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Postprint: Reverse Polarity Effect in Liquid-Solid Electromigration of Ni/Sn-9Zn/Ni Solder Joints

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Abstract

The effect of liquid-solid electromigration on the interfacial reactions in Ni/Sn-9Zn/Ni linear solder joints under conditions of 230 °C and 5$×10^{3}$ A/cm^2 was investigated. During liquid-solid electromigration, Ni/Sn-9Zn/Ni solder joints exhibited a pronounced reverse polarity effect, wherein the intermetallic compound (IMC) at the cathode interface continuously grew thicker and remained consistently thicker than the IMC at the anode interface. Since back stress effects were excluded, the anomalous migration behavior of Zn atoms in the Sn-9Zn liquid solder was attributed to their effective charge number being positive at high temperatures; that is, under the electron wind force, Zn atoms migrated directionally toward the cathode interface, thereby inducing the reverse polarity effect in the solder joint during liquid-solid electromigration. After reflow soldering, a thin Ni5Zn21 layer formed on both interfaces of the Ni/Sn-9Zn/Ni solder joint. During the liquid-solid interfacial reaction process (without current), the IMCs at both interfaces of the solder joint grew thicker with time, thereby consuming Zn atoms from the solder and altering the phase equilibrium at the interface, which caused the interface IMC to transform from Ni5Zn21 to [Ni5Zn21+(Ni, Zn)3Sn4]. In contrast, during liquid-solid electromigration, the type of IMC at both the cathode and anode interfaces remained Ni5Zn21, and no transformation of IMC type occurred. This was because, under the electron wind force, the Zn atom content in the solder near the cathode interface was sufficient for Zn to react with Ni to form Ni5Zn21-type IMC; simultaneously, the electron wind force also hindered the diffusion of Zn atoms toward the anode interface, thereby suppressing IMC growth at the anode interface and resulting in a thinner interface IMC, consequently preventing IMC type transformation at the anode interface as well. Furthermore, proof by contradiction was employed to further verify that the effective charge number of Zn is positive at high temperatures.

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Full Text

Study on the Reverse Polarity Effect in Ni/Sn-9Zn/Ni Solder Joints Undergoing Liquid-Solid Electromigration

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Abstract

This study investigates the effect of liquid-solid electromigration on the interfacial reaction in Ni/Sn-9Zn/Ni linear solder joints under conditions of 230 ℃ and 5$\times10^{3}$ A/cm^2. During liquid-solid electromigration, the Ni/Sn-9Zn/Ni joints exhibit a pronounced reverse polarity effect, wherein the intermetallic compound (IMC) layer at the cathode continuously grows thicker and remains consistently thicker than that at the anode.

By eliminating the influence of back-stress, the anomalous migration behavior of Zn atoms in liquid Sn-9Zn solder is attributed to their positive effective charge number at elevated temperatures. Specifically, under the electron wind force, Zn atoms migrate directionally toward the cathode interface, thereby inducing the reverse polarity effect during liquid-solid electromigration. After reflow soldering, thin Ni_5Zn_{21} layers form at both interfaces. During liquid-solid interfacial reaction without electric current, the IMC layers at both interfaces grow thicker with time, consuming Zn atoms from the solder and altering the phase equilibrium at the interface, which causes the interfacial IMC to transform from Ni_5Zn_{21} to [Ni_5Zn_{21} + $(Ni, Zn)_3Sn_4$]. In contrast, during liquid-solid electromigration, the IMC type at both anode and cathode remains Ni_5Zn_{21} without transformation. This occurs because, under the electron wind force, the Zn atom content in the solder near the cathode interface remains sufficient for Zn to react with Ni and form Ni_5Zn_{21}-type IMC. Simultaneously, the electron wind force impedes Zn diffusion toward the anode interface, suppressing IMC growth there and resulting in a thinner IMC layer, which prevents IMC type transformation at the anode. Furthermore, proof by contradiction is employed to verify that the effective charge number of Zn is positive at high temperatures.

KEY WORDS: reverse polarity effect, Sn-9Zn solder joint, electromigration, interfacial reaction, intermetallic compound

1. Introduction

Electronic packaging technology continues to develop toward miniaturization, high performance, and high reliability. The increasing power density and continuously shrinking bump size cause the average current density through individual bumps to rise dramatically (10^4–10^6 A/cm^2) [1], making electromigration a critical reliability concern in electronic packaging [2–4]. The physical essence of electromigration is that when electric current passes through an interconnect conductor, the directional movement of electrons collides with metal atoms and transfers momentum to them, causing metal atoms to migrate toward the anode and resulting in mass transport [3,5].

