Thermomigration in solder joints

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In 3D IC technology, the vertical interconnection consists of through-Si-vias (TSV) and micro solder bumps. The size of the micro-bump is approaching 10 μm, which is the diameter of TSV. Since joule heating is expected to be the most serious issue in 3D IC, heat flux must be conducted away by temperature gradient. If there is a temperature difference of 1 °C across a micro-bump, the temperature gradient will be 1000 °C/cm, which can cause thermomigration at the device operation temperature around 100 °C. Thus thermomigration will become a very serious reliability problem in 3D IC technology. We review here the fundamentals of thermomigration of atoms in microbump materials; both molten state and solid state thermomigration in solder alloys will be considered. The thermomigration in Pb-containing solder joints is discussed first. The Pb atoms move to the cold end while Sn atoms move to the hot end. Then thermomigration in Pb-free SnAg solder joints is reviewed. The Sn atoms move to the hot end, but the Ag atoms migrate to the cold end. Thermomigration of other metallization elements, such as Cu, Ti and Ni is also presented in this paper. In solid state, copper atoms diffuse rapidly via interstitially to the cold end, forming voids in the hot end. In molten state, Cu thermomigration affects the formation of intermetallic compounds.

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1. Introduction

Thermomigration has been studied since 1856 [1]. When an inhomogeneous binary alloy is annealed at an elevated temperature, it will become homogenous. On the other hand, when a homogeneous binary alloy is annealed under a temperature gradient, i.e., one end of it is hotter than the other end, the alloy will become inhomogeneous. This de-alloying phenomenon is called Soret effect, which is a cross-effect in irreversible processes between heat conduction and atomic diffusion [1–3]. The effect is caused by thermomigration or atomic diffusion driven by temperature gradient [4].

Thermomigration occurs in a pure metal such as Al, Zr, Cu and Zn [5–8]. We would expect that an Al utensil in kitchen, such as a cooking pot, should expand in size after years of use. This is because if the outside of the pot is about 500–600 °C and the inside is about 100 °C due to boiling water in cooking, the thermal gradient in the wall of 1 mm thick of the pot will be approximately 5000 °C/cm, Al atoms would have migrated from the outside to the inside and the latter should have expanded. Yet, this does not seem to happen! The reason is that the lattice diffusion in Al occurs through vacancy mechanism. The outside of the pot which is hotter will have a higher concentration of vacancies than that in the inside. The vacancy concentration gradient induces a counter atomic flux which might have compensated nearly all of the flux of Al atoms driven by the temperature gradient. The net change may be too small to be noticed.

Solder is typically a binary alloy [9–12], so Soret effect can be observed. Actually, Soret effect has been reported in PbIn alloy which forms solid solution over a wide range of concentration. Due to joule heating in 3D IC devices, the heat flow must induce temperature gradient in microbumps of Pb-free solders. Thermomigration will occur, not only because Pb-free solder is a low melting point alloy, but also because the alloying elements of Ag, Cu, and even Ni in the Pb-free solder diffuse interstitially in Sn. The fast interstitial diffusion will enhance the flux of thermomigration.

Furthermore, due to joule heating, electromigration may have caused a non-uniform temperature distribution in a flip chip solder joint [13–17], thus thermomigration may occur because of electromigration. Due to current crowding, the chip side of the flip chip solder joint is hotter than the substrate side. In other words, electromigration in flip chip solder joint is accompanied by thermomigration when a large current density is applied and when the current distribution is non-uniform in the solder joint due to
current crowding. The temperature gradient exists over the entire chip, hence it exists for those unpowered solder joints too. This can be regarded as an advantage in experimental study so that we can couple as well as decouple electromigration and thermomigration in our study. No doubt, we have to conduct experiments to study thermomigration alone, without electromigration.

In addition to 3D IC technology, thermomigration can occur in solder joints used in Si based solar cell technology. Under the sun, there will be a temperature gradient in the Pb-free solder joints which are used to join the Ag interconnects on the front surface of the cell. Thermomigration of Ag in molten Pb-free solder occurs rapidly. In solid state, thermomigration of Ag in Sn will be two to three orders of magnitude slower even at temperatures slightly above room temperature, because Ag is known to diffuse interstitially in Sn.

Thermomigration is a cross effect or interaction between heat flow and mass flow. In the analysis of thermomigration on the basis of irreversible processes, the heat flow $J_Q$ driven by temperature gradient and the mass flow $J_M$ driven by chemical potential gradient can be expressed as below:

$$J_Q = - L_{Q_0} \frac{1}{T} \frac{dT}{dx} - L_{Q_1} T \frac{d(\mu/T)}{dx} \quad (1)$$

$$J_M = - L_{M_0} \frac{1}{T} \frac{dT}{dx} - L_{M_1} T \frac{d(\mu/T)}{dx} \quad (2)$$

We note that the second term in Eq. (1) and the first term in Eq. (2) are the cross terms. When a sample is kept in a temperature gradient until a concentration gradient is established to balance the temperature gradient, it reaches a steady state where the mass flow $J_M$ will be zero. Taking $J_M = 0$, we have from Eq. (2):

$$\frac{1}{T} \frac{dT}{dx} = L_{Q_1} T \frac{d(\mu/T)}{dx} \quad (3)$$

By eliminating $\frac{dT}{dx}$, we have

$$d\left(\frac{\mu}{T}\right) = \frac{L_{Q_0}}{L_{M_1}} \frac{dT}{T^2} \quad (4)$$

Then, by differentiation, we obtain

$$d\left(\frac{\mu}{T}\right) = \frac{1}{T} \frac{d(\mu/T)}{dx} = \frac{1}{T} \frac{d\mu}{dx} - \frac{1}{T^2} \frac{dT}{dx} \quad (5)$$

Using the following thermodynamic relations,

$$d\mu = -SdT + VdP$$

and substituting them into the previous equation, we obtain

$$d\left(\frac{\mu}{T}\right) = \frac{VdP}{T} - H \frac{dT}{T^2} = - \frac{L_{M_0}}{L_{M_1}} \frac{dT}{T^2} \quad (7)$$

thus

$$\frac{VdP}{T} = \left( H - \frac{L_{M_0}}{L_{M_1}} \right) \frac{dT}{T^2} \quad (8)$$

For a better understanding of the meaning of $L_{Q_0}/L_{M_1}$ in the last equation, we consider the ratio of heat flow to mass flow under isothermal condition, that is, when $dT/dx = 0$. We have

$$\frac{J_Q}{J_M} = \frac{L_{Q_0}}{L_{M_1}} = L_{Q_1}$$

(9)

by using Onsager’s relation that $L_{Q_0} = L_{M_1}$.

