Effect of entropy production on microstructure change in eutectic SnPb flip chip solder joints by thermomigration

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(Received 30 August 2006; accepted 21 September 2006; published online 27 November 2006)

Thermomigration in flip chip solder joints of eutectic SnPb has been studied at an ambient temperature of 100 °C. Redistribution of Sn and Pb occurs with Pb moving to the cold end. A stepwise concentration profile is observed. Significantly, the lamellar microstructure becomes much finer after thermomigration. Since the lamellar interface is disordered and is a fast path of diffusion, it indicates a high rate of entropy production in the thermomigration, in agreement with Onsager's principle of irreversible processes. The effect of entropy production on microstructure change is shown here. The molar heat of transport of Pb has been calculated to be −25.3 kJ/mole. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2385205]

Recently, thermomigration has been reported to accompany electromigration in flip chip solder joints.[1–5] A temperature difference of 10 °C across a 100 μm diameter solder joint will produce a temperature gradient of 1000 °C/cm, which is sufficient to induce thermomigration from our previous calculation.[3] Hopkins and Co-workers used marker motion and void formation to detect the net effect of combining electromigration and thermomigration.[1,2] It was found that a redistribution of Sn and Pb occurred due to thermomigration, inferring that Sn has moved to the Si side (the hot side) and Pb to the substrate side (the cold side).[3] In a recent study by Chunang and Liu, they observed thermomigration in a bulk sample of eutectic SnPb alloy under a thermal gradient of 1000 °C/cm and found that the Pb phase was depleted in the hot side.[4] In this letter, we report the direct observation of thermomigration in eutectic SnPb flip chip solder joints. Redistribution of Sn and Pb occurred, with Pb moving to the cold end. It is a surprise to find that there is no linear concentration gradient of either Pb or Sn, as expected from the Soret effect, rather a stepwise concentration profile was observed. More significantly, the two-phase lamellar structure becomes much finer than that before thermomigration. Since the lamellar interfaces are disordered, it indicates a process of large entropy generation. Also since atomic diffusion along interfaces is faster than that in the lattice, the formation of fine lamellar structure may enhance the rate of entropy generation during the thermomigration. All these findings are in agreement with Onsager's principle of irreversible process in nonequilibrium thermodynamics. The finding of refinement of lamellar structure is a direct indication of the effect of entropy production on microstructure evolution.

Eutectic 37Pb63Sn flip chip solder joints were used in the study reported here. The under-bump-metallization (UBM) thin films on the chip side were Al (~0.3 μm)/Ni(V) (~0.3 μm)/Cu (~0.7 μm) deposited by sputtering. The bond-pad metal layers on the substrate side were Ni (5 μm)/Au (0.05 μm) prepared by electroplating. The height of the eutectic SnPb bump between the UBM and the bond-pad is 90 μm. The contact opening of the bump on the chip side has a diameter of 90 μm.

Figure 1(a) is a schematic diagram of the test sample having an array of 11 solder bumps. Among them, only one pair was stressed by electric current. When a dc of 0.95 A was applied through this pair of bumps (Nos. 6 and 7) at 100 °C, the average current density at the contact opening was 1.5×10^4 A/cm^2. Since the on-chip Al interconnects are the source of joule heating and Si is a good thermal conductor, a temperature gradient was produced across all the solder bumps[6,7] and caused thermomigration in all of them .[8] Therefore, the unpowered bumps in the sample were used to study thermomigration. After current stressing, the sample was polished to the center of the bumps with SiC papers and Al_2O_3 powder consecutively for cross-sectional examination. Optical microscope and SEM with backscattering mode were used to examine the microstructure change and image of composition redistribution of the cross section. Energy dispersive x-ray and electron probe microanalysis (EPMA) were used to analyze composition profiles across the cross section.

