1. Introduction

The reliability of flip chip packages has emerged as a critical concern because of the demand for increasing current density with decreasing solder bump size. A common failure mode for flip chip packages is the open-circuit failure due to void formation at the intermetallic compounds. Failures of this type have been reported after prolonged current stressing at an elevated temperature and have been identified as a result of electromigration (EM) damage [1,2]. Under electromigration, IMC growth can be significantly enhanced and accompanied by Kirkendall void formation which plays an important role in controlling the lifetime of solder joints in flip chip packages [3,4]. Gan and Tu reported distinct characteristics for IMC growth at both anode and cathode and formulated a kinetic model to account for the current polarity effect on IMC growth [5]. In their model, the two intermetallic phases, Cu3Sn and Cu6Sn5, formed at the solder/UBM interface were not distinguished but treated as a single phase for simplicity. Following this study, Orchard and Greer analyzed the EM effect on compound growth at interfaces, taking into account the effect of interfacial reaction barriers but still treated only a single intermetallic phase [6]. Gurov and Gusak were the first to consider the formation of dual intermetallics under an electric field in the kinetic analysis and presented asymptotic solutions at steady state [7]. These authors found that the growth kinetics of the dual intermetallics can follow distinct growth modes depending on the balance of the interdiffusion and electromigration fluxes in individual compound layers.

This paper reports a comprehensive analysis framework for the study of EM enhanced IMC kinetics and void formation of Pb-free solders with two intermetallic compounds. The analysis was applied to analyze experimental results on IMC growth observed under EM between a Cu UBM and a Sn-based Pb-free solder. The kinetics of the two compound layers in a Cu–Sn diffusion couple was treated by taking into account the concentration-driven and current-driven mass transport of Cu and Sn atoms. The complexity of the model necessitates the use of simulated annealing (SA) for an efficient derivation of the many diffusion and EM parameters needed for the analysis. A vacancy transport model and a solder crack propagation model were included to study the EM enhanced void formation which is the most dominant factor controlling the EM lifetime of the flip chip connection. This provides a kinetic framework to analyze void and crack formation and the final failures of the solder joints under accelerated EM tests.
2. Kinetic formulation

A Cu–Sn diffusion couple was considered in which two intermetallic phases Cu3Sn and Cu6Sn5 formed between pure Cu and pure Sn phases. The two intermetallic phases have very narrow composition ranges, and the values of the boundary composition in atomic fraction are listed in Table 1. Fig. 1a shows the schematic composition profile of the diffusion couple. Within each phase, Cu and Sn atoms diffuse simultaneously and, in addition, they are subjected to an EM driving force due to the electron current from the under bump metallization (UBM) toward the top surface metallurgy (TSM). Darken’s equation for interdiffusion [8] can be modified to apply to this case, taking into account the atomic flux induced by both chemical potential and external electric field. The atomic flux due to chemical diffusion can be expressed as

\[
J^\text{chem}_{\text{Cu}} = -D_{\text{Cu}} \frac{\partial C_i}{\partial x}
\]

\[
J^\text{chem}_{\text{Sn}} = -D_{\text{Sn}} \frac{\partial C_i}{\partial x}
\]

where \( C_i \) is the concentration, and the subscript Cu is omitted for simplification unless otherwise denoted. The running index \( i \) denotes the phase in which interdiffusion takes place. The concentration is described as:

\[ C_i = C_0 n_i \]

where \( C_0 \) is the atomic density and \( n \) is the atomic fraction of Cu. In this paper, the atomic densities were assumed to be the same for all phases for simplification. It was also assumed that the vacancy concentration is low and therefore \( n_{\text{Cu}} \approx n_{\text{Sn}} = 1 \). The current induced atomic flux due to chemical diffusion is expressed as

\[
J^\text{EM}_{\text{Cu}} = C_0 D_{\text{Cu}} \frac{kT}{e} \rho j \phi = C_0 D_{\text{Cu}} \phi_{i,j} j
\]

\[
J^\text{EM}_{\text{Sn}} = C_0 D_{\text{Sn}} \frac{kT}{e} \rho j \phi = (C_0 - C_i)D_{\text{Sn}} \phi_{i,j} j
\]

where \( \phi = \frac{kT}{e} \rho j \) is the electromigration factor, \( Z' \) is the effective charge number, \( e \) is the electron charge, \( \rho \) is the resistivity, and \( j \) is the current density.

