56 \times 10^{-10}$ m$^2$ s$^{-1}$. The palladium diffusion rate is somewhat higher than that of the silver and was found to be 14.45, 9.63, and 4.81 nm s$^{-1/2}$ for the ageing temperatures 150, 100 and 70°C, respectively.

To evaluate the usefulness of the above results, some samples supplied by Hybrid Microcircuits and made from the same material system under the same conditions were investigated. These test samples had been stored at room temperature for about 3, 5, 6, and 8 years. The measured silver diffusion depth in the solder joints and the predicted depth, assuming stored at
30°C, calculated from Eq. (3) using the parameters determined above are compared in Fig. 11. The silver diffusion rate for the surface mounted thick film solder joints on the real industrial assemblies roughly agrees with that predicted from our ageing experiments. This means that the diffusion parameters we obtained may be used to predict the diffusion depth in industrial thick film solder joints. Hence the influence of silver diffusion on the reliability of real surface mounted thick film solder joints after electronic assembly operated at different thermal conditions for various times may be evaluated.

### 3.3. Intermetallics growth

The intermetallic growth within solder joints is not entirely understood. While the presence of intermetallic compounds is an indication that a good metallurgical bond has formed, however, too thick an intermetallic layer at the solder/conductor interface may affect the reliability of the solder joints [10]. X-ray diffraction patterns from a cross-section of the solder joint which had undergone 47 days isothermal ageing at 100°C are shown in Fig. 12. The XRD data reveals the coexistence of intermetallic compounds.
Fig. 7. Backscattered SEM picture and X-ray elements mapping of a cross sectional view of a solder joints after 47 days ageing at 150°C.

4. Conclusions

Interdiffusion and intermetallics formation between metallization conductor Pd–Ag and solder 62Sn-36Pb-2Ag have been studied. It is observed that diffusing tin reaches the interface of the conductor/substrate after 120 h of ageing at 150°C. Silver and palladium dot mapping images of solder joints aged at 150°C demonstrate that the metallization layer disappears after ageing for 11 days. It is observed that silver-rich areas exist in the bulk of the 62Sn-36Pb-2Ag solder after ageing.
but palladium-rich areas are not evident. The diffusion rate of the silver in the solder joints for this material system was found to be 14.16, 7.05, and 3.01 nm s$^{-1/2}$ for the ageing temperatures 150, 100, and 70°C, respectively, giving an activation energy and pre-exponential factor for the silver diffusion of about 0.475 eV and $0.56 \times 10^{-10}$ m$^2$ s$^{-1}$, respectively. The palladium diffusion rate is somewhat higher than that of the silver and was found to be 14.45, 9.63, and 4.81 nm s$^{-1/2}$ for the ageing temperatures 150, 100, and 70°C, respectively. The usefulness of these diffusion parameters were assessed through comparing the measured diffusion rate in surface mounted thick film solder joints in real industrial assemblies aged at room temperature with
Fig. 10. Arrhenius plot for the silver diffusion in the thick film solder joints studied.

that calculated using the parameters. These values are useful in predicting the silver diffusion depth in the thick film solder joints after electronic assembly operated at different thermal conditions for various times and hence contribution of diffusion depth to the reliability factor of the surface mounted thick film solder joints. X-ray diffraction results reveal the formation of the intermetallic compounds Ag₃Sn, Ag₅Sn, Pd₃Sn₂, PdSn, PdSn₂, PdSn₄, PbPd₃, and Pb₃Pd₅. Element interdiffusion, intermetallics formation, and consequent disappearance of the metallization layer may be the main factors affecting the adhesion strength and reliability of the surface mounted thick film solder joints on ceramic substrate.

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References