Figure 1(b) displays SEM images of the cross section of the row of 11 bumps after the current stressing for 27 h and 20 min. The direction of electron flow was marked by arrows. The lighter color in the SEM image is the Pb-rich phase and the darker color is the Sn-rich phase. Compared to the as-received sample shown in Fig. 1(b), the results show that the Pb-rich phase has moved to the substrate side (the cold side) in the unpowered neighboring bumps of Nos. 1–4 and Nos. 10 and 11. Also, the unpowered neighboring bumps of 5, 8, and 9 show the dendritic structure of crystallization of a liquid phase, indicating that they melted. In the pair of powered bumps, Nos. 6 and 7, they showed very different microstructure changes. The No. 6 bump, with electrons

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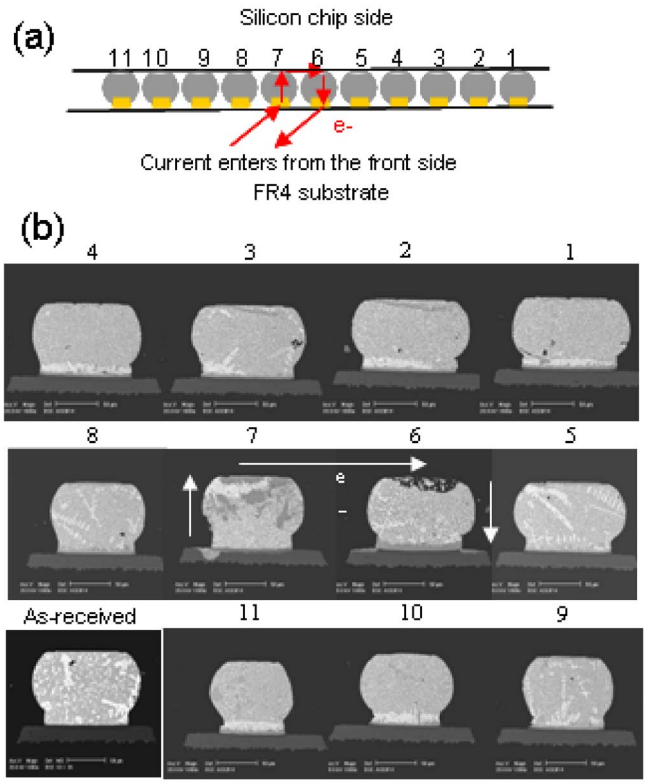

FIG. 1. (Color online) (a) Schematic diagram of 11 solder bumps with one pair of solder bumps under current stressing. (b) The cross-sectional SEM pictures of eutectic solder bumps after current stressing at 1.5×10^4A/cm^2 at 100 °C for 27 h, and 20 min.

flowed from the chip side to the substrate side, has a large pancake type of void at the cathode side and also shows evidence of melting. The No. 7 bump, with electrons flowed from the substrate side to the chip side, has no evidence of melting; instead a large amount of intermetallic compound (IMC) has formed at the anode side. A plausible reason of the difference between No. 6 and No. 7 is that in the latter the direction of thermomigration is opposite to electromigration, but in the former they are in the same direction.

From our previous systematic study, we have found that a critical current density of approximately 1.6×10^4 A/cm^2 exists. If the applied current density is 5% above the critical value, bumps will melt very soon. On the other hand, when the applied current density is below 1×10^4 A/cm^2, electromigration occurs in the powered bumps, yet the neighboring unpowered bumps hardly show any thermomigration. Therefore, we conclude that thermomigration occurs very close to the melting temperature in eutectic SnPb flip chip solder joints.

Besides thermomigration, the effect of back stress or stress gradient should be considered in the solder joint. Since the experiment occurred very near the melting point, stress relaxation occurs quickly. Even if a temperature gradient is produced across the bump, the cold end (substrate side) is still very hot for fast stress relaxation. Therefore, the back stress of solder joint in thermomigration is not as important as that in electromigration.