The ratio of $L_{Q_0}/L_{M_1}$ represents the energy flow associated with a mass flow. Defining $Q^* = L_{Q_0}/L_{M_1}$, we have

$$\frac{VdP}{T} = (H - Q^*) \frac{dT}{T^2} = Q^* \frac{dT}{T^2} \quad (10)$$

where we define the heat of transport, $Q^* = H - Q$. We see that the heat of transport represents the difference between the energy associated with the materials that flows ($Q$) and the enthalpy of the materials ($H$) in the reservoir from which the flow starts. It is clear that if $H > Q^*$, the heat of transport $Q^*$ is positive, which means the reservoir temperature is higher than the temperature of the diffusing atom, or the atom is diffusing from hot to cold. On the other hand, if $Q^*$ is negative, atomic diffusion will be from cold to hot. In iron–carbon alloys, Shewmon showed that under a temperature gradient carbon moved to the hot side and a steady state was established. The value of $Q^*$ for carbon in α-iron is about $-24$ kcal/mol near 700°C. The sign of $Q^*$ will be discussed further in the next section.

2. Driving force of thermomigration

In thermoelectric effect where a temperature gradient can drive electrons, similarly a temperature gradient can also drive atoms in thermomigration. Essentially, the electrons in the high-temperature region have higher energy in scattering for interaction with a diffusing atom. On driving force of atomic diffusion, we recall Fick’s first law that the atomic flux driven by composition gradient or chemical potential gradient can be given as $[4,18,19]$

$$J = C\langle \psi \rangle = CMF = \frac{C}{kT} \left( - \frac{\partial \mu}{\partial x} \right) \quad (11)$$

where $\langle \psi \rangle$ is drift velocity, $M = D/kT$ is mobility, and $\mu$ is chemical potential energy.

Considering temperature gradient as the driving force, we have

$$J = \frac{C}{kT} \left( Q^* \frac{dT}{T} \right) \quad (12)$$

where $Q^*$ is defined as heat of transport. Comparing the last two equations, we see that $Q^*$ has the same dimension as $\mu$, so it is the energy or heat per atom. Furthermore, the sign of $Q^*$ can be determined by Eq. (12).

We recall the Fick’s first law of diffusion that $J = -D(\partial \mu/\partial x)$, where the atomic flux diffuses from high concentration to low concentration or downhill diffusion, the diffusivity $D$ is positive. The negative sign is conventional since the slope of $dC/dx$ is negative in the plot of $C$ vs. $x$. Typically, we draw a straight line of $C$ from upper left corner to lower right corner. The coordination of $x$ increases from left to right, but the $C$ decreases from left to right, so the slope is negative. On the other hand, in uphill diffusion where the atomic flux diffuses from low concentration to high concentration, $D$ is negative. The same applies to Eq. (12). If atomic flux diffuses down the temperature gradient, $Q^*$ is positive. But if atomic flux diffuses against the temperature gradient, $Q^*$ is negative. Therefore, we can conclude that if we find atomic flux moves from hot to cold, the $Q^*$ is positive. On the other hand, if atomic flux moves from cold to hot, the $Q^*$ is negative.

Hence the driving force of thermomigration is given as

$$F = \frac{Q^*}{T} \left( \frac{dT}{dx} \right) \quad (13)$$

To make a simple estimation of the magnitude of the driving force, we take $\Delta T/\Delta x = 1000$ K/cm, and consider the temperature difference across an atomic jump distance and take the jump distance to be $a = 3 \times 10^{-8}$ cm. We have a temperature change of $3 \times 10^{-5}$ K across an atomic spacing. So the thermal energy change will be

$3kT \Delta T = 3 \times 1.38 \times 10^{-23} (J/K) \times 3 \times 10^{-5} K \approx 1.3 \times 10^{-27}$ J.

As a comparison, we shall consider the driving force, $F$, of electromigration at a current density of $1 \times 10^4$ A/cm$^2$ or
1 × 10^8 A/m², which we know experimentally has induced electromigration in solder alloys.

\[ F = Z \times eE = Z \times e \rho j \]  \hspace{1cm} (14)

We shall take \( \rho = 10 \times 10^{-8} \Omega \text{m}, \) \( Z^* \) of the order of 10, and \( e = 1.602 \times 10^{-19} \text{C,} \) and we have \( F = 10 \times 1.6 \times 10^{-19} \text{C} \times 10 \times 10^{-8} \Omega \text{m} \times 10^8 \text{A/m²} = 1.6 \times 10^{-17} \text{C V/m} = 1.6 \times 10^{-17} \text{N}. \)

The work done by the electrical force in a distance of atomic jump of \( 3 \times 10^{-10} \text{m} \) will be \( \Delta w = 4.8 \times 10^{-27} \text{N m} = 4.8 \times 10^{-17} \text{J} \), which is close to the thermal energy change we have calculated for thermomigration. Thus, we can conclude that if a current density of \( 10^8 \text{A/cm}^2 \) can induce electromigration in a solder joint, a temperature gradient of 1000 °C/cm will induce thermomigration in a solder joint.

On heat of transport, we note that \( Q^* \) can be positive or negative. In Fe–C system, C was found to move to the hot end interstitially with a negative heat of transport [20]. In alloys of SnPb, when thermomigration drives Pb to move from the hot zone to the cold zone, it moves down the temperature gradient. But the thermomigration drives Sn to move in the opposite direction; it moves against the temperature gradient. The \( Q^* \) for Pb is positive or the heat decreases: it means Pb atoms move from hot end to cold end. But for Sn, the \( Q^* \) is negative since it gains heat; it means Sn atoms move from cold end to hot end. This can occur because we have one temperature gradient in thermomigration for both species, unlike interdiffusion in a diffusion couple, in which the concentration gradient of the two interdiffusing species is in opposite direction, so the chemical potential change can be positive for both species. It is worth mentioning when we analyzed flux motion in a two-phase structure of SnPb, we found that Pb is the dominant diffusing species and diffuses from the hot end to the cold end [21,22], and owing to conservation of mass, Sn is being pushed backward and it diffuses from the cold end to the hot end. However, when thermomigration of Sn occurs in Pb-free solders, it moves from cold to hot too, so the heat of transport of Sn is negative.

To measure \( Q^* \), if we know the atomic flux, we can use the flux equation to determine \( Q^* \) when diffusivity, the average temperature, and temperature gradient are known, as described by Eq. (12). Therefore, measurement of the average temperature and temperature gradient are critical to the calculation of \( Q^* \). In the following, we will review the thermomigration of constituent atoms of solder, Sn and Pb, as well as the other alloying elements.