A unique and important characteristic of electromigration is the polarity effect, wherein the intermetallic compound (IMC) layer at the anode interface continuously thickens during electromigration, always remaining thicker than that at the cathode interface. Chen et al. [6,7] reported the polarity effect in electromigration processes. Gan and Tu [8] studied the polarity effect in V-groove solder joints during electromigration, finding that IMC growth kinetics at the anode interface followed a parabolic law, while cathode interface IMC growth was more complex.

However, the polarity effect of metal atoms during electromigration is not absolute. Some researchers [9–14] have discovered a reverse polarity effect in Sn-Zn based solders. Zhang et al. [9,10] found that Cu/Sn-9Zn/Cu joints exhibited a reverse polarity effect during solid-solid electromigration, attributing it to Sn atoms migrating toward the anode and generating back-stress that directed Zn atoms toward the cathode. Our research group observed the reverse polarity effect in Sn-Zn solder joints during liquid-solid electromigration through studies of Cu/Sn-9Zn/Cu and Cu/Sn-9Zn/Ni joints [11–14]. By experimentally eliminating back-stress effects and using synchrotron radiation real-time imaging to observe the entire reaction process, we determined that the reverse polarity effect resulted from directional Zn atom migration from anode to cathode (opposite to the normal direction that would produce the polarity effect), with the positive effective charge number of Zn atoms at high temperatures being the sole cause. However, in our study of Cu/Sn-9Zn/Ni joints during liquid-solid electromigration [11], regardless of current direction, Zn atoms always migrated directionally toward the Cu side due to the coupling of chemical potential gradient and electron wind force, forming a Cu_5Zn_8 layer with continuously increasing thickness, and no obvious reverse polarity effect was observed.

To exclude the influence of Cu atoms on Zn directional migration, this study employs Ni/Sn-9Zn/Ni linear joints to investigate the reverse polarity effect and its underlying mechanism during liquid-solid electromigration. The symmetric structure of linear joints simultaneously eliminates current crowding effects and Joule heating interference, making the experimental results more reliable.

2. Experimental Methods

This study prepared Ni/Sn-9Zn/Ni linear solder joints using a reflow soldering method. Before reflow soldering, the bonding surfaces of two Ni blocks were ground and polished. A Sn-9Zn solder foil was placed between the two Ni blocks, and two stainless steel wires with a diameter of 200 m were used to control the joint gap. The assembled sample was then placed in a reflow furnace and soldered at 270 ℃ for 4 min. The soldered samples were sectioned into linear joint specimens, and their four sides were ground and polished to prepare strip samples with a cross-section of 300 m × 300 m, as shown in [Figure 1: see original paper]. Finally, the prepared joints were sealed with adhesive.

Electromigration experiments on Ni/Sn-9Zn/Ni joints were conducted at a joint temperature of (230±4)℃*andcurrentdensityof*5.0×10^{3} A/cm^2 for durations of 1, 4, and 8 h. For comparison, liquid-solid interfacial reaction experiments (without current) were also performed at the same temperature. The electromigration experiments were carried out in an oil bath with silicone oil temperature set at 216 ℃. Due to Joule heating effects, the linear joint temperature rose to 230 ℃ within 5 min. During the experiments, a K-type thermocouple was periodically placed on the joint surface for temperature measurement.

After liquid-solid interfacial reaction and electromigration, specimens were ground, polished, and etched. A Zeiss Super 55 scanning electron microscope (SEM) with attached energy-dispersive X-ray spectroscopy (EDX) was used to analyze the morphology and composition of interfacial IMCs. AutoCAD software was employed to measure IMC layer thickness, with three fields measured per interface and three measurements taken per field, then averaged.

