PRECIPITATE DRIFTING AND COARSENING
CAUSED BY INTERFACE ELECTROMIGRATION

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ABSTRACT

A mechanism is proposed to explain electromigration-enhanced precipitate coarsening in Al-Cu alloy interconnects. The interface between the α-phase matrix and a θ-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 towards 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 surface tension-induced 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.

INTRODUCTION

It is believed that Cu atoms reduce the Al mobility along fast diffusion paths, such as grain boundaries and interfaces, by clogging ledges or binding vacancies [1]. Because Cu atoms at these fast diffusion paths can be easily washed-out by the electric current, it is necessary to have Cu sources in the line to supply fresh Cu atoms. This is achieved by adding Cu significantly beyond its solubility limit in aluminum, so that most of the Cu atoms are gathered into the stable θ-phase Al_2Cu precipitates.

During heat treatment, the precipitates undergoes the usual coarsening process [2,3]. When an electric current is supplied in addition to heat, coarsening proceeds at a significantly higher rate. It is particularly puzzling that even precipitates inside the grains agglomerate [3]. The resulting large precipitates are distantly separated, leaving the rest of the line depleted of Cu. Since the lifetime is largely governed by the time needed for copper depletion, it is perhaps most effective to reduce the coarsening rate in order to prolong the lifetime. The Ostwald ripening, governed by grain boundary diffusion and interface tension, has been reconsidered recently [4]. Yet the process by itself explains neither the enhanced coarsening rate under the electric field nor the coarsening of the precipitates trapped inside of grains where no fast diffusion paths are available. A complementary process will be described in this paper. Briefly, driven by the electric current, both Cu and Al atoms diffuse along the matrix-precipitate interface which, in turn, causes a precipitate to migrate.

PRECIPITATE MIGRATION IN ELECTRON WIND

Figure 1 illustrates a θ-phase Al_2Cu precipitate and the α-phase matrix, subjected to an electric field. The electron wind exerts a force on each atom in the interface

$$F_i = -Z_i e E_t \qquad (1)$$

Here subscript i denotes either Al or Cu, Z_i (> 0) the effective valence of the atom, e (> 0) the magnitude of the electron charge, and E_t 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.
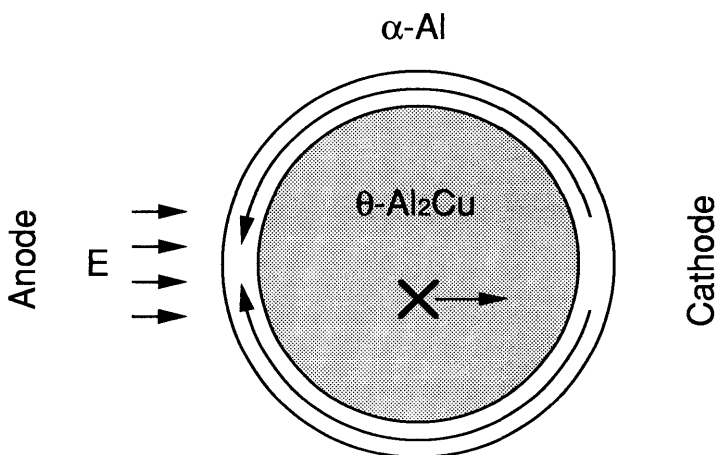
Fig. 1 A spherical θ-phase particle in an infinite α-phase matrix, subjected to an electric field. As the current induces electromigration of Al and Cu atoms along the interface from the cathode side to the anode side, the precipitate accommodates the process by undergoing rigid body translation toward the cathode as shown by the marker (X).
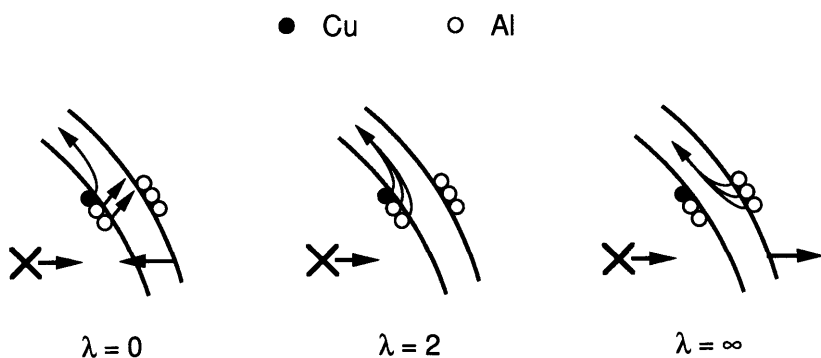

Fig. 2 The direction of interface movement is controlled by the relative mobility of Al and Cu atoms along the interface. Three limiting cases are illustrated, in which the interface moves left ($\lambda = 0$), remains stationary ($\lambda = 2$), or moves right ($\lambda = \infty$).