The thermal gradient may be created during accelerated electromigration tests [23,24], in which the solder is in the solid state. Section 3 will review the thermomigration behaviors in the solid state. On the other hand, a thermal gradient may be generated during reflow/joining process, in which the solder are heated over their melting points. Thermomigration in the molten state of solder will be presented in Section 4.

### 3. Thermomigration in solid state solders

A solder joint consists of many materials, besides the solder alloy itself, there are under-bump metallizations (UBMs) on both sides of the joint, and all of them tend to migrate under a thermal gradient. Fig. 1 shows the schematic drawing of a typical solder joint. An adhesion layer is needed between the Al or Cu wiring trace and the UBM layer on the chip. Titanium is often adopted as the adhesion layer. The Ti film also serves as a diffusion barrier layer and its thickness is about 100 μm. For the UBM materials, Cu or Ni or a bilayer of them is chosen because they have excellent wettability with solders [12]. The solder may be SnPb, SnAg, or SnAgCu alloys. On the substrate side, the bond-pad metallization layer may be Cu or Ni again. Therefore the materials that may be subjected to thermomigration are, Pb, Sn, Cu, Ni, Ag and Ti in this system. We will review the thermomigration behavior of these elements.

Large thermal gradients may be created in the solder joints subjected to current stressing as well as in the neighboring unpowered joints. Fig. 2(a) shows the schematic drawing for the stressing circuit, in which Bump 2 and Bump 3 were applied by a direct current, but Bump 1 and Bump 4 were unpowered. On the...
chip side, an Al trace connects the four bumps together. Its dimension is 2550 μm long, 100 μm wide, and 1.5 μm thick. In this structure, an asymmetrical joule heating takes place during the current stressing. The Al wiring trace in the chip side has a small cross-sectional area of 100 μm × 1.5 μm. On the other hand, the solder joint and the Cu line on the substrate side have a cross-sectional area of π × 40 μm × 40 μm, and 100 μm × 25 μm, respectively. Therefore, the joule heating effect in the Al wiring trace is much higher than that in the solder joint and in the Cu line. Temperature simulation by finite element analysis was carried out to simulate the temperature distributions in the four bumps. The parameters used in this simulation are listed in Table 1.

Fig. 2(b)–(e) shows the temperature distributions in four solder joints in which Bump 2 and Bump 3 were applied by 1.8 A of direct current. Temperature gradients build up across the solder joints due to the asymmetrical joule heating, with hot end on the chip side and the cold end on the substrate side. The temperature gradient is denoted as the temperature difference across the solder, divided by the solder height, which is 50 μm in the present case. The temperature gradient has been simulated to be 1000 °C/cm and 1100 °C/cm in Bump 2 and Bump 3, respectively. It is noteworthy that the asymmetrical joule heating also generates large temperature gradients in Bump 1 and Bump 4, although no currents passed through.

Table 1

<table>
<thead>
<tr>
<th></th>
<th>Al</th>
<th>Cu</th>
<th>Ni</th>
<th>Ni3Sn4</th>
<th>Sn2.5Ag</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resistivity (μΩ·cm)</td>
<td>3.2</td>
<td>1.7</td>
<td>6.8</td>
<td>28.5</td>
<td>12.6</td>
</tr>
</tbody>
</table>

Fig. 3. Thermomigration in Pb-containing solders. (a) Schematic representation of experimental setup for thermomigration test: one pair of solder bumps (Nos. 4 and 5) under current stressing, and other un-stressed bumps under the influence of temperature gradient. (b) Cross-sectional SEM images of 2 of the stressed bumps (Nos. 4 and 5) and 4 of the un-stressed bumps (Nos. 2, 3, 6 and 7). The lighter color in the images is the Pb-rich phase and the darker color is the Sn-rich phases.
through them. This is because Si possesses an excellent thermal conductivity of 147 W/m K. The thermal gradient is 580 °C/cm and 600 °C/cm for Bump 1 and Bump 4, respectively. Therefore, these two bumps are quite suitable for thermomigration study without electromigration, whereas Bump 2 and Bump 3 can be used to examine the combined effect of thermomigration and electromigration on the microstructure changes of solder joints.

Furthermore, there also exist a lateral thermal gradient in the Bumps during current stressing. Fig. 2(b) shows the temperature distribution in Bump 2. Because the major heating source is the AI trace between the Bump 2 and Bump 3, the upper-right corner of the joint appears hotter than that on the lower-left corner. Yet, for Bump 3, the temperature on the upper-left corner is hotter than that on lower-right corner, as illustrated in Fig. 2(c). The temperature distribution in Bump 1 is similar to that in Bump 2, as depicted in Fig. 2(d), except the gradient is smaller. Fig. 2(e) shows that temperature map for Bump 4, which is similar to that in Bump 3. But the hot-spot temperature and the thermal gradient are lower than those in Bump 3. Experimental verification was reported by Hsiao et al. using infrared microscopy [25]. The temperature distribution will have an obvious effect on the thermomigration of atoms. We will discuss this in details later.

3.1. Thermomigration of Pb atoms

Thermomigration in eutectic SnPb solder was first reported by Ye et al. in 2003 [26]. They proposed that the SnPb solder migrate to the cold end of the solder joints. Huang et al. reported that Pb atoms were the dominated diffusion species for thermomigration in SnPb solder joints [27]. They proposed that it requires a thermal gradient over 1000 °C/cm in order to observe thermomigration behavior during electromigration tests. In order to measure heat of transport, Chung and Liu performed a thermomigration test in a bulk sample of eutectic Sn Pb solder under a constant thermal gradient of 1000 °C/cm [28]. They also observed that the Pb-rich phase was depleted in the hot side and the heat of transport was calculated to be +22.16 kJ/mol. Later, Ouyang et al. reported a direct observation of thermomigration in eutectic SnPb flip chip solder joints [29]. They found redistribution of Sn and Pb occurred, with Pb moving to the cold end. They also calculated the heat of transport of Pb to be +25.3 kJ/mol by measuring the thickness of Pb accumulation at the cold side. More significantly, the two-phase lamellar structure was found to become much finer than that before thermomigration. Since the lamellar interfaces are disordered, it indicates a process of large entropy generation. The finding of refinement of lamellar structure is a direct indication of the effect of entropy production on microstructure evolution due to thermomigration.