3. Results and Discussion

3.1 Initial Microstructure of Linear Joints

[Figure 2: see original paper] shows the microstructure of Ni/Sn-9Zn/Ni joints after reflow soldering. As shown in Figure 2a, the Sn-9Zn solder bonded well with the Ni substrate without defects such as voids. Figures 2b and c reveal thin, layered interfacial IMCs formed at both interfaces. EDX analysis identified these as Ni_5Zn_{21} with an average thickness of 0.68 m. Since the initial IMC thickness after reflow was very thin, it would not affect subsequent liquid-solid interfacial reaction and electromigration experiments. Liou et al. [15] studied the interfacial reaction between Sn-9Zn and Ni substrate at 255 ℃ and similarly found Ni_5Zn_{21} as the interfacial IMC after short reaction times. Additionally, Figures 2b and c show fine eutectic microstructure in the solder because Ni reacts slowly with the solder, forming only a thin interfacial IMC and consuming few Zn atoms, leaving the solder composition nearly unchanged.

3.2 Liquid-Solid Interfacial Reaction (Without Current)

[Figure 3: see original paper] presents the microstructure of Ni/Sn-9Zn/Ni joints

after liquid-solid interfacial reaction at 230 ℃ for 1, 4, and 8 h. The IMC layers at both interfaces grow continuously with time, and no massive IMC precipitation occurs in the solder. After 1 h of liquid-solid interfacial reaction (Figures 3a and b), continuous, relatively thick layered IMCs form at both interfaces. EDX analysis determined their composition as 22.52 at% Ni - 77.48 at% Zn, corresponding to Ni_5Zn_{21} without Sn atoms, with thickness increasing from the initial 0.68 m to 1.39 m. Due to Zn consumption by interfacial reaction, the solder has become hypoeutectic. After 4 h (Figures 3c and d), the interfacial IMC remains layered, with EDX composition of 22.02 at% Ni - 73.56 at% Zn - 4.42 at% Sn, indicating Ni_5Zn_{21} (with 4.42 at% Sn dissolved), and thickness further increases to 2.62 m. After 8 h (Figures 3e and f), two distinct IMC layers with different contrasts form at both interfaces. The thinner, brighter layer adjacent to the Ni substrate is a new phase formed after 8 h of reaction, while the thicker, darker layer near the solder side has similar contrast to the IMCs after 1 and 4 h. EDX analysis determined the compositions as 21.16 at% Ni - 23.02 at% Zn - 55.82 at% Sn and 20.90 at% Ni - 72.28 at% Zn - 6.82 at% Sn for the layers near the Ni substrate and solder side, respectively, corresponding to $(Ni_{0\cdot48}, Zn_{0\cdot52})_3Sn_4$ and Ni_5Zn_{21} (with 6.81 at% Sn dissolved), with thicknesses of 1.06 m and 4.19 m, respectively, giving a total interfacial IMC thickness of 5.25 m. In summary, during liquid-solid interfacial reaction of Ni/Sn-9Zn/Ni joints at 230 ℃, the interfacial IMC type gradually transforms from Ni_5Zn_{21} to $[Ni_5Zn_{21} + (Ni, Zn)_3Sn_4]$ with increasing reaction time.

As the liquid-solid interfacial reaction progresses, the layered IMC thickens, gradually reducing Zn content in the solder and altering the phase equilibrium at the interface. Consequently, after 8 h of reaction, the interfacial IMC transforms from Ni_5Zn_{21} to $[Ni_5Zn_{21} + (Ni, Zn)_3Sn_4]$. Wang and Chen [16] investigated interfacial reactions between Sn-xZn solders and Ni at 250 ℃, reporting that after 48 h of reaction between Sn-9Zn and Ni, the interfacial IMC remained Ni_5Zn_{21} with a thickness of 24 m because bulk solder provided sufficient Zn atoms without significant depletion. In contrast, Sn-3Zn/Ni reaction produced two IMC layers, $(Ni, Zn)_3Sn_4$ and Ni_5Zn_{21}, after just 1 h, and Sn-1Zn/Ni reaction yielded $(Ni, Zn)_3Sn_4$ IMC after only 5 min. This suggests that after 8 h of liquid-solid interfacial reaction, the Zn content in the solder was approximately 3 wt%. EDX analysis measured an average Zn content of 2.3 wt% in the solder, consistent with literature reports.

3.3 Liquid-Solid Electromigration

[Figure 4: see original paper] shows the microstructure of Ni/Sn-9Zn/Ni joints after liquid-solid electromigration at 230 ℃ and 5.0$\times10^{3}$ A/cm^2 for various times, with Figures 4a, c, and e showing cathode interface IMC morphology and evolution, and Figures 4b, d, and f showing anode interface IMC morphology and evolution. A clear reverse polarity effect is observed in Ni/Sn-9Zn/Ni joints, where the cathode interface IMC is thicker than the anode interface IMC, becoming more pronounced with increasing electromigration time.

