Precipitate drifting and coarsening caused by electromigration

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A mechanism is proposed to explain electromigration-enhanced precipitate coarsening in Al-Cu alloy interconnects. The interface between the $\alpha$-phase matrix and a $\beta$-phase $Al_2Cu$ precipitate is incoherent, along which both Al and Cu atoms diffuse under an applied electric field. Depending on the relative mobility of Al and Cu, the diffusion causes the precipitate to migrate toward either the positive or the negative electrode. The velocity of a spherical precipitate is proportional to the electric field and the mobilities and inversely proportional to its radius. A critical electric field or precipitate radius exists, above which the precipitate can penetrate a grain boundary. Consequently, the precipitates agglomerate by the synergism between the Ostwald ripening and the current-induced migration. The resulting particles are distantly separated, depleting Cu atoms from the rest of the interconnect. The mechanism appears to limit the lifetime of interconnects having bamboo-like grains, tested below 300 °C, less than half of the melting temperature of Al. Experiments taking advantage of migration of various inhomogeneities are suggested which may illuminate several basic issues in the field of electromigration.

I. INTRODUCTION

Shortly after electromigration was identified as a failure mechanism of aluminum interconnects, a method to delay the failure was also discovered: adding a few percent of copper to an interconnect extends its lifetime by about 80 times. The discovery, as well as the perpetual urge to shrink integrated circuits, has inspired much of the subsequent work. Much is known about the Al-Cu films now, but the enhancement mechanism of copper remains controversial. Furthermore, when the width of the interconnects falls below the grain size, the grain boundaries no longer connect into a network. In the limit, a bamboo-like structure forms where all the grain boundaries lie normal to the current direction. The bamboo-like interconnects have longer lifetimes than wide films, but still fail by void and hillock formation, indicating long-range mass-transport.

If the grain boundaries do not facilitate long-range diffusion in the bamboo-like interconnects, then what do? Lattice diffusion is slow provided the interconnects operate below 150 °C. Among the mass-transport mechanism considered recently are cavity migration by atoms diffusing on the cavity surface, diffusion on metal-passivation interfaces, and dislocation climb and multiplication by core diffusion.

The effect of heat treatment on interconnects follows the classical rules. Precipitates appear due to the low equilibrium solubility of copper in the $\alpha$-phase. Initially formed are coherent, metastable Guinier–Preston zones which, after a sequence of metastable phases, become incoherent, stable $\beta$-phase $Al_2Cu$ particles. The precipitates may (a) undergo Ostwald ripening by grain boundary diffusion, (b) prefer to reside in grain boundaries and triple points to reduce total surface area, and (c) be trapped inside the grains if no fast diffusion path is available. When an electric current is supplied in addition to heat, coarsening proceeds at a significantly higher rate: even precipitates inside the grains agglomerate. The resulting large precipitates are distantly separated, leaving the rest of the line depleted of Cu.

Hypotheses on the role of copper fall into two types: either Cu atoms or $Al_2Cu$ precipitates slow down the Al diffusion. In wide films, grain boundaries facilitate diffusion below one half of the melting temperature of Al. It is believed that Cu atoms reduce the Al mobility on the grain boundaries, e.g., by clogging ledges or binding vacancies. Similar mechanisms may slow down cavities, prismatic loops, and interface diffusion in the bamboo-like lines. The atomistic details by which Cu atoms clog the fast diffusion paths are still unclear. Nonetheless the present writers are unaware of any experimental evidence inconsistent with this hypothesis. Under this hypothesis, the precipitates act merely as reservoirs to replace the Cu atoms depleted by the field.