Combining the chemical diffusion flux and current induced flux into Fick’s 2nd law gives the governing equation of current enhanced interdiffusion:

\[
\frac{\partial C_i}{\partial x} = -D_{\text{Cu}} \frac{\partial C_i}{\partial x} + \phi \left( \frac{\partial C_i}{\partial x} \right)
\]

(3)

\[
\phi = \frac{\partial}{\partial x} \left( \frac{\partial C_i}{\partial x} \right)
\]

(4)

\( \phi \) is the effective interdiffusion–electromigration coefficient of phase \( j \). Fig. 1b shows the concentration profile across the interface between \( \alpha \) and \( \beta \) phases and its associated movement. The velocity of interface migration can be described in Eq. (5) based on the mass conservation principle. Both chemical diffusion and current induced diffusion cause the interfaces to move. Each compound phase grows or shrinks as a result of the migration of its interface boundaries.

\[
v_i = \frac{d \lambda_i}{dt} = v_i^\text{Chem} + v_i^\text{EM}
\]

(5)

where

\[
v_i^\text{Chem} = \frac{1}{C_{i+1} - C_{i-1}} \left( \frac{d \lambda_i}{dt} \frac{C_{i+1} - C_{i-1}}{D_{i+1} \frac{\partial C_i}{\partial x}} - \frac{d \lambda_i}{dt} \frac{C_{i-1} - C_{i+1}}{D_{i-1} \frac{\partial C_i}{\partial x}} \right)
\]

(6)

Table 1

<table>
<thead>
<tr>
<th>Atomic fraction of Cu at interfaces</th>
</tr>
</thead>
<tbody>
<tr>
<td>( n_{12} )</td>
</tr>
<tr>
<td>0.993</td>
</tr>
</tbody>
</table>

Due to the narrow range of the composition in IMC, it is a valid assumption that the composition profile would be reasonably close to steady state, that is, linear profile. If steady state assumption is made, Eq. (6) becomes:

\[
v_i^\text{EM} = \frac{j}{C_0(C_{i+1} - C_{i-1})} \left[ C_{i+1}(C_{i+1} - C_{i-1})\phi_{i+1} - C_{i-1}(C_{i+1} - C_{i-1})\phi_i \right]
\]

(7)

When deriving the parameters, Eq. (8) was used because it is a reasonable approximation and it provided the necessary computation efficiency. After these parameters were obtained, they were applied to a finite difference model that calculated the chemical diffusion component of the intermetallic compound growth using Eq. (6), which rendered a more rigorous representation of the IMC composition profile. The finite difference model is described in next section.

3. Numerical simulation

The numerical simulation was programmed with a Matlab 6.5 program using the finite difference method. The simulated domain was uniformly meshed by fixed grids that have a spacing of 25 nm. At the two boundaries of each phase, an extra cladding node was attached to the end of the nodal array in order to represent the moving boundary, as shown in Fig. 2. Overall, the simulation domain contained fixed nodes that describe the concentration in each phase and movable nodes that describe the migration of the interfaces. The fixed nodes had constant positions but variable concentration, while the movable nodes had variable positions but constant concentration.

Eq. (3) was applied in each phase and solved for the boundary conditions listed in Table 1. In dealing with the cladding interfacial
its thickness was directly measured on the micrographs. Therefore, the actual solder temperature in this experiment was 140°C over the nominal temperature 140°C, while purging with Ar gas to prevent oxidation. The intermetallic growth was also determined by measuring the thickness of each phase in cross-sectional scanning electron microscope (SEM) images.

4. Measurements of intermetallic growth

4.1. Electromigration experiment

EM experiments were performed on Sn–3.5Ag lead-free solder bumps with a Cu-based UBM stack as shown in Fig. 3a to measure current enhancement effects on IMC growth kinetics and void formation [2]. The test structures were subjected to a high current density (4.12 x 10^4 and 5.16 x 10^4 A/cm²) at elevated temperatures (140–150°C) for a prolonged period of time (>400 h). The joule heating effect was found to cause the actual solder temperature to rise about 10–15°C over the nominal temperature 140°C. Therefore, the actual solder temperature in this experiment was around 150–155°C.

In the EM tests, electron current flowed from the under bump metallurgy (UBM) to the top surface metallurgy (TSM). Cross-sectional images were taken using SEM to investigate the evolution of IMC phases and void formation. Each phase was identified by energy-dispersive X-ray analysis (EDX) performed in a scanning electron microscope. Due to the non-planar nature of the Cu6Sn5 layer, the coefficient of self-diffusion in pure Cu and pure Sn phases are readily available in ASM and diffusion handbooks [10–12]. Sn has been identified to have a tetragonal crystal structure [13] and anisotropic diffusion coefficients were reported [10]. Since the interdiffusion model in this paper is one dimensional, the anisotropy is neglected and only an average self-diffusion coefficient is used [11]. Dyson et al. reported the extremely rapid and anisotropic mobility of Cu in the pure Sn phase due to its fast diffusion by an interstitial mechanism [14].