Fig. 3 displays backscattered electron microscope (SEM) images of the cross-section of the row of 8 bumps after thermomigration. The 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 arrows depict the electron flow direction. Among the 8 solder bumps, only one pair of bumps, No. 4/5, was current-stressed of 1.58 × 10^4 A/cm² for 21.5 h. Electrons entered the left solder bump from the bond-pad on the substrate and exited the bump from its upper right corner; they entered the Al interconnect on the top of the bump. The electrons then flowed along the Al line and entered another current-stressed solder bump from it upper left corner. When the solder bumps were under current stressing, the joule heating generated from the on-chip Al interconnects was greater than that from the Cu bond-pads on the substrate side, and thus the joule heating difference between substrate and chip established a temperature gradient across the solder bumps. This temperature gradient was transferred to the un-stressed bumps because Si chips are very good heat conductors. Hence, the un-stressed neighboring bumps in the flip chip samples were used to study the thermomigration induced by a temperature gradient. We can see that a Pb-rich phase was redistributed in the un-stressed bumps after thermomigration. For un-stressed bumps (Nos. 2 and 7) away from the current-stressed bumps, Pb-rich phase was observed to be accumulated on the substrate side, suggesting temperature gradient has driven the Pb atoms moving to the cold side. In additional to the vertical temperature gradient, a lateral temperature gradient was found to be established across the bumps. As shown in Fig. 3(b), a Pb-rich phase was redistributed to the upper-left-hand corner after 21.5 h. Since the upper-left-hand region is adjacent to the current-stressed bump, the above results suggest that Pb atoms were pushed to colder side.

It is of interest to find out if a concentration gradient of Pb exists, for either down-hill or up-hill diffusion. The accumulation of Pb at the cold side clearly shows that Pb moves with the temperature gradient and is the dominant diffusing species in thermomigration. If Sn was the dominant diffusing element, it should have been accumulated at the hot end. The Pb would be left behind and the average concentration of Pb in the bulk would increase. Fig. 4(a) and (b) shows respectively the concentration profiles of Pb and Sn across the bump after thermomigration using electron probe micro-analyzer (EPMA). Three straight lines across the bumps were scanned. Three kinds of curves – solid, broken, and dotted curves are shown in Fig. 4. Every line is the average of three
sets of data points, and each point was taken at every 5 µm interval steps from the chip side to the substrate side. The results show that the composition has a stepwise distribution across the solder joint. Since the diameter of the EPMA probe was of a few microns and is larger than the lamellar spacing, the measured composition was an average over several lamellae. Thus whether the Pb matrix is supersaturated of Sn or not could not be determined. In the meantime, the EPMA analysis indicates 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$_5$Sn$_3$ intermetallic compounds (IMC).

What is unusual in Fig. 4 is that no clear concentration gradient across the bump was found; except a stepwise change from a rather uniform region to a high-Pb region. Although the distribution of Pb and Sn in the bulk part of the samples shows local fluctuation due to the two-phase structure, the average distribution of Pb and Sn in these regions is still quite uniform. We recall that Shewmon showed a linear concentration gradient of C in thermomigration of C in the Fe–C system [13], 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 can be explained...
by the fact that the binary eutectic system is a constant chemical potential when the isothermal line is with the miscibility gap and below the eutectic temperature. It means that this binary eutectic system is independent of the concentration or volume fraction of the two primary phases according to equilibrium thermodynamics; therefore, the two-phase structure has no resistance to redistribution of concentration or volume fraction. Strictly speaking, we may not use the concept of equilibrium thermodynamics to explain the observation due to the presence of a temperature gradient in our system. But, in our experiment, $\Delta T / T \sim 10/450$ is small, so the behavior of the two-phase structure is near-equilibrium.

Compared to original SEM image of eutectic SnPb solder (Fig. 5), the lamellar structure after thermomigration is much finer than that before thermomigration. Additionally, the bulk part of the fine eutectic microstructure in the solder joint is quite uniform, as shown in Fig. 6(a). Fig. 6(b) shows a higher magnified image of the Pb-rich phase on the substrate side. It remains a two-phase microstructure, but has a much finer microstructure, too. In principle, when a eutectic two-phase microstructure is annealed at constant temperature, coarsening, instead of refinement, of the two-phase lamellar structure should occur to reduce the surface energy. Similar results were also observed in high Pb/eutectic SnPb composite solder joints [27], eutectic SnPb and SnBi solders [30,31].

Therefore, we suggest a possible mechanism on the formation of structural refinements (a more disordered state) by a thermal gradient. 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 [32]. During thermomigration, the major entropy production is attributed to heat propagation under a temperature gradient, thus

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

(15)

where $V$ is volume, and $S$ is entropy. If we take heat conductivity in solder as $k \approx 50 \, \text{J/m s K}$, $dT/dx = 1000 \, \text{K/cm}$, and $T = 400 \, \text{K}$, we obtain $(T/V)(dS/dt) = 1.2 \times 10^{11} \, \text{J/m}^2 \cdot \text{s}$. Other source of entropy production during thermomigration would be much smaller.

The entropy production by atomic migration, the cross-effect, can be estimated as

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

(16)

where the driving force $F$ was roughly assumed to be $3k(dT/dx)$ in which $k$ is Boltzmann's constant, $3kT(x)$ – local thermal (vibrational) energy per atom. By taking $dT/dx = 1000 \, \text{K/cm}$, we obtain $(T/V)(dS/dt) = 3 \times 10^{7} \, \text{J/m}^2 \cdot \text{s}$, which is much smaller than that due to heat propagation.

If we take the lamellar interfacial energy to be $0.235 \, \text{J/m}^2$ (235 erg/cm$^2$) obtained from cellular precipitation in Pb (Sn) alloy [33–35], the total interfacial energy in the microstructure as shown in Fig. 3 can be estimated 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.

On the basis of the 2nd law of thermodynamics, not all the heat supplied to a system could be used to do work because a part of it has to be wasted. Joule heating is a kind of waste heat in electrical conduction. While a large amount of thermal energy was wasted, it seems that a small amount of configurational entropy was created in forming the nanoscale lamellar interfaces. While thermal entropy cannot convert into configurational entropy, the former could induce tremendous increase in the temperature of Si chip. Since interfacial diffusion is faster than lattice diffusion, the formation of a large number of lamellar interfaces may have enhanced the rate of entropy production during thermomigration, in agreement with Onsager’s principle of irreversible process in non-equilibrium thermodynamics.

To separate the effect of thermomigration from electromigration, Hsiao et al. adopted alternate current to stress eutectic SnPb solder joints [36]. Because the alternate current generates the same of joule heating as the direct current does, but it does not introduce electromigration. They also use infrared microscope to measure the thermal gradient across the solder bump. In addition, markers were used to measure thermomigration flux, so that the heat of transport of Pb can be measured to be $+26.6 \, \text{kJ/mol}$.