A second hypothesis holds that the precipitates themselves act as diffusion barriers. In wide films, for a precipitate to partially block a grain boundary, the diffusivity along the matrix/precipitate interface should be lower than that along the grain boundary. Furthermore, since the precipitates on a grain boundary are discontinuous, additional mechanism must be invoked to block diffusion between the precipitates. In the bamboo-like lines, arrays of precipitates may set up periodic stress gradients to arrest the diffusion. Existing experiments do not discriminate between the two hypotheses, because the Cu atoms and the $Al_2Cu$ precipitates always coexist on the grain boundaries. Interpretation of the existing data is further complicated by the change of Cu concentration during a given test. Hypothesis debate aside, a correlation has long been observed between precipitate coarsening and void forma-
II. CURRENT-INDUCED PRECIPITATE MIGRATION

Consider a segment of an interface between a \( \theta \)-phase \( \alpha_2 \text{Cu} \) precipitate and the \( \alpha \)-phase matrix, Fig. 1. The electron wind exerts a force on each atom in the interface

\[ F_i = -Z_i e E_i \quad (1) \]

Here subscript \( i \) denotes either Al or Cu, \( Z_i(>0) \) the effective valence of the atom, \( e(>0) \) the electron charge, and \( E_i \) the electric field component tangential to the interface. The negative sign indicates that the direction of the force coincides with that of the electron flow. The flux of each species, i.e., the number of atoms of a species per unit time crossing unit length in the interface, is

\[ J_i = L_i F_i \quad (2) \]

Here \( L_i \) are the phenomenological coefficients related to the interface diffusivities.\(^{12}\) It is assumed that \( L_i \) are constant in the interface. The relative mobility is denoted as

\[ \lambda = \frac{J_{\text{Al}}}{J_{\text{Cu}}} = \frac{L_{\text{Al}} Z_{\text{Al}}}{L_{\text{Cu}} Z_{\text{Cu}}} \quad (3) \]

Note that \( \lambda \) is a material constant independent of the electric field. It will be evident that the value of \( \lambda \) governs the migration direction of the interface.

Unless otherwise stated on one occasion, the matrix will be held as the immobile reference. Fixed on the precipitate is an inert marker, which moves relative to the matrix when the precipitate undergoes a rigid body translation. The interface can also migrate relative to the matrix. It is the flux divergence, not the flux itself, that moves the interface and the marker: they would remain stationary were no net atoms diffusing out of or into the interface segment in Fig. 1. As atoms diffuse out of the interface segment, the marker moves toward the matrix to fill the space; the interface remains stationary if \( \lambda = 2 \), moves toward the matrix if \( \lambda > 2 \), or away from the matrix if \( \lambda < 2 \). All the directions are reversed if atoms diffuse into the interface segment. The remainder of this section analyzes this situation in detail.

The arrangement of atoms and vacancies near the interface is inconsequential to the following considerations—so long as the species adjust rapidly to maintain local equilibrium. That is, as the species diffuse along the interface, maintained at any point near the interface are (a) the stoichiometry of \( \alpha_2 \text{Cu} \) in the precipitate, (b) the purity of Al in the matrix, and (c) the equilibrium composition in the interface. Furthermore, the conclusions are independent of the interface composition. That the Cu concentrations in the two phases near the interface are given by the Gibbs-Thomson relation will only modify the following results slightly. The assumption of local equilibrium is justified provided a small group of atoms near a given point of the interface shuffle at a much higher rate than the diffusion around a precipitate particle. The latter, in turn, requires that the particle be sufficiently large, or the applied electric field be sufficiently small.

First consider the case where Cu has a much higher mobility than Al (\( \lambda \rightarrow 0 \)). For each Cu atom diffusing out of the interface segment, the precipitate must dissolve one unit of \( \alpha_2 \text{Cu} \), donating the Cu atom to the interface to restore its equilibrium, and the two Al atoms to the matrix to recover the stoichiometry of the precipitate. Consequently, the interface migrates away from the matrix; to compensate for the vacancy left by the diffused Cu atom, the marker moves toward the matrix by a rigid body translation of the precipitate. These operations restore the equilibrium in the three phases—no vacancy or interstitial is created or destroyed anywhere. Parallel conclusions hold for each Cu atoms diffusing into the interface element.

Figure 2 illustrates a \( \theta \)-phase particle in an infinite \( \alpha \)-phase matrix subjected to an electric field.
electric field is applied. As Cu atoms diffuse from the cathode side to the anode side, the \( \theta \)-phase dissolves on the cathode side and reprecipitates on the anode side. Consequently, the spherical interface moves toward the anode, but the marker toward the cathode. The nonuniform Cu flux along the interface is so distributed that the particle remains to be spherical as it moves, as will be shown in Sec. III.