The diffusion coefficients of Cu and Sn atoms in the intermetallics are not well documented although the interdiffusion coefficients of the Cu–Sn intermetallics have been reported. Both Mei et al. [15] and Onishi and Fujibuchi [16] have deduced the interdiffusion coefficients based on intermetallic growth in annealing experiments. Although the intrinsic diffusivities and activation...
energies they deduced were different, their interdiffusion coefficients were reasonably consistent at the temperature of interest. Bader et al. investigated the formation and growth of IMC in thin Cu–Sn–Cu tri-layers and reported the interdiffusion coefficient for Cu3Sn in thin films [17]. Tu derived the diffusion coefficients of Cu–Sn thin films by investigating the aging effect of Cu–Sn bilayer [18].

The EM driving force is measured by a dimensionless parameter, the effective charge number \( Z^* \) as defined below [19]:

\[
F_{\text{eff}} \equiv |e| Z^* E
\]  

(9)

Self electromigration has been reported for both Cu and Sn and their effective charge numbers have been reported [20–23]. However, this parameter has not been reported for Cu and Sn as dilute solute in each other. Hsieh and Huntington reported the effective charge number \( Z^* \) of Cu in Pb in the range of 0.6–3.25 [24]. The effective charge number \( Z^* \) of Cu in Pb and in Sn is expected to be similar because Pb and Sn are both quadrivalent metals in group IV with similar electronic configuration and Cu atoms diffuse interstitially in both host metals. The effective charge number of Cu in pure Pb is herein taken as that in pure Sn with reservation.

In addition to the interdiffusion coefficients of the intermetallic phases, the diffusivity and effective charge numbers of both diffusants Cu and Sn are required to calculate EM enhanced IMC growth according to Eq. (4). Although many of the parameters are not readily available in literature, the diffusion coefficients can be obtained together with effective charge numbers by virtue of the solution of the inverse problem of the experimental intermetallic growth [25].

5.2. Derivation of parameters using simulated annealing

Simultaneous derivation of these parameters is challenging. As reported in previous paragraphs, while some have been documented in literature, many more of these parameters have not yet been determined. Second, a closed form solution of the phase transformation kinetics of Eq. (5) is not available. Although it is possible to use empirical laws to interpret the experiment data, the rate constants used in empirical laws do not shed light on the diffusion behavior of the intermetallic system as do the diffusivity and the effective charge numbers. Therefore, in order to accurately obtain these parameters, a mathematical algorithm is required which can efficiently tackle an inverse problem with multiple variables and without closed form solution.

Simulated annealing (SA) utilizes an analogy between the process of physical annealing and the mathematical solution of the global minimum (stable state) of a function in which local minima (metastable states) may be present [26]. In this study, simulated annealing is used to find the set of best fit parameters which minimize the misfit function of intermetallic compound thickness, Eq. (10):

\[
S(m) = \frac{1}{N} \sum_{n} \sigma \left[ \frac{d_n(m) - \bar{d}_n}{d_0} \right]^2
\]  

(10)

where \( N \) is the total number of observables (IMC thickness), \( n \) is the running index for individual observable, \( d_n \) is the initial IMC thickness as measured from SEM images of intact solders, \( \bar{d}_n \) is the IMC thickness measured using SEM at a given time, \( m \) is the model parameter set (diffusion coefficients \( D \) and effective charge numbers \( Z^* \)), and \( \sigma \) is a weight parameter. \( d_0 \) is the theoretical IMC thickness as derived from numerical integration of Eq. (5). For simulated annealing, Eq. (8) that assumes steady state composition was used to calculate the chemical diffusion component of the interfacial velocity. Fig. 4 shows the experimental data used in this study to derive the parameters. The trend lines in Fig. 4 were empirically fit.

In order to minimize the misfit function, the simulative system was subsequently subject to random walks over the variable space, the predetermined variation range of the parameter set \( m \), in search of the optimal fit in a heuristic fashion. These random walks were accepted or rejected based on the favorability of the simulated energy criterion proposed by Metropolis [27].
P_{AB} = \min \left( 1, e^{-\frac{(S_A - S_B)}{\Theta}} \right) \tag{11}

where \( P_{AB} \) is the probability of acceptance of the transition from the model space \( A \) to the model space \( B \) and \( \Theta \) is the nominal temperature. The nominal temperature \( \Theta \) was gradually decreased and it was adjusted so that the acceptance rates of the unfavorable moves reached approximately 50% at the onset and <0.5% at the end of the simulation. The rationale of the controlled cooling schedule is to prevent the system from being trapped at metastable states (local minima) so that the stable state (global minimum) will be invariably reached. A periodic boundary condition was applied to the entire variable space to ensure equal probability for all possible states.

5.3. Discussion

The parameters were obtained very efficiently using simulated annealing. The results are listed in Table 2. The first step to verify the deduced diffusion coefficients was to calculate the interdiffusion coefficients of the intermetallic compounds and compare them with the literature reported values. In Table 2, \( D_{150} \) are the deduced diffusion coefficients. The interdiffusion coefficients calculated accordingly were found to be very consistent with the literature reported values. This suggests that the deduced diffusion coefficients have reasonable values.