Fig. 8. Cross-sectional SEM images showing the microstructure evolution during thermomigration under a thermal gradient of $2829 \, ^\circ\text{C/cm}$. (a) 0 h; (b) 300 h; (c) 550 h; and (d) 800 h. Tin atoms was observed to move upward to the chip, which is the hot end.
Furthermore, the thermomigration of Pb in solder joints can be also illustrated in Fig. 7. Fig. 7(a) shows the cross-sectional image of SEM for a eutectic SnPb joint before thermomigration tests. The UBM on the chip side is 5 μm Cu/3 μm Ni. The metallization on the substrate side is 3 μm electroless Ni on 20 μm Cu lines. The Pb-rich phase and the Sn-rich phase are distributed uniformly before alternate current (AC) stressing. After the current stressing at 1.88 A in Bump 2 and Bump 3 at room temperature for 6 h, the stressing circuit became open. No current passed through Bump 1 and Bump 4. But significant thermal gradient was built up in them due to the current stressing in Bump 2 and Bump 3. Fig. 7(b) shows the cross-sectional SEM image for Bump 1. The Pb-rich phase has migrated to the lower-left corner, which was the cold end. The temperature distribution for Bump 1 is similar to the one in Fig. 2(d). Yet, the Pb-rich phase in Bump 4 has moved to the lower-right corner, which was the cold end as shown in Fig. 7(c). Its temperature distribution is similar to the one in Fig. 2(e). The above results demonstrate that Pb atoms migrate to the cold end under a thermal gradient in solder joints.

3.2. Thermomigration of Sn atoms

It is intriguing that Sn atoms migrate to the hot end in both Pb-containing and in Pb-free solder joints. The thermomigration of Sn in eutectic SnPb solder is hard to be detected because Pb is the dominate diffusion species. However, the thermomigration of Sn can be studied in Pb-free solders. Hsiao et al. stressed Pb-free SnAg joints by alternate current at 100 °C [37]. They reported that Sn atoms migrated to the hot end and formed Sn hillocks there. Fig. 8(a) shows the cross-sectional SEM image for the eutectic SnAg solder joints before current stressing. The UBM on the chip side is 5 μm Cu/3 μm Ni. The metallization on the substrate side is 5 μm electroless Ni on 20 μm Cu lines. The solder consists of 3.5 wt% of Ag and 96.5 wt% of Sn. To measure the thermomigration flux, arrays of markers were indented by focused ion beam (FIB) on both the cold and hot ends. The joint was stressed by 0.57 A and the joule heating effect created a thermal gradient as high as 2829 °C/cm, with hot end on the chip side and cold end on the substrate side. After stressing for 300 h, hillocks of pure Sn started to emerge on the hot end, as illustrated in Fig. 8(b). As the stressing time increased to 550 h, the hillocks grew bigger, as depicted in Fig. 8(c). The Sn hillocks become more obvious after the thermomigration test for 800 h. Fig. 8(d) presents the microstructure change for the bump after 800 h. The arrows and the dotted lines in the figures indicate the position of the markers. Tin atoms moved upward to the chip, the markers moved downward to the substrate side. Therefore, the Sn atoms move toward the hot end. By measuring the displacement of the markers and the known thermal gradient, the heat of transport of Sn can be determined to be −1.36 kJ/mol. This value is much smaller than the heat of transport of Pb atoms, which is approximately +25 kJ/mol [28,29,36]. Therefore, Sn atoms are less susceptible to migrate in a thermal gradient. Ouyang and Kao performed in situ observation of thermomigration of 96.5Sn–3Ag–0.5Cu solder joints, and they confirm that Sn atoms migrate to the hot end [38]. In addition, the molar heat of transport of the Sn atoms is measured to −3.38 kJ/mol by marker displacement method.

Fig. 9 shows the schematic diagram of Pb-free 96.5Sn–3Ag–0.5Cu flip chip solder joints for thermomigration tests. The underbump-metallization (UBM) thin films on the chip side, Ti (ca.

![Fig. 9. Schematic representation of experimental setup for thermomigration test: one pair of solder bumps (Nos. 1 and 4) under current stressing, and bumps of No. 2 and No. 3 under the influence of temperature gradient.](image)

![Fig. 10. Cross-sectional SEM images of the same solder bump (No. 2) after in situ thermomigration at an ambient temperature of 150 °C for (a) 0, (b) 62 h. (c–d) Enlarged cross-sectional SEM images of bump No. 2 near (c) the chip side after thermomigration for 62 h and (d) the substrate side after thermomigration for 62 h.](image)
0.3 µm)/Ni(V) (ca. 0.3 µm)/Cu (ca. 0.7 µm), were deposited through sputtering. The bond-pad metal layers on the substrate side, Ni (5 µm)/Au (0.05 µm), were prepared through electroplating. The height of the 96.5Sn–3Ag–0.5Cu bump between the UBM and the bond-pad was 100 µm. Because the current passed behind the top of bump No. 1 and entered the top of bump No. 4, the bump No. 2 and No. 3 could be used to study thermomigration. Fig. 10(a) and (b) displays the evolution of the microstructure of solder joint No. 2 at an ambient temperature of 150 °C after thermomigration for 0 and 62 h (condition #1). Compared with the as-received sample in Fig. 10(a), Fig. 10(b) reveals that a mass protrusion appeared in the higher temperature region after 62 h, suggesting that Sn atoms were pushed to the hot side. Void formation was also evident on the substrate side. To provide a clearer view of the microstructures after thermomigration, Fig. 10(c) and (d) presents enlarged images of the hot and cold regions of bump No. 2 after 62 h of thermomigration, respectively.

In addition to the temperature gradient, the actual temperature of the sample is another important factor to trigger thermomigration in flip chip solder joints. Fig. 11 reveals the microstructural changes of the un-powered bump No. 2 under a current density of 1.4 × 10⁴ A/cm² at an ambient temperature of 125 °C before and after 341 h of thermomigration (condition #2). Notably, no significant microstructural change occurred in the un-powered bumps, even after 341 h of thermomigration. Furthermore, no evidence for void formation appears in the enlarged images of the substrate side (cold end) in Fig. 11(c). Because we used the same circuit design and same DC current magnitude, the joule heating generated under conditions #2 was the same as that under conditions #1; nevertheless, no thermomigration occurred because the ambient temperature for the former conditions (125 °C) was much lower than that for the latter. Thus, a critical temperature existed, between “125 °C + joule heating” and “150 °C + joule heating,” to trigger thermomigration. This situation might have arisen because current-induced joule heating at 125 °C was insufficient to raise the temperature close to the critical temperature for thermomigration. Similar results were also reported in the eutectic Pb–In solders [39], showing that thermomigration induced failure only occurs when temperature difference exceeded 8.5 °C at elevated temperatures.