Figure 2(a) shows an enlarged SEM picture of bump No. 11. Significantly, the lamellar structure after thermomigration as shown in Fig. 2(a) is much finer than that before thermomigration as shown in Fig. 1(b). Figure 2(b) shows a higher

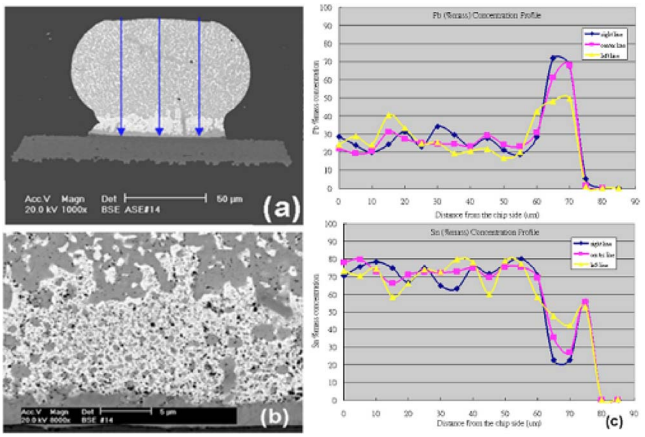

FIG. 2. (Color online) (a) Cross-sectional SEM picture of bump No. 11 after thermomigration at 100 °C. (b) Enlarged cross-sectional SEM picture of bump No. 10 near the substrate side. (c) The EPMA concentration profile across bump No. 11 from the chip side to the substrate side.

magnified image of the Pb-rich phase in the substrate side. It maintains a two-phase microstructure, but has a much finer microstructure too. We note that Fig. 5 in Ref. 5 has also shown the refinement of microstructure after electromigration and thermomigration.

The redistribution of Sn and Pb due to the accumulation of Pb to the substrate side (the cold side) can be seen in Fig. 2(a), yet there is no clear accumulation of Sn to the chip side (the hot side); it is likely that Sn may have reacted with Cu to form Cu–Sn IMC. The composition has a stepwise distribution. Figure 2(c) shows two concentration profiles of Pb and Sn respectively across the bump measured by EPMA. Three profile lines across the bumps were scanned and every line is the average of three sets of data points. Each point was taken at every 5 μm interval steps from the chip side to the substrate side. The results show that the accumulated concentration of Pb on the substrate side is about 73%, and in the rest the average concentration of Sn from the chip side to the substrate side ranges from 70% to 80%. Beyond the high-Pb region, the higher concentration of Sn at the bottom of the substrate side is due to the formation of Cu_6Sn_5 IMC.

What is unusual in Fig. 2(c) is that there is no clear concentration gradient across the bump, except a stepwise change from a rather uniform region to a high-Pb region. Away from the substrate side and the chip side, the average distribution of Pb and Sn in the bulk part of the sample is quite uniform, except for local fluctuations because of the two-phase microstructure. We recall that in thermomigration of C in the Fe–C system, Shewmon showed a linear concentration gradient of C,[9] which is expected from the Soret effect. To explain the flat concentration distribution observed here, we note that thermomigration is not driven by a concentration gradient. The concentration gradient observed in the Soret effect is induced by temperature gradient. However, in the eutectic two-phase structure, thermomigration will not induce or be counteracted by a concentration gradient. This is because below the eutectic temperature, the isothermal line within the miscibility gap in a binary eutectic system is a constant chemical potential line, independent of the concentration or volume fraction of the two primary phases according to equilibrium thermodynamics. Hence, the two-phase structure has no resistance to redistribution of concentration or volume fraction. Strictly speaking, we have a temperature

gradient so we may not use the concept of equilibrium thermodynamics to explain the observation. But, in our experiment, $\Delta T/T \sim 10/450$ is small, so the behavior of the two-phase structure is near equilibrium.

Onsager defined the conjugated flux and force in irreversible processes so that their product is equal to the product of temperature and entropy production per unit volume.[10] In thermomigration, the major entropy production is due to heat propagation under a temperature gradient, so

$$\frac{T}{V}\frac{dS}{dt} = \left(-\kappa\frac{dT}{dx}\right)\left(-\frac{1}{T}\frac{dT}{dx}\right), \tag{1}$$

where V is volume and S is entropy. If we take heat conductivity in solder as $\kappa \cong 50$ J/m s K, $dT/dx = 1000$ K/cm, and $T = 400$ K, we obtain $(T/V)(dS/dt) = 1.2 \times 10^9$ J/m^3 s. Other source of entropy production during thermomigration will be much smaller. The entropy production by atomic migration, the cross effect, can be estimated as