At the cathode interface, after 1 h of liquid-solid electromigration (Figure 4a), a dense layered IMC forms with EDX composition of 20.50 at% Ni - 73.34 at% Zn - 6.16 at% Sn, corresponding to Ni_5Zn_{21} (with 6.16 at% Sn dissolved) and thickness of 1.41 m. After 4 h (Figure 4c), the layered IMC thickness increases to 2.83 m with composition of 23.80 at% Ni - 70.82 at% Zn - 5.38 at% Sn (Ni_5Zn_{21} with 5.38 at% Sn dissolved). After 8 h (Figure 4e), the layered IMC thickness further increases to 5.45 m with composition of 20.43 at% Ni - 74.03 at% Zn - 5.54 at% Sn (Ni_5Zn_{21} with 5.54 at% Sn dissolved).

At the anode interface, after 1 h (Figure 4b), a dense layered IMC forms with composition of 22.21 at% Ni - 73.52 at% Zn - 4.27 at% Sn (Ni_5Zn_{21} with 4.27 at% Sn dissolved) and thickness of 1.38 m, slightly thinner than the cathode interface IMC. After 4 h (Figure 4d), the layered IMC thickness increases to 2.35 m with composition of 20.38 at% Ni - 74.47 at% Zn - 5.15 at% Sn (Ni_5Zn_{21} with 5.15 at% Sn dissolved). After 8 h (Figure 4f), the layered IMC grows to 3.22 m, significantly thinner than the cathode interface IMC, with composition of 23.03 at% Ni - 71.55 at% Zn - 5.42 at% Sn (Ni_5Zn_{21} with 5.42 at% Sn dissolved). Additionally, EDX analysis after 8 h of liquid-solid electromigration shows that Zn content in the solder decreased from the initial 9 wt% to 1.72 wt%.

As shown in [Figure 5: see original paper], Ni/Sn-9Zn/Ni joints exhibit a reverse polarity effect during liquid-solid electromigration, with cathode interface IMC thickness exceeding that at the anode. This suggests that Zn atoms migrate directionally toward the cathode interface during liquid-solid electromigration, creating a Zn-rich zone near the cathode interface while the anode interface becomes Zn-depleted. This hypothesis is directly confirmed by Zn composition analysis of the joint after electromigration. [Figure 6: see original paper] shows the overall microstructure of joints after different electromigration times. After 1 h (Figure 6a), Zn content in solder near the cathode interface decreases to 6.41 wt% while that near the anode interface decreases to 5.20 wt%. After 4 h (Figure 6b), Zn content near cathode and anode interfaces decreases to 4.41 wt% and 2.36 wt%, respectively. After 8 h (Figure 6c), Zn content near cathode and anode interfaces decreases to 3.61 wt% and 0.93 wt%, respectively. The consistently higher Zn content near the cathode interface provides strong evidence that Zn atoms migrate directionally toward the cathode during liquid-solid electromigration.

3.4 Mechanism Analysis

The following analysis addresses why Zn atoms migrate directionally toward the cathode during liquid-solid electromigration. Zhang et al. [9] proposed that the reverse polarity effect in Cu/Sn-9Zn/Cu joints during solid-solid electromigration resulted from back-stress caused by Sn atom migration toward the anode, which drove Zn atoms toward the cathode. However, the reverse polarity effect observed during liquid-solid electromigration cannot be explained by the back-stress mechanism because back-stress does not exist in liquid solder. Therefore, another mechanism must be introduced to explain the reverse polarity effect in

Ni/Sn-9Zn/Ni joints during liquid-solid electromigration.

The atomic electromigration flux induced by an electric field is generally expressed as [17]:

$$J_{em} = C \cdot F_{em} \cdot M \tag{1}$$

where J_{em} is the atomic diffusion flux due to electromigration, C is atomic concentration, F_{em} is the force acting on atoms, and M is atomic mobility.

Atomic mobility M can be expressed using the Nernst-Einstein equation [18]:

$$M = \frac{D}{kT} \tag{2}$$

where D is the diffusion coefficient, k is the Boltzmann constant, and T is thermodynamic temperature.