The reason for this is most probably due to the presence of stress gradient. For a solder joint under a temperature gradient, thermomigration induced mass transport of Sn from the cold to the hot end and thus the latter will be in compression and the former in tension, resulting in a stress gradient. Since this stress gradient is in the opposite direction of temperature gradient, the driving force of thermomigration is counteracted by this stress gradient. This reasoning is similar to the back stress model of electromigration by Blech and Herring, in which the back stress gradient retards electromigration and a critical length of interconnect is obtained, below which no electromigration occurs [40].

Thus the net driving force of Sn due to the presence of temperature gradient and stress gradient could be expressed as

\[ F_{\text{Th}} - F_{\text{back.stress}} = Q^* \left( -\frac{dT}{dx} \right) \frac{d\sigma}{dx} + \Omega \]

(17)

where \( Q^* \) is the heat of transport, \( d\sigma \) is stress gradient, and \( \Omega \) is atomic volume.

Note that both driving forces listed in Eq. (17) are gradient dependent. After rearranging Eq. (17), the threshold temperature difference needed to trigger thermomigration is

\[ \frac{\Delta T}{T} = \exp \left[ \frac{\Omega}{Q^*} (\sigma_1 - \sigma_2) \right] - 1 \]

(18)

where \( \sigma_1 \) and \( \sigma_2 \) are maximum hydrostatic stresses that material can sustain at each end of bump. Eq. (18) suggested that the threshold temperature difference is a function of temperature. Additionally, we can see that the threshold temperature difference will be larger at lower working temperature, which is consistent to what we have observed in the Pb-free solder.

3.3. Thermomigration of Cu atoms

Thermomigration of Cu in Cu has been studied by Meechan and Lehman in 1962 [41]. They examined Cu thermomigration using a pure Cu disc maintaining one end at 1249 °C and the other end at 530 °C. The temperature gradient was 1194 °C/cm. The measured
heat of transport is \(+53 \pm 5\) kcal/mol. Later, Stracke and Herzig investigated Cu thermomigration in Pb at the temperature range of 181–303 °C [42]. They also reported that Cu migrated to the cold end and obtained the heat of transport to be +5.1 kcal/mol. The Cu interstitial diffusion in Sn matrix is extremely fast especially driven by a large thermal gradient [43,44]. Based on previous literature [45], Cu atom has the tendency to move to the cold end in solder in thermomigration. Therefore, thermomigration of Cu in Pb-free solder may become a serious problem in solder joints. Thermomigration induced failure was first reported by Chen et al. [46]. They performed

Fig. 12. Thermomigration of Cu in Cu/SnAg/Ni solder joints. Direct current of 0.55 A was applied through Bump 2 and Bump 3 at 150 °C. (a) Bump 1 before the thermomigration test. (b) Bump 4 before the thermomigration test. (c) Bump 1 after the thermomigration test for 76 h. (d) Bump 4 after the thermomigration test for 76 h. The Cu6Sn5 IMCs detached from the chip side after the thermomigration test.

Fig. 13. Thermomigration of Ni in Ni/SnAg/Ni solder joints. Direct current of 0.55 A was applied through Bump 2 and Bump 3 at 150 °C for 180 h. (a) Bump 1, no current passing through. (b) Bump 2 with downward electron flow. (c) Bump 3 with upward electron flow. (d) Bump 4, no current passing through. No damage due to thermomigration was observed.
Electromigration tests in eutectic SnAg solder joints with a 5 μm Cu UBM on the chip side, but serious Cu migration was found on the bumps without current stressing.

Fig. 12(a) and (b) shows the solder joints with 5 μm Cu UBMs before electromigration and thermomigration tests. The two joints to be tested were Bump 1 and Bump 4, respectively. Cu5Sn3 IMCs adhered to the Cu UBM very well. The solder joints were cross-sectioned and polished first to about their centers. Similar to the stressing layout in Figs. 2 and 7, electrical current of 0.55 A was applied through Bump 2 and Bump 3 at 150 °C on a hot plate, which corresponds to an average current density of 9 × 1012 A/cm² in the UBM opening. Therefore, the Bumps 1 and 4 did not have current passing through. Yet, the four bumps have experienced almost the same joule heating, because the Si die possess excellent heat conduction. The thermal gradient was approximately 1000 °C/cm for these two bumps [46]. After the current stressing for 76 h, the samples were polished slightly again for SEM observation, so that the shapes of the joints changed slightly. We observed that the Cu5Sn3 IMCs in both bumps migrated to the cold/substrate end after thermomigration. Fig. 12(c) and (d) shows the microstructure changes in the Bump 1 and Bump 4, respectively, after the thermomigration tests. There was almost no Cu UBM left on the hot/chip end for both bumps. An isothermal annealing at 165 °C at oven was performed to examine whether the aging can cause the Cu migration toward the substrate. The results indicate that Cu5Sn3 IMCs grew thicker after the isothermal annealing, but they still adhere to the remaining Cu UBM very well [47]. Abdulhamid et al. also observed thermomigration of Cu to the cold end in unstressed SnAgCu solder [48]. Therefore, Cu atoms migrate to the cold end in the solder joints.

3.4. Thermomigration of Ni atoms

Ni atoms also migrate toward the cold end [49]. However, theoretical calculation indicates that Ni atoms migrate slower than Cu in SnPb solder under thermal gradients. If we take the effective charge number of Ni to be 67 [43], resistivity as 6.4 × 10⁻⁸ Ω m, and the current density as 9.7 × 10¹³ A/m², the electromigration force is estimated to be 6.7 × 10⁻¹⁷ N using Eq. (4). The work done by the force in an atomic jump distance of 3 × 10⁻¹⁰ m is 2.01 × 10⁻²⁰ J. When the thermomigration force is balanced with electromigration force, a temperature difference of ΔT = 2.415 × 10⁻⁴ K is needed across an atomic jump, which is equivalent to 8050 °C/cm. That is, it needs a thermal gradient over 8050 °C/cm to observe thermomigration of Ni atoms during electromigration.