Next consider the other limiting case \( \lambda \to \infty \) when Al diffusion dominates. For each Al atom diffusing out of the interface segment in Fig. 1, the matrix donates an Al atom to the interface to restore the equilibrium of the interface; the \( \theta \)-phase does not dissolve or reprecipitate. To compensate for the vacancy left in the matrix, the interface moves toward the matrix, and so does the precipitate which undergoes a rigid translation. Consequently, both the interface and the marker of the particle in Fig. 2 moves toward the cathode at the same velocity if Al diffusion dominates. Concurrent Al and Cu diffusion \( (0 < \lambda < \infty) \) can be similarly analyzed. The marker always migrates toward the cathode, which indicates a rigid body translation of the precipitate to accommodate the space as both Al and Cu atoms diffuse on the interface toward the anode. The spherical interface migrates toward the cathode if \( \lambda < 2 \), and toward the anode if \( \lambda > 2 \). Since the particle maintains the spherical shape, the translation velocity of the interface coincides with that of the mass center of the particle.

The present phenomenon involves two atomic species but differs, in several significant ways, from the Kirkendall effects in interdiffusion couples.\(^{13}\) First, the diffusion is driven by the electric current, not by concentration gradients; in fact, the concentrations at any point never change to an observer traveling with the spherical interface. Second, both Al and Cu diffuse along the interface in the same direction, rather than normal to the interface in the opposite directions. Third, as atoms diffuse from the cathode side to the anode side, the space mismatches on both sides are compensated by a rigid body translation of the particle: neither vacancies nor interstitials need be created. The case \( \lambda = 2 \) is particularly illuminating. Material with a Al\(_2\)Cu stoichiometry relocates from one side to the other toward the anode, which is compensated by a rigid body translation of the precipitate toward the cathode. Relative to the matrix, the marker moves toward the cathode, but the interface remains stationary and so does the mass center of the particle.

### III. INTERFACE VELOCITY AND MARKER VELOCITY

We now focus on the spherical precipitate, of radius \( a \), embedded in an infinite matrix, subjected to an electric field \( E \), Fig. 2. Two velocities relative to the matrix are of concern: the translating velocity of the spherical interface \( V_I \), which coincides with that of the mass center of the particle; the velocity of the marker \( V_M \), which indicates the rigid body translation of the particle. The flux divergence causes the interface at each point to migrate in the direction normal to the interface. It turns out that the normal velocities, varying from point to point, are such that the entire interface translates like a rigid spherical shell. The situation is analogous to migration of other defects, such as prismatic loops,\(^{7}\) cavities, and inclusions.\(^{14}\)

The interface migration can be monitored by counting the number of Al atoms removed from the matrix. Consider a cap of radius \( r \) measured from the symmetry axis. Each Al atom diffusing out of the cap removes one Al atom from the matrix; each Cu atom diffused out of the cap adds two Al atoms to the matrix. Thus, the volume of Al atoms per unit time removed from the matrix, crossing the perimeter of the cap, is \( 2\pi r\Omega_{\text{Al}}(J_{\text{Al}}-2J_{\text{Cu}}) \). Here \( \Omega_{\text{Al}} \) is the volume occupied by an Al atom in the matrix. As the cap moves at velocity \( V_I \), the matrix loses volume per unit time \( \pi r^2V_I \). Mass conservation requires that

\[
J_{\text{Al}}-2J_{\text{Cu}} = V_I/2\Omega_{\text{Al}}. \tag{4}
\]

It is well known that, due to the difference in the resistivity, the electric field is nonuniform in the matrix but uniform inside the spherical particle. The latter differs from the applied field by \( \beta = 3\rho_P/(2\rho_P + \rho_m) \), where \( \rho_P \) and \( \rho_m \) are the resistivity of the precipitate and the matrix, respectively. Consequently, the electric field component tangential to the interface is

\[
E_I = -\beta Er/a. \tag{5}
\]

Assuming the precipitate has a larger resistivity than the matrix, one finds that \( 1 < \beta < 1.5 \). The atomic fluxes can be computed by substituting (5) into (1) and (2). The identical \( r \) dependence in (4) and (5) indicates that a spherical particle will migrate with the same shape.