In this paper, the parameters were estimated by fitting the compound kinetics data instead of being derived from explicit functional relationships. Therefore, questions arise regarding the ranges of the deduced parameters. The results in Table 2 represent the optimum fit to the experimental data. However, if the variance of the experimental data was taken into consideration, the deduced diffusivities fell within the ranges that span approximately 1 order of magnitude [28]. Therefore, we were not able to identify the fast diffusant in the intermetallic compounds since the component diffusivities in the IMC were found to be similar to each other. In addition, the effective charge numbers were not determined unequivocally due to their narrow variable ranges compared to the diffusivities. Therefore, the effective charge numbers represent only a rough estimate and should be regarded with caution.

The uncertainty was mainly attributed to the variance in the experimental data. In addition, restrictions of the fitting approach and secondary effects neglected by the model can also play a role. Further studies are necessary to include more experimental data points under various test conditions to improve the accuracy of the deduced parameters. Nevertheless, simulated annealing in conjunction with kinetic modeling was demonstrated to enable the investigation of the diffusion and EM parameters using the experimentally observed IMC growths.

For the derived diffusivities, it is interesting to note that the diffusivities of Cu and Sn in the intermetallics were found to be close to each other within one order of magnitude. It has been argued that diffusion in highly ordered intermetallic compounds occurs via more complex mechanisms because the simple nearest-neighbor jump of a vacancy will inevitably lead to disordering of the atomic structure. The concept of correlated nearest-neighbor vacancy jumping that maintains the atomic ordering was first proposed for the B2 atomic structure by Elcock and McCombie [30] and Huntington et al. [31] and was named as six-jump cycle (6JC) or Huntington–McCombie–Elcock (HME) mechanism. The result of the correlated jump mechanisms is the strong coupling between the component diffusivities of the intermetallics. Bakker [32] indicated that the 6JC mechanism imposes limits on the ratio of the component diffusivities as follows:

\[ 0.5 < \frac{D_A}{D_B} < 2 \tag{12} \]

where \( D_A \) and \( D_B \) are the component tracer diffusion coefficients. Due to the experimental errors that invariably occur, the diffusivities derived in this paper were not sufficiently definite to substantiate this relation. However, the ratios of the component diffusion coefficients (\( \frac{D_{Cu}}{D_{Sn}} \)) were 0.16 and 1.08 for Cu$_5$Sn and Cu$_5$Sn$_5$ respectively and they were not far off if not within the limits described by Eq. (12). Special attention deserved to be paid to the ratio for Cu$_5$Sn$_5$. Although the Cu$_5$Sn$_5$ structure is of B8-type, its composition range is approximately 0.54–0.55, which is close to the ideal composition, 0.5, of a B2-type structure. One would therefore...
expect the component its diffusivities to follow a relation close to Eq. (12) and the ratio obtained for Cu₆Sn₅ in this paper appears to be reasonable in this respect. The result regarding the ratio of the diffusivities of Cu and Sn is in good agreement with other findings in the literature [33,34].

6. Results and discussion

6.1. Kinetics of intermetallic growth

To investigate the intermetallic compound growth, kinetic modeling was conducted using the model developed in Sections 2 and 3 and the parameters derived in Section 5. Under thermal aging, Eq. (6) suggests that diffusion controlled growth rate is proportional to the concentration gradient. As the intermetallic thickens the concentration gradient across the phase decreases, so the growth rate decays over time following a parabolic law in general. The electromigration term in Eq. (5) is Eq. (7). The growth rate is a function of the current density and the concentration across the interface. Hence, under a steady current density, EM-induced growth remains at a constant rate even when the intermetallic thickens.

It is important to pay attention to two assumptions that were made in the formulation. First, the intermetallic compounds grow and shrink due to the phase transformations that take place at the interfaces. Second, the rate of the transformation is only controlled by the fluxes, that is, the reactions can occur as rapidly as the local diffusion can provide the atoms for reactions. The concentration at the interface therefore plays a critical role in the phase kinetics under electromigration through the action of the electron wind force. It contributes to a linear kinetics because it is an equilibrium factor and remains constant during the reactions.

However, it can not be ruled out that linear kinetics can also be a result of other factors such as the interfacial barriers that could limit the rate of transformation. This effect was first proposed by Gösele and Tu [35] and the simultaneous action of the electron wind force and the interfacial barriers was subsequently studied by Orchard and Greer [6]. The interfacial barriers were not included in this study because their effect could not be distinguished from the diffusivities during the parameters derivation.

The growth behavior for the two limiting cases can be readily deduced. At high current density, current induced growth dominates and the overall rate follows a linear law. At low or zero current density, however, current induced growth is absent and therefore the IMC growth should follow a parabolic law. In general, the growth behavior will be more complicated, depending on the balance of the mass fluxes driven by interdiffusion and EM.