The flux of each specie, i.e. the number of atoms of a specie per unit time crossing unit length in the interface, is

$$J_i = L_i F_i \qquad (2)$$

Here L_i are the phenomenological coefficients related to the interface diffusivities [5]. It is assumed that L_i are constant in the interface. Although two atomic species are involved in the interface diffusion, the chemical concentration does not change along the interface and is invariant with time. This is different from the Kirkendall interdiffusion couples. The relative mobility is denoted

$$\lambda = \frac{J_{Al}}{J_{Cu}} = \frac{L_{Al} Z_{Al}}{L_{Cu} Z_{Cu}} \qquad (3)$$

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

The particle is assumed to take a spherical shape in equilibrium before the electric field is applied. The nonuniform atomic flux along the interface is so distributed that the particle remains to be spherical as it moves, as will be shown later. Since atoms diffuse from right to left under current, the inert marker (X in Fig. 1) fixed on the precipitate always migrates towards 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 towards the anode.

To understand the interface movement, we assume that 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 Al_2Cu in the precipitate, b) the purity of Al in the matrix, and c) the equilibrium composition in the interface. Three special cases are illustrated in Fig. 2. If Cu has a much higher mobility than Al ($\lambda = 0$), for each Cu atom diffusing out of the interface segment, the precipitate must dissolve one unit of Al_2Cu, 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. For the case $\lambda = 2$, only the precipitate participates in the electromigration; material of stoichiometry of Al_2Cu relocates from one side of the precipitate to the other leaving the interface stationary. In the third case $\lambda = \infty$, only Al atoms and hence the matrix participate in the process. So the interface moves towards the cathode. General cases ($0 < \lambda < \infty$) can be similarly analyzed. The spherical interface migrates towards the cathode if $\lambda < 2$, and towards 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 marker and the interface move at different velocities relative to the matrix. The velocity of the spherical interface V_I coincides with that of the mass center of the particle. The velocity of the marker V_M 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 [6], cavities and inclusions [7].

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 (Fig. 3). Each Al atom diffused out of the cap removes one Al atoms from the matrix; each Cu atom diffused out of the cap adds two Al atoms to the matrix. Thus, the number of Al atoms per unit time removed from the matrix, crossing the perimeter of the cap, is $2\pi r \Omega_{Al}(J_{Al}-2J_{Cu})$. Here Ω_{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 $\pi r^2 V_I$. Mass conservation requires that

$$J_{Al} - 2J_{Cu} = \frac{r V_I}{2\Omega_{Al}} \qquad (4)$$

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 factor $\beta = 3\rho_p/(2\rho_p+\rho_m)$, where ρ_p and ρ_m are the resistivity of the precipitate and the matrix, respectively. Consequently, the electric field component tangential to the interface is

$$E_t = -\beta E \frac{r}{a} \qquad (5)$$

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 preserve the shape as it migrates.

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

Fig. 3 The interface cap moves as a result of the matrix loosing or gaining Al atoms.

$$V_I = 2(\lambda - 2)\Omega_{Al}L_{Cu}Z_{Cu}\beta Ee / a \qquad (6)$$

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 particle drifts towards the cathode if Al mobility prevails $(\lambda > 2)$, and towards the anode if Cu mobility prevails $(\lambda < 2)$. The available experimental observations seem to support the latter.

The marker velocity can be similarly derived

$$V_M = 2[\Omega_\theta + (\lambda - 2)\Omega_{Al}]L_{Cu}Z_{Cu}\beta Ee / a \qquad (7)$$

where Ω_θ is the volume occupied by unit Al_2Cu. Because both Al and Cu diffuse towards the anode, the marker moves, and therefore the particle makes a rigid body translation, towards the cathode to accommodate the space.

DISCUSSION

Precipitate coarsening is accelerated by the synergism of the two forces: the interface tension and the electron wind. At temperatures of practical interest, the Ostwald ripening, driven by interface tension, 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 paper. 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. 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. The coarsening rate is determined by the electron wing force Z_iEe, the interface diffusion parameter $\delta_I D_I$, and the diffusion distance ($\sim a$) and