The force F_{em} acting on atoms can be expressed as [19,20]:

$$F_{em} = eZ^*E \tag{3}$$

where e is electron charge, Z^* is the effective charge number of metal atoms, and E is electric field intensity.

The electric field E in equation (3) can be expressed as:

$$E = \rho j \tag{4}$$

where ρ is solder resistivity and j is current density through the joint.

Substituting equations (2), (3), and (4) into equation (1) yields the expression for electromigration flux:

$$J_{em} = \frac{eZ^*\rho jCD}{kT} \tag{5}$$

The effective charge number Z^* reflects the migration direction and capacity of atoms under electromigration conditions, making its intrinsic meaning crucial for understanding. Typically, the effective charge number is not constant but a temperature-dependent variable [21], related to temperature by:

$$Z^* = Z_{el} - c\rho \tag{6}$$

where Z_{el} is the nominal valence of atoms and c is a constant. Since resistivity ρ increases with temperature, the absolute value of Z^* decreases with increasing temperature.

During liquid-solid electromigration of Ni/Sn-9Zn/Ni joints, the reaction temperature reaches 230 ℃, suggesting that the Z^* of Zn atoms is positive at elevated temperatures. Consequently, Zn atoms continuously migrate directionally toward the cathode interface during liquid-solid electromigration, producing the reverse polarity effect.

To further verify that the effective charge number of Zn atoms is positive at 230 ℃, proof by contradiction can be applied. Assuming the effective charge number Z^* of Zn atoms remains negative, [Figure 7: see original paper] schematically illustrates Zn atomic fluxes during liquid-solid electromigration. Because Ni-Zn IMC formation at the joint interfaces consumes Zn atoms, the Zn content in solder near the interfaces is higher than at the interfaces, creating chemical potential gradients pointing toward the interfaces at both anode and cathode. Since the solder is molten, no back-stress exists, and Zn diffusion is driven by electron wind force and chemical potential gradients.

Assuming atomic flux toward the interface is positive, the Zn atomic flux expressions at anode and cathode interfaces are:

$$J_{anode} = J_{chem} + J_{em} \tag{7}$$

$$J_{cathode} = J_{chem} - J_{em} \tag{8}$$

where J_{anode} and $J_{cathode}$ are Zn atomic fluxes toward anode and cathode interfaces, respectively, and J_{chem} and J_{em} are Zn atomic fluxes induced by chemical potential gradient and electromigration, respectively.

Combining equations (7) and (8) yields:

$$J_{cathode} - J_{anode} = -2J_{em} \tag{9}$$

Since the reverse polarity effect occurs during liquid-solid electromigration, $J_{cathode} - J_{anode} > 0$, requiring J_{em} to be negative, meaning J_{em} must oppose the assumed direction in [Figure 7: see original paper]. This derivation confirms that the effective charge number Z^* of Zn is positive at 230 ℃.

4. Conclusions

(1) After reflow soldering, thin Ni_5Zn_{21} IMC layers formed at both interfaces of Ni/Sn-9Zn/Ni joints. During liquid-solid interfacial reaction without current, the interfacial IMCs gradually transformed from Ni_5Zn_{21} to [Ni_5Zn_{21} + $(Ni, Zn)_3Sn_4$]. This IMC type transformation resulted from continuous IMC growth consuming large amounts of Zn atoms from the solder, altering the phase equilibrium at the interface.

(2) Ni/Sn-9Zn/Ni joints exhibited a reverse polarity effect during liquid-solid electromigration, where the cathode interface IMC thickness continuously increased and remained greater than that at the anode. This phenomenon arises from Zn atoms migrating directionally toward the cathode under electron wind force and participating in interfacial reactions to form IMC. The IMC type at both anode and cathode remained Ni_5Zn_{21} without transformation. Under electron wind force, sufficient Zn atoms near the cathode interface enabled formation of Ni_5Zn_{21}-type IMC, while simultaneously impeding Zn diffusion toward the anode, suppressing anode interface IMC

growth and preventing IMC type transformation at the anode. Additionally, due to interfacial reaction consumption, Zn concentration in the solder decreased from the initial 9 wt% to 1.72 wt% after 8 h of liquid-solid electromigration.

(3) The positive effective charge number of Zn atoms at high temperatures is the fundamental reason for directional Zn migration toward the cathode in Ni/Sn-9Zn/Ni joints during liquid-solid electromigration, fundamentally differing from Zn migration induced by back-stress during solid-solid electromigration.

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