Kinetic analysis was first conducted for the thermal aging condition, that is, when there is no current stressing (j = 0). Fig. 5 shows the variation of intermetallic thickness due to thermal aging at 150 °C along with the experimental data from a Cu–Sn thin film aging experiment [9]. The simulation results were in good agreement with the empirical data and the IMC growth kinetics apparently followed a parabolic law.

Simulation was conducted for IMC growth under EM at a nominal temperature 140 °C (joule heating corrected temperature ~150 °C) and two current stressing conditions: 4.12 × 10⁴ A/cm² and 5.16 × 10⁴ A/cm². Fig. 6a and b shows the simulated time dependency of the thickness of Cu₃Sn and Cu₆Sn₅ under the two EM conditions.

In Figs. 5 and 6, Cu₃Sn thickened with time both under electromigration and thermal aging. It seems that Cu₃Sn exhibits more significant thickening under thermal aging than under electromigration. However, this in part results from the fact that the initial thicknesses of the aging sample and the EM sample are different since the aging experiment was done with thin film samples whereas the EM experiment was done with solder joints in a package.

The overall intermetallic thickness of the EM sample was much thicker than that of the thermal aging sample because the initial intermetallic thickening of the EM sample was done during solder reflow. The fact that Cu₃Sn remains a very thin conformal layer

### Table 2

<table>
<thead>
<tr>
<th>Phase</th>
<th>Diffusant</th>
<th>Z</th>
<th>(D_{150}) (m²/s)</th>
<th>Interdiffusion coefficient (m²/s)</th>
<th>Interdiffusion coefficient literature (m²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu₆Sn₅</td>
<td>Cu</td>
<td>27</td>
<td>(3.7 \times 10^{-17})</td>
<td>1.87 \times 10^{-16}</td>
<td>2.87 \times 10^{-17} [16]-3.81 \times 10^{-16} [17]</td>
</tr>
<tr>
<td></td>
<td>Sn</td>
<td>24</td>
<td>(2.4 \times 10^{-16})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu₃Sn₅</td>
<td>Cu</td>
<td>26</td>
<td>(7.0 \times 10^{-16})</td>
<td>6.74 \times 10^{-16}</td>
<td>1.61 \times 10^{-16} [16]-4.19 \times 10^{-16} [29]</td>
</tr>
<tr>
<td></td>
<td>Sn</td>
<td>36</td>
<td>(6.5 \times 10^{-16})</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 5. IMC growth for thermal aging (a) plotted against time and (b) plotted against square root of time (experimental data courtesy of Siewert et al. from Ref. [9]).
The thickening of Cu$_6$Sn$_5$ was significantly enhanced by EM, as that the thickening of Cu$_6$Sn$_5$ not only is significantly enhanced both EM and aging experiments. Most important of all, it shows /C2\ Reflow Solid/liquid Layer Scallop Flux driven ripening Reaction Critical interface IMC morphology Mechanism Kinetics Ref

Table 3
Reactions at solder/IMC interface.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Critical interface</th>
<th>IMC morphology</th>
<th>Mechanism</th>
<th>Kinetics</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reflow</td>
<td>Solid/liquid</td>
<td>Layer</td>
<td>Scallop</td>
<td>Flux driven ripening</td>
<td>$t^{1/3}$</td>
</tr>
<tr>
<td>Aging</td>
<td>Solid/solid</td>
<td>Layer</td>
<td>Layer</td>
<td>Diffusion controlled</td>
<td>$t^{1/2}$</td>
</tr>
<tr>
<td>EM</td>
<td>Solid/solid</td>
<td>Layer</td>
<td>Electron path</td>
<td>Drift controlled</td>
<td>$t$</td>
</tr>
</tbody>
</table>

Fig. 6. Electromigration enhanced IMC growth under (a) $4.12 \times 10^4$ A/cm$^2$ and (b) $5.16 \times 10^4$ A/cm$^2$ (experimental data from Ref. [2]).

between Cu UBM and the adjacent phase adds to the difficulty of experimental determination of Cu$_3$Sn thickness. However, in general, the simulation still predicted the Cu$_3$Sn thickening within the error bars of the experimental data.

While the EM effect on the thickening of Cu$_3$Sn is not yet clear, the thickening of Cu$_3$Sn, was significantly enhanced by EM, as shown in Fig. 6. Simulation predicted the thickening of Cu$_6$Sn$_5$ of both EM and aging experiments. Most important of all, it shows that the thickening of Cu$_3$Sn not only is significantly enhanced by EM but has a linear time dependency.