A combination of (1)-(5) gives the translation velocity of the spherical interface relative to the matrix:

\[
V_I = 2(\lambda - 2)\Omega_{\text{Al}}L_{\text{Cu}}Z_{\text{Cu}}\beta E r/a. \tag{6}
\]

The velocity is proportional to the applied field and the mobility, but inversely proportional to the precipitate size. A small particle has a short diffusion length and therefore drifts fast. The particles drifts toward the cathode if Al mobility prevails \( (\lambda > 2) \), and toward the anode if Cu mobility prevails \( (\lambda < 2) \). The available experimental observations seem to support the latter. The dimensional group in (6) is representative: only the prefactor varies for precipitates of other shapes.

Next we take the marker and therefore the particles as the reference, against which the interface migrates and the matrix may undergo a rigid body translation (Fig. 2). For each Cu atom diffusing out of the cap, the precipitate must dissolve a unit of Al\(_2\)Cu, donating the Cu atom to the interface and the two Al atoms to the matrix. Thus, the interface moves toward the precipitate, and so does the matrix. For each Al atom diffusing out of the cap, the precipitate makes no adjustment, the interface accepts an Al atom from the matrix and remains stationary, and the matrix moves toward the particle. Consequently, only the Cu flux contributes to the velocity of the interface relative to the marker, \( V_{IM} \). Mass conservation for the cap requires that

\[
J_{\text{Cu}} = -(V_I - V_M)/2\Omega_\theta. \tag{7}
\]
Here $\Omega_\theta$ is the volume occupied by Al-Cu in the $\theta$-phase lattice, and $V_{IM} = V_I - V_M$. Consequently, the velocity of the marker relative to the matrix is

$$V_M = 2[\Omega_\theta + (\lambda - 2)\Omega_{Al}]L_{Cu}Z_{Cu}aEe/a.$$  \hspace{1cm} (8)

Because both Al and Cu diffuse toward the anode, the marker and therefore the particle make a rigid body translation toward the cathode to accommodate the space.

The interface translation velocity can be readily measured by in situ experiments. The marker velocity may also be measured if a defect on the particle is visible. If both the marker and the interface velocity can be measured, the Al and Cu mobilities can be deduced from (6) and (8).

**IV. FORCES ON A PRECIPITATE**

Precipitates are assumed to migrate in a perfect lattice in the previous section. In bamboo-like interconnects, grain boundaries may trap the precipitates to reduce surface area. The applied field needed for the precipitate to break away from a grain boundary can be calculated. For simplicity, it is assumed that the precipitate remains spherical when crossing the grain boundary.

Denote $f_I$ and $f_M$ as the drag forces applied to, respectively, the interface (or the center of mass) and the marker (or the rigid particle). A sign convention is adopted such that the forces are positive if directed toward the cathode. In equilibrium the two forces balance the electron wind force, so that the interface diffusion and particle translation stop. Equation (2) should be modified to include the influence of the drag, but the relative mobility in (3) still holds. If a particle in equilibrium is given a virtual motion, the total virtual work vanishes:

$$\int \{F_{Al}J_{Al} + F_{Cu}J_{Cu}\} dS + f_IV_I + f_MV_M = 0.$$  \hspace{1cm} (9)

The integral extends over the spherical interface. Here the wind force on each atom $F_I$ is related to the applied field by (1) and (5). The four virtual kinetic quantities, $J_{Al}$, $J_{Cu}$, $V_I$, and $V_M$, are compatible, as required by the relative mobility (3) and mass conservation (4) and (7). These equations are rearranged to express in terms of the virtual velocity of the center of mass $V_I$ the other three quantities:

$$J_{Al} = \frac{\lambda}{\lambda - 2} \left( \frac{rV_I}{2\Omega_{Al}} \right),$$

$$J_{Cu} = \frac{1}{\lambda - 2} \left( \frac{rV_I}{2\Omega_{Al}} \right),$$

$$V_M = \left( 1 + \frac{\Omega_\theta}{\lambda - 2} \frac{\Omega_{Al}}{\Omega_{Al}} \right)V_I.$$  \hspace{1cm} (10a)

All the kinetic quantities are determined once one of them is: the problem has only one degree of freedom. Note that in the virtual work considerations $F_I$ and $J_I$ need not be related by constitutive equations like (2).