Fig. 13(a) through (d) show the cross-sectional SEM images of the four bumps with 3 μm Ni/5 μm Cu UBMs after stressed by 0.55 A at 150 °C for 180 h. The electrical layout is identical to that in Fig. 12. When they were stressed by 0.55 A, the measured thermal gradient was 857, 1286, 1429 and 857 °C/cm [47]. Voids formed only in Bump 3, which had a downward electron flow. These voids are caused by electromigration and they formed in the interface of the solder and the Ni3Sn4 IMCs. The resistance of this bump increased to 1.5 times of its initial value. It is interesting that there were no damages or voids observed in Bumps 1, 2, and 4, except that the thickness of Ni–Sn IMCs increased from 0.9 μm to 1.7 μm. The thermal gradients in the four bumps are much smaller than this value in the study. Therefore, migration of Ni–Sn compounds was not observed in the SnAg solder joints. We only observe electromigration damages during current stressing. Thus, no thermomigration of Cu and Ni was found in the joints with Ni UBMs. The results also suggested that the Ni UBMs serve as an excellent diffusion barrier for Cu thermomigration. It is speculated that the low Ni solubility in Pb-free solder also slow down the occurrence of the thermomigration of Ni atoms. Zeng and Tu reported that the solubility of Ni is only 0.28 wt% in Pb-free solders at 250 °C. However, the solubility of Cu is 1.54 wt% in Pb-free solders at 260 °C [50]. Therefore, the thermomigration of Ni is much less than that of Cu.

3.5. Thermomigration of Ag atoms

The two of the most popular Pb-free solders are SnAg and SnAgCu alloys, in which Ag concentration are about 2.0–3.5 wt%. Whether Ag atoms would migrate in a thermal gradient in the solder joint is of interests. It is reported that Ag atoms migrate to the cold end under a thermal gradient. Fig. 14(a) shows the cross-sectional SEM image for a solder joint before current stressing. The UBM on the chip side is 5 μm Cu/3 μm Ni. The metallization on the

![Image of thermomigration of Ag atoms](image-url)
substrate side is 5 μm electroless Ni on 20 μm Cu lines. The solder consists of 3.5 wt.% of Ag and 96.5 wt.% of Sn. Fig. 14(b) shows the distribution of Ag atoms analyzed by electron probe X-ray microanalyzer (EPMA). The Ag atoms dispersed in the Sn matrix uniformly in the as-fabricated sample. The joint was stressed by 0.57 A of an alternate current and the joule heating effect created a thermal gradient as high as 2829 °C/cm, with hot end on the chip side and cold end on the substrate side. The samples and the stressing conditions were identical to those in Section 3.2. After stressing for 800 h, some pure Sn accumulated on the hot end due to thermomigration, as illustrated in Fig. 14(c). However, the Ag atoms migrated to the cold end after the AC stressing, as shown by the EPMA mapping of Ag atoms in Fig. 14(d). They precipitated as large particles of Ag₃Sn intermetallic compounds there. The results indicate that the Ag atoms migrate to the cold end under the thermal gradient. Nevertheless, the Ag concentration was only 3.5 wt.% The migration of the Ag atoms may not cause any void formation. It deserves further study whether it will cause other reliability problems.

3.6. Thermomigration of Ti atoms

Ti has been widely adopted as the diffusion barrier between the Al trace and the Cu UBM. It is also an excellent adhesion layer between SiO₂ and Al or Cu films. It is reported that Ti has a large heat of transport value of 768 kJ/mol (if Ti moves to the cold end, it should positive value) [51,52] and is susceptible to migrate under a thermal gradient. Chen et al. reported that Ti atoms migrate to the cold end rapidly under a thermal gradient, resulting in severe deterioration of the interface between the Cu and Al layers as shown in Fig. 15 [53]. The samples for thermomigration tests were identical to the ones for thermomigration tests in Section 3.2, which were eutectic SnAg solder joints with 5 μm Cu UBMs. Fig. 15(a) shows the cross-sectional transmission electron microscope (TEM) for the UBM structure on the chip side. On the Al wiring trace, a Ti film of 0.12 μm thick was deposited between the Al trace and the 5 μm Cu UBM layer, which was labeled by the dotted lines in the figure. This Ti layer served as a diffusion and adhesion layer for Cu UBM and it adhered quite well to the Al and Cu films before thermomigration tests. Before the test, the sample was polished to its center first. Electromigration tests were performed at 0.55 A at 150 °C for 82 h. Then FIB was adopted to etch a cross section for the observation of the interface in Bump 1, which had no current passing through. After thermomigration tests at approximately 1000 °C/cm, the microstructure changes are shown in Fig. 15(b). Cold end locates on the right-hand of the figure because of the Al trace serving the major heating source. Some Cu₆Sn₅ IMCs still adhered to the Al trace. However, it is intriguing that the Al and the Ti layers were damaged and severe void formation occurred in the Al trace. It is speculated that the Ti layer had migrated into the Cu and Cu₆Sn₅ IMCs due to the thermal gradient because of it is very susceptible to migrate under a thermal gradient. Then the Al trace diffused into the Cu UBM because Al can easily diffuse into the Cu UBM to form Al–Cu solid solution or to react with Cu to form intermetallic compounds, resulting in the voids in the original location of the Al trace. Fig. 15(c) presents another sample after the thermomigration test for 82 h. The 5 μm Cu UBM was migrated to the substrate side due to thermomigration of Cu. Serious voids also formed in the Al trace after the thermomigration test. Therefore, Ti thermomigration also endangers the reliability of the solder joints.

4. Thermomigration in molten solders

In the processing of solder joints in flip-chip technology and microbumps in 3D IC, the solder bumps need to go through several reflows and each of them for about 1 min. For example, in flip chip technology the first reflow is needed to transform the plated solder cylinders into solder balls on the Si chip. Then, the Si chip is flipped over to align to a polymer substrate, and then they are refloved for chip-join [19]. For microbump fabrication, a Si chip is aligned to another Si chip and they are refloved for about 1 min [54,55].
During the joining processes, the solder needs to be melted to react with UBM to form IMCs. More reflows may be required when multiple chips are joined together. There may exist a temperature gradient during reflow process in oven or on a hot plate. In addition, hot compression method is sometimes adopted to join microbumps [56,57]. There will be a thermal gradient across the microbumps for hot compression because heat is applied through one of the chips. The thermal gradient across the solder should be much smaller than that during electromigration tests. However, the Cu and Ni diffusivities in molten solder is in the order of $10^{-3} \text{ cm}^2/\text{s}$, which is several orders in magnitude larger than that in solid state. Therefore, the thermomigration of Cu and Ni in molten solder may occur during reflow process when there is a small thermal gradient present in the joint. The migration of Ni and Cu atoms will affect the growth of interfacial IMCs and thus influence the reliability of the solder joints and microbumps.