This kinetic model successfully rendered an accurate prediction of intermetallic growth and movement, which was consistent with the experimental observation. However, there was still some discrepancy between simulation and experimental results. First, in the simulation, the Cu$_3$Sn phase did not extend itself as far into the solder and reach the TSM as was evidently observed in Fig. 3d. The discrepancy arose from the fact that the model was 1-D while the solder bumps under test were three dimensional structures. In a 3D solder bump, Cu$_6$Sn$_5$ not only grows along the electron current path due to current crowding [1,2] but also shrinks along lateral direction due to dissolution of the Cu UBM.

It is also important to extend some discussion regarding the intermetallic morphology observed in samples subjected to current stressing, Fig. 3d, and those subjected only to thermal aging, Fig. 3c. The distinct morphologies of the two intermetallic phases of reflowed solders are well known: a layer-type Cu$_3$Sn phase and a scallop-type Cu$_6$Sn$_5$, as shown in Fig. 3b. However, under high current stressing, the morphological development of the intermetallic phases noticeably followed the distribution of current flux divergence, as shown in Fig. 3d. This indicated that kinetics under EM dominated the evolution of the intermetallic morphology.

In order to understand the non-planarity of IMC, it is critical to distinguish the reflow reaction, one that occurs at solid/liquid interfaces, and the subsequent aging and EM reactions, ones that occur at solid/solid interfaces.

For reflow reaction, Kim et al. indicated that the size of Cu$_6$Sn$_5$ scallops approximately follows $t^{1/3}$ dependence kinetics, $t$ being the reflow time, and the scallops form by Ostwald ripening reactions [36]. Görlich et al. indicated that the wetting angle between adjacent scallops is an equilibrium feature at the reflow temperature and is related to the surface tension balance between molten solder/Cu$_6$Sn$_5$ interface and the grain boundary [37]. Based on these studies, it became clear that during reflow reactions, the IMC morphology and its growth kinetics is different from the phase growth in the solid state.

For solid state aging, Tu et al. found that, for post-reflow eutectic SnPb solder, the Cu$_6$Sn$_5$ morphology can gradually change from scallop-type to layer-type at a very slow rate [38]. They also indicated that the solid state aging kinetics follow a parabolic law. It is confirmed in the present paper that the parabolic kinetics can be attributed to the diffusion driven IMC growth model. In EM, however, we show that Cu$_6$Sn$_5$ growth can be significantly enhanced by current along the electron path and that the growth kinetics follows a linear law.

The comparisons between the Cu$_3$Sn reactions during reflow, aging, and EM are summarized in Table 3. Although the equilibrium IMC morphologies of these reactions are different, their kinetic behaviors can be explained by flux-driven approaches. Gusak and Tu devised a flux-driven ripening theory to explain the growth kinetics and size distribution of Cu$_6$Sn$_5$ scallops during solder reflow reactions [39]. We presented in this paper the kinetic model that takes into account both diffusion and EM-induced flux. This model can therefore explain the kinetic behaviors of solid state aging and EM based on the current density given.

It is worth noting the effect that the reaction history has in the analysis of the solder/UBM IMC structure. As indicated by Tu et al., the kinetics of reflow reactions can be four orders of magnitude faster than the solid state aging [38]. Therefore, Cu$_6$Sn$_5$ phase of reflowed solders exists in scallop shapes even after a prolonged solid state aging. However, high current stressing can substantially
increase the solid state kinetics and completely alter the morphology within the same reaction time.

6.2. EM enhanced void formation

As shown in Fig. 3d, crack formation in the intermetallics was the dominant failure mode of solder joints under EM [2–4]. This failure mode has been attributed as the result of Kirkendall void formation accompanying the IMC growth due to reaction of Cu and Sn [3]. To understand EM-induced void formation due to intermetallic growth, we incorporate in the kinetic analysis the evolution of vacancy concentration in the kinetic analysis. For this purpose, vacancy transport was considered in the following continuity equation:

$$\frac{\partial C}{\partial t} = -\frac{\partial J}{\partial X}$$  (13)

$$J = (D_{Cu} - D_{Sn}) \frac{\partial C}{\partial X} - J_{EM}^{Cu} - J_{EM}^{Sn}$$  (14)

The vacancy concentration increases at the infinitesimal distance when

$$(D_{Cu} - D_{Sn}) \frac{\partial^2 C}{\partial X^2} - f(D_{Cu} \phi_{Cu} + D_{Sn} \phi_{Sn}) \frac{\partial C}{\partial X} < 0$$  (15)

It is clear that both the first and second derivative of the concentration play a role in terms of the time variation of the vacancy concentration. Results from this analysis are shown in Fig. 7. Fig. 7a shows the simulated composition profile of each phase after a prolonged and significant current stressing ($5.16 \times 10^6$ A/cm$^2$ and >300 h). Vacancy accumulation was also estimated by numerically integrating Eq. (13) and the results are plotted in Fig. 7b. Eq. (13) did not take into account the vacancy annihilation and only provides an overestimation that describes the history of vacancy accumulation at a given location. Fig. 7b indicates that significant vacancy accumulation takes place in the Cu$_6$Sn$_5$ phase near the Cu$_3$Sn/Cu$_6$Sn$_5$ interface during the intermetallic compound growth. Vacancy accumulation can significantly contribute to nucleation and growth of the voids in this region due to excessive vacancy concentration in conjunction with the presence of defects such as boundaries, interfaces, and surfaces. In the electromigration experiment, the voids were indeed found to form in this region, as shown in Fig. 7c. Unfortunately, the actual vacancy concentration could not be estimated in this study because the rate of vacancy annihilation was not known. Therefore, Fig. 7b was normalized to the maximum value.