$$\frac{T}{V}\frac{dS}{dt} = \left(C\frac{D}{kT}F\right)F = C\frac{D}{kT}\left(3k\frac{dT}{dx}\right)^2, \tag{2}$$

where we have roughly assumed the driving force $F = 3k(dT/dx)$, where k is Boltzmann's constant, and $3kT(x)$ the local thermal (vibrational) energy per atom, and by taking $dT/dx = 1000$ K/cm, we obtain $(T/V)(dS/dt) = 3 \times 10^2$ J/m^3 s, which is much smaller than that due to heat propagation.

Now, if we take the lamellar interfacial energy to be 235 ergs/cm^2 as obtained from cellular precipitation in Pb(Sn) alloy,[11–13] we can estimate that the total interfacial energy in the microstructure as shown Fig. 2(b) is about 1–10 J/cm^3. This means that it takes less than 1 s in entropy production to produce more of the energy needed to create the disordered interfaces. However, in order to refine the microstructure, it requires atomic diffusion in thermomigration which takes time.

The accumulation of Pb at the cold side shows that Pb moves with the temperature gradient. We have estimated the heat of transport of Pb in the thermomigration by using the flux equation below:[9,10]

$$J = C\frac{D}{kT}\frac{(Q^*/N)}{T}\left(-\frac{\partial T}{\partial x}\right), \tag{3}$$

where Q^* is defined as heat of transport, which is the difference between heat carried by a moving atom per mole to the heat of atoms per mole at the hot end. C is concentration, D is diffusivity, N is Avogadro's number, and kT is thermal energy.

By measuring the accumulation width of Pb (12.5 μm) on the substrate side from Fig. 2(a), the total volume of atomic transportation can be obtained from the product of the width and the cross section of the solder joint. Therefore, we calculate the net atomic flux of Pb due to thermomigration as follows:

$$J_{\mathrm{TM}} = \frac{(\Delta C_{\mathrm{Pb}} AX)\rho/MN}{At}, \tag{4}$$

where ΔC_{Pb} is the change of Pb concentration (atomic fraction) in this accumulation layer, 0.32; X is the accumulation width of Pb; A is the cross section of the solder, 12 100 μm^2; ρ is the density of 27Sn73Pb, 10.25 g/cm^3; M is the molecular weight of 27Sn73Pb, 183.3 g/mole; and t is the operation time for thermomigration, 27 h and 20 min. Thus, we obtain $J_{\mathrm{TM}} = 1.36 \times 10^{14}$ at./cm^2 s.

Assuming a temperature gradient of 1000 K/cm, and a temperature of 180 °C, which is very close to the melting temperature of eutectic SnPb, and a diffusivity of $D_{\mathrm{Pb}} = 4.4 \times 10^{-13}$ cm^2/s, which is calculated from the data of Gupta *et al.*,[14] we substitute these values into Eq. (3) and obtain the molar heat of transport $Q^*_{\mathrm{Pb}} = -25.3$ kJ/mole. Compared to the reported molar heat of transport of eutectic SnPb alloy, −22.16 kJ/mole,[4] our value is a little bit larger. The discrepancy or the accuracy of determination of Q^* may be affected by the measurement of flux in Eq. (3) since the concentration distribution is nonuniform. The assumed temperature gradient may be incorrect. However, more serious is the basic assumption in the analysis that both Pb and Sn move with the temperature gradient. Actually if Pb is the dominant diffusing species and moves from the hot side to the cold side, the Sn will be pushed back in the opposite direction if we assume a constant volume process. The effect of reverse flux of Sn on the calculation of heat of transport in a two-phase microstructure should be studied, and we will need marker motion.

In conclusion, thermomigration was conducted in eutectic 37Pb63Sn flip chip solder joints at an ambient temperature of 100 °C. Redistribution of Sn and Pb occurred, having a stepwise concentration profile. Refinement of lamellar microstructure was observed. The molar heat of transport of Pb has been calculated to be −25.3 kJ/mole.

The authors at UCLA would like to thank the support from NSF Contract No. DMR-0503726.

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