4.1. Thermomigration of Cu atoms in molten solders

The samples used for thermomigration study in molten solders are different from those described above in solid state. Sandwich structures of Si/Cu/SnAg/Cu/Si were fabricated. The Sn2.5Ag solder of 19 $\mu$m thick was electroplated on patterned Cu UBMs, which were 100 $\mu$m in diameter and 20 $\mu$m in thickness. The fabrication of the microbumps were described in our previous publications [58,59]. The wafer was reflowed at 260°C for 1 min to form solder cap on the Cu UBM. To fabricate the test samples, a Si die was flipped over to align with another die and reflowed at 260°C for 3 min. In order to investigate the Cu thermomigration in molten state, the flip-chip samples underwent additional reflow of 5, 10, 20, 40 min on a hot plate or in an oven maintained at 260°C. Then the samples were cooled in air and the cooling rate was about 5°C/s.

Thermomigration Cu in molten solders was first reported by Guo et al. [60]. In our samples, Fig. 16(a) shows the cross-sectional SEM image for the as-fabricated sample. The bump height was approximately 30 $\mu$m. This sample experienced 3 min reflow at 260°C on a hot plate, where the bottom die contacted the hot plate and the top die was exposed to the air. Therefore, the bottom die was the hot end and the top die was the cold end, as labeled in the figure. IMCs of Cu$_6$Sn$_5$ formed at both Cu/solder interfaces. The measured thickness for the interfacial IMCs was 2.3 $\mu$m and 2.9 $\mu$m on the hot end and cold end, respectively. It shows that the IMC on the cold end is thicker. Fig. 16(b) presents the cross-sectional SEM image for the sample after an additional 10 min reflow at 260°C. The Cu$_6$Sn$_5$ IMCs on the cold end grew to 5.2 $\mu$m, whereas it is only 3.5 $\mu$m on the hot end. As the reflow time
increased to 20 min, as shown in Fig. 16(c), the IMCs on cold end increased to about 6.7 μm. Yet the IMCs on the hot end did not grow at all, remaining about 3.4 μm. When the reflow time increased to 40 min, Fig. 16(d) shows that the asymmetrical growth appears more significantly. The IMCs on the cold end grew to 12.3 μm, yet it is still 3.6 μm on the hot end. As a controlled experiment for comparison, samples were reflowed in an oven of uniform temperature for various periods. No obvious difference in IMC thickness was found on both ends. Fig. 17 summarizes the thickness of Cu6Sn5 IMCs as a function of reflow time on the hot end and cold end. In addition, the average IMC thickness for the sample reflowed in the oven was also plotted in the figure. The results indicate that the IMCs on the cold end have the fastest growth and the IMCs on the hot end grow slower than that in the oven.

The thermal gradient in the molten solders appears to be much lower than that in solid solder discussed above. Fig. 18 shows the temperature distribution in the molten solder when convection coefficient was set to 15 W/m²K. The thermal gradient was only 51 °C/cm across the molten solder.

4.2. Thermomigration of Ni atoms in molten solders

Sandwich structures of Si/Ni/SnAg2.5/Ni/Si were fabricated for the study of thermomigration of Ni in molten solders. The Ni layers were 5 μm thick fabricated by electroplating. The solder thickness is close to that used in Cu thermomigration in molten solders. Fig. 19(a) shows the as-fabricated microbumps. The cold end locates on the top side, whereas the hot end sits on the bottom side. There is no detectable difference in Ni5Sn3 thickness for the as-fabricated sample. As the reflow time increased to 20 min and 40 min at 260 °C, as shown in Fig. 19(b) and (c), there is no obvious thickness difference between the IMCs on the both ends. Therefore, the Ni migrates much slower than Cu in a thermal gradient and there is no detectable thermomigration of Ni during reflow process on a hot plate.

To further verify Ni will move to cold end or hot end in molten solder, the thermal gradient in the molten solder was increased by placing a blank Si chip on top of the microbumps. The schematic drawing for the experimental setup is shown in Fig. 20. Since Si is a good heat conductor, it will dissipate heat away from the top Si die.
of the microbump. Thermal paste of thermal conductivity of 4.5 W/m K was applied between the blank Si and the microbump to lower the thermal resistance of the entire structure. By this arrangement, the thermal gradient in the molten solder can be increased to approximately 300 °C/cm. Fig. 21(a) shows the interfacial IMCs growth after 10 min reflow at 260 °C. The thickness of the Ni3Sn4 IMCs was 1.74 ± 0.04 µm and 1.76 ± 0.03 µm for the IMCs on cold end and on the hot end, respectively. However, the thickness of the IMCs on the cold end grew thicker than that on the hot end after 40 min, as presented in Fig. 21(b). It is 3.03 ± 0.27 µm and 1.93 ± 0.08 µm for the IMCs on the cold end and on the hot end, respectively. As the reflow time increased to 100 min, the difference becomes more significantly, as shown in Fig. 21(c). The Ni3Sn4 IMCs grew as thick as 4.61 ± 0.34 µm on the cold end. Yet, it is only 2.12 ± 0.06 µm for the Ni3Sn4 IMCs on the hot end. Fig. 22 shows the Ni3Sn4 IMCs thickness as a function of reflow time for the both ends. The results indicate the thermomigration of Ni starts to affect the growth of the interfacial Ni3Sn4 IMCs after 20 min reflow. In addition, Ni atoms diffuse to the cold end under a thermal gradient, although the diffusion rate is much slower than that of Cu.

![Fig. 21](image)

**Fig. 21.** Thermomigration of Ni in molten solder at approximately 300 °C/cm. Cross-sectional SEM images showing the evolution of interfacial IMCs after various reflow times at 260 °C on a hot plate. (a) After 10 min reflow. (b) After 40 min reflow. (c) After 100 min reflow. The Ni–Sn IMC grew thicker on the cold end than that on the hot end.

5. Conclusion

Thermomigration is expected to be a serious reliability issue in microbumps in 3D IC technology due to joule heating. Thermomigration behaviors in solder joints were reviewed in this paper. In Pb-containing solders, Pb atoms are the dominated diffusion species and they migrate to the cold end under a thermal gradient. The heat of transport is measured to be +22 to +26 kJ/mol. However, Sn atoms migrate to the hot end in the thermal gradient. Its heat of transport is measured to be −1.36 to −3.38 kJ/mol. Thermomigration of Cu diffuse to the cold end very quickly in solder in both solid and molten solders. On the other hand, the thermomigration of Ni is much slower in both solid and molten solders. Thermomigration of Ti is a serious issue, since it may damage the contact interface between the Al trace and the Cu UBM because it migrates to the cold end. Ag atoms also migrate to the cold end in solid solder.

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