6.3. Void-induced crack growth

Although Kirkendall voids can form during solder reflow and solid state aging, EM-induced voids have little relation to the reflow or aging induced voids and are predominantly driven by the current flux [2]. Fig. 8 shows the SEM images of two solder joints taken from the identical specimen of 140 °C 263 h accelerated EM testing. The solder joint in Fig. 8a was not subjected to any current stressing while the solder joint in Fig. 8b was subjected to 1.01 A current stressing. It is apparent that reflow or aging induced voids are present in both images and they are located in proximity to the Cu UBM. Nevertheless, the EM-induced voids, which only appeared in the current stressed solder, can grow considerably larger in size and are clearly separated from the smaller reflow and aging induced voids [2].

![Fig. 7.](image1)

(a) Composition profile after prolonged high current stressing ($5.16 \times 10^6$ A/cm$^2$ and >300 h), (b) vacancy accumulation derived from vacancy transport model and (c) expanded SEM image of a failing solder joint showing the interfaces of intermetallic phases. (Chao et al. in Ref. [43]).

![Fig. 8.](image2)

Kirkendall void formation due to (a) solder reflow and aging only, and (b) reflow, aging and EM (Chae et al. in Ref. [2]).
Further observation of Fig. 8b also suggests that the final EM failure of the solder joints could result from concerted action of EM-induced void formation and crack extension through the structure weakened by these voids. This is made obvious by the characteristic sharp, fracture-like edges connecting the voided areas in the EM failed samples.

Fig. 9 shows the EM damage evolution in the solder joint subject to current stressing. As the EM damage progresses, the Cu UBM gradually dissolves and shrinks, and both intermetallic phases grow in size but into distinct morphology. Cu3Sn remains as a layer-type morphology and conformal to the shape of the Cu UBM, whereas the growth of Cu6Sn5 follows the electron flux path. EM-induced voids were found to form mainly in the Cu6Sn5, and their sizes were small and comparable with the reflow- and aging induced voids adjacent to the Cu UBM.

In the later stages, the sizes of the EM-induced voids grow considerably and fracture-like cracks can be clearly observed between them. The final failure appears to result from EM voiding and crack propagation between these voids, as shown in Fig. 9d.

To understand the crack extension behavior in the voided solder joint due to EM enhanced Kirkendall effect, the crack driving force was studied with a finite element (FE) model of a voided IMC layer with an existing crack, as shown in Fig. 10. The energy release rate (ERR), also known as crack driving force, is the indicator of the propensity for crack propagation.

During EM testing, two types of loadings are likely to contribute to the crack driving force of the solder fracture. First, thermomechanical loading arises due to chip-to-substrate CTE (coefficients of thermal expansion) mismatch after the package is cooled down from the solder reflow temperature. Substrate warpage can cause stresses and fracture mode mixity that vary significantly with respect to the solder joint position under the chip. The center bumps are more prone to mode I cracking, whereas the edge bumps are subject to both modes I and II cracking.

In addition to thermomechanical loading, volume change induced by IMC formation also generates substantial stresses in the solder joints. The IMC growth is usually accompanied by an atomic volume change which reaches −4.8% for Cu6Sn5. As shown in Fig. 9c, IMC roughly maintains layer-type morphology when crack propagation initiates. Therefore, the volume change induced stress is mainly perpendicular to the interface, driving the crack to propagate as a mode I crack.

In order to fully correlate the EM experiment with the calculation of crack driving force, a comprehensive model is required to address both types of loadings. However, in a preliminary crack driving force analysis, we focused on the mode I cracking condition which is more applicable to the solder joints near the center of the chip. A finite element (FE) model of a finite region in the intermetallic compound (Cu3Sn or Cu6Sn5) was established. A void 250 nm in diameter and a crack of prescribed length was added to the model, as shown in Fig. 10. Constant stresses were applied at both top and bottom boundaries of model region driving the crack to propagate in the direction of the nearest void to the crack tip.

Fig. 11 shows the Von Mises stress calculated in the vicinity of the void. When subject to the specified loading, huge tensile stress concentration can be generated in front of the crack tip near the voided area. The tensile stress state is expected to facilitate the extension of the cracks.