Integrating (9) over the spherical surface gives the equilibrium equation among $E$, $f_I$, and $f_M$:

$$\int \{F_{Al}J_{Al} + F_{Cu}J_{Cu}\} dS + f_IV_I + f_MV_M = 0.$$  \hspace{1cm} (9)

The force on the precipitate due to the grain boundary is computed in the same way as that in Zener’s model. As the precipitate moves away from the boundary, the grain boundary strives to maintain itself normal to the interface (Fig. 3). The surface tension of the boundary, $\gamma_B$, exerts a force at the circular intersection between the interface and the grain boundary. The resultant force is the conjugate to $V_I$. Thus, $f_M = 0$ and

$$|f_I| = 2\pi a \gamma_B \cos \phi \sin \phi.$$  \hspace{1cm} (13)

The force is maximum when $\phi = \pi/4$. The maximum force exerted on the precipitate by the surface energy of the grain boundary is

$$|f_I| = \pi a \gamma_B.$$  \hspace{1cm} (14)

The force is directed toward the direction opposing the particle escape.

The balance between the electron wind and the grain boundary tension yields

$$Ea^2 = \text{constant}.$$  \hspace{1cm} (15)

The constant is material specific as determined by equating (11) and (14). Consequently, a critical value of $Ea^2$ exists, above which the precipitate penetrates the grain boundary. Subjected to a given electric field, small particles will be trapped by the grain boundary, but bigger ones will escape. The qualitative conclusion applies to other traps, such as......
V. DISCUSSION

The experimental data available to us do not permit quantitative comparison with the results derived in this article. We will try to place the present model in the general context of electromigration failure. It is hoped that some experiments may succeed shortly in solving the problems suggested here, which are of fundamental nature to the field of electromigration.

A. The role of Cu on fast diffusion paths

As pointed out in Sec. I, the existing electromigration experiments do not distinguish the beneficial effects of the Cu atoms dissolved in the grain boundary and the Al2Cu precipitates. It appears to us that the effect of the dissolved Cu atoms may be proved or disproved by observing other fast diffusion mechanisms, e.g., cavity or prismatic loop migration, in aluminum lattices with and without copper doping. In a lattice of aluminum doped with a low concentration of copper so that precipitates do not form, cavities or dislocations are affected by Cu atoms only. The concentration of Cu on the cavities or dislocations is higher than that in the matrix. This experiment also removes another uncertainty in testing diffusivity of grain boundaries. It is impossible to maintain a fixed Cu concentration on a grain boundary as electromigration proceeds. However, cavities and prismatic loops can migrate with a fixed Cu concentration on the surface or dislocation core. As such, comparing the migration velocities with and without Cu doping would unambiguously settle the effect of the dissolved Cu atoms on short-circuit Al diffusion.

B. The atomic mobilities on metal-passivation interfaces

It has long been speculated that metal-passivation interfaces may be fast diffusion paths. Diffusion along these interfaces may become significant in narrow, bamboo-like interconnects, where other fast diffusion paths are unavailable and the interface to bulk ratio increases. The Cu atoms, as well as the species from the passivation (H, O, N, C, Si), may affect the mobility of Al on the interfaces. Little data are available now to assess the significance of these effects, apparently due to the experimental difficulty in measuring the atomic mobilities along the interfaces. The phenomenon described in this article may provide an accurate method. As an example, consider the mobility of Al on the Al-Al2O3 interface. The alumina particle can form inside an Al matrix by internal oxidation. The mobilities on the interface may be deduced once the particle velocities are measured by in situ experiments. Results in this article can be readily modified so that the atomic mobilities on the interfaces can be deduced from the measured particle velocities.

C. Precipitate coarsening in bamboo-like interconnects

Precipitate coarsening is accelerated by the synergism between the interface tension and the electron wind. At temperatures of practical interest, Ostwald ripening is facilitated by diffusion along grain boundaries, metal-passivation interfaces, and possibly dislocations. A large fraction of precipitates may be trapped inside the grains due to the lack of diffusion paths. Subjected to an electric current, the precipitates inside the grains migrate by the self-accommodating dissolution and reprecipitation process described in this article. The mass transport rate is limited by the mobilities of Al and Cu on the precipitate-matrix interface. Precipitates can agglomerate by several processes. A precipitate in the matrix migrates at a velocity inversely proportional to its radius. A large precipitate would drift slowly, waiting for the smaller ones to catch up with it. The coarsening rate is limited by the relative migration velocity of the precipitates, and therefore governed by the interface diffusivities and the precipitate radius. Once two precipitates touch one another, they will sinter into a single spherical particle, driven primarily by the interface tension and facilitated by the interface diffusion.

If a drifting precipitate does not encounter another one, it will hit a grain boundary in the bamboo-like line. The precipitate then participates in Ostwald ripening on the grain boundary, by a combination of grain boundary and interface diffusion, driven by the interface tension. Once one of the precipitates becomes large enough, it escapes into the lattice. As the precipitates agglomerate, consuming small precipitates in both the grains and the boundaries, Cu will be depleted from the rest of the interconnect. The interconnect can fail by fast diffusion of Al by mechanisms for pure Al lines, such as cavity or dislocation migration.

It is sometimes observed that voids are attached to precipitates and grow as the precipitates migrate. This is not inconsistent with the model described here. Features unaccounted for in the present model may cause the voids to grow. For example, L1 may be nonuniform in the interface leading to a flux divergence. Interstitial dislocation loops near the precipitate may act as the atomic sink. The cavity-precipitate interaction may have analogous effects of dislocation-precipitate interaction discussed in Ref. 7. The interactions among various defects may yield information of practical significance which will be presented elsewhere.

D. Special results for high Cu mobility

If Cu has a much higher mobility than Al on the interface, as it appears to from the available experimental observations, the spherical interface moves toward the anode and the marker toward the cathode. The drift velocity of the interface relative to the matrix becomes

$$V_f = -4 L_{Cu} Z_{Cu} \Omega_A \beta E e / a.$$  \hspace{1em} (16)

Thus, the mobility of Cu is determined once the velocity is measured.

The equilibrium equation for the particle becomes
For a given mechanism of drag, the forces \( f_I \) and \( f_M \) can be measured independently. In an in situ experiment, the equilibrium can be attained by adjusting the field \( E \). The experiment can be used to determine the effective valence on the interface \( Z_{Cu} \). This information is important in various instability phenomena, such as a particle breakaway from a grain boundary.

The critical condition for the precipitate to escape from a grain boundary becomes

\[
Ea^2 - \frac{3}{2} \frac{\Omega_{Al} \gamma_B}{\beta e Z_{Cu}} = 0.
\]

Note that the right hand side is a material constant. Using \( \Omega_{Al} = 1.66 \times 10^{-25} \text{ m}^3 \), \( \gamma_B = 0.5 \text{ J/m}^2 \), \( Z_{Cu} = 10 \), \( \beta = 1.5 \), and \( e = 1.6 \times 10^{-19} \text{ C} \), one obtains

\[
Ea^2 = 5.2 \times 10^{-12} \text{ V m}.
\]

For example, the field needed for a particle of radius \( a = 0.1 \mu m \) to penetrate a grain boundary is \( E = 520 \text{ V/m} \). This field is of the same order of magnitude typically used in electromigration tests. Uncertainties arise from the difficulties in determining accurate values for the grain boundary tension and the effective valence; the estimate here is only tentative.

**VI. CONCLUDING REMARKS**

Subjected to an electric field, a \( \theta \)-phase particle moves in an \( \alpha \)-phase matrix as atoms diffuse on the particle-matrix interface. A critical value of \( Ea^2 \) is identified, above which a precipitate can penetrate a grain boundary. Precipitates in interconnects agglomerate by a synergism between the electron wind and interface tension. Both processes operate via fast diffusion paths, and therefore are important at temperatures of practical significance (\( T < 450 \text{ K} \)). The analysis uses electric current as the driving force, but the results with suitable modifications are applicable to precipitate migration under a stress gradient. The phenomenon can be tested by in situ transmission electron microscope TEM observations. Experiments are suggested which may help to settle several long-standing issues in the field of electromigration.

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