The energy release rate calculated in this model is plotted against the void to crack tip distance in Fig. 12. Both intermetallic phases Cu3Sn and Cu6Sn5 were considered in the model since Kirkendall voids can be present in either of these two phases. The solid lines represent the energy release rate directly obtained from the model in Fig. 10. However, this result is in part affected by the change of the crack length used in the model when the void to crack tip distance is adjusted. Therefore, a reference model was also created with identical crack length and without the void. The effect of the void can subsequently be manifested by comparing the result of the void model and void free model. The result after correction against the void-free reference model is plotted in the dotted lines in Fig. 12.

It is clear from Fig. 12 that the energy release rate increases significantly as the void to crack tip distance decreases. This indicates a strong tendency for micro cracks to advance and connect the

---

Fig. 9. Electromigration (EM) damage evolution in the solder joint with Cu under bump metallization (UBM). (a) Initial stage of Cu depletion, (b) void initiation prior to the resistance jump, (c) crack propagation subsequent to the resistance jump and (d) final open failure. Electron flux direction specified in (a) (Chae et al. in Ref. [2]).
Kirkendall voids on the crack propagation path when the density of the voids increases. And after a crack is initiated, the ERR will increase to sustain the crack propagation. These two factors will cooperate resulting in crack-induced solder failure under accelerated EM tests.

In EM experiments, the mechanical loading on the solder joint is straightforward. However, complex loading conditions are expected during the usage of the products especially for the increasingly popular mobile devices. Drop reliability test is a common practice to evaluate the robustness of the solder joints. It was reported that extensive Kirkendall void formation can significantly undermine the solder joint and compromise the joint reliability during mechanical drop tests [40]. However, their effects on the solder drop reliability are very complex. Peng and Marques showed that Kirkendall void formation due to thermal aging did not have a significant impact on the drop performance [41]. They concluded that the weakening effect of the Kirkendall voids is likely counteracted by the grain coarsening that occurs during thermal aging. Furthermore, thermally induced IMC growth also plays a role in the change of drop reliability during thermal aging. The effect of EM-induced crack formation on the drop reliability of solders raises an interesting question and has yet to be investigated.

7. New challenges in 3D Interconnects

3D interconnect technology has stimulated great interests recently due to its remarkable potential in superior form factor, increased electrical performance, heterogenous integration, and low cost. Various stacking techniques have been proposed in the
wafer or chip levels. However, Cu–Sn–Cu bonding has emerged as one of the most promising candidates because of its affinity to the more mature flip chip technology.

Fig. 13 shows the EM damage in a Cu–Sn–Cu microconnect [42]. Similar to the observation in EM testing on solder joints, these microconnects failed predominantly due to extensive Kirkendall void formation. However, the Sn solder used for these microconnects is substantially thinner compared to the flip chip solder joints. Rapid intermetallic formation can completely consume the pure Sn phase and forms a Cu–IMC–Cu connection after reflow. In addition, the delamination is also peculiar that occurs both at the TiW/dielectric and TiW/Cu3Sn interfaces. Thus, the underlying pure Sn phase and forms a Cu–IMC–Cu connection after reflow. Rapid intermetallic formation can completely consume the pure Sn phase and forms a Cu–IMC–Cu connection after reflow.

8. Conclusion

A comprehensive framework was established for the analysis of EM enhanced IMC kinetics and void formation in Pb-free solders with two intermetallic compounds. The analysis comprises four components: EM-enhanced IMC kinetics model, derivation of the diffusion and EM parameters, vacancy transport model and the crack propagation model. These components were applied to evaluate experimental results on IMC formation observed under EM between a Cu UBM and a Sn-based Pb-free solder. The EM kinetic model takes into account Cu–Sn interdiffusion and current stress. The complexity of the model necessitates the use of simulated annealing (SA) to efficiently obtain the diffusion and EM parameters. The derivation of these parameters provided not only the foundation for the kinetic model but also important insight into the diffusion behaviors that could occur in the intermetallic compound. The EM enhanced void formation is the most dominant factor controlling the EM lifetime of the flip chip connection and was studied with the vacancy transport model and the solder crack propagation model in this paper. The vacancy transport model indicated vacancy accumulation at the Cu6Sn5 side of the Cu6Sn5/Cu3Sn interface where the voids were observed in EM experiments. The crack propagation model promotes understanding of the collective behaviors of voiding and crack extension that results in the final failures of the solder joints observed in the accelerated EM tests. Additionally, the analysis approach in this paper can be readily applied to the investigation of EM kinetics and damage of the Cu–Sn–Cu bonding in 3D interconnect technology.

Acknowledgments

This research was supported in part by the Semiconductor Research Corporation. The authors would like to thank Dr. Peng Su, Trent Uehling, and Lakshmi N. Ramanathan of Freescale Semiconductor for funding support and assistance in experiments and also like to thank Professor Venkat Ganesan at the University of Texas at Austin for useful discussion of numerical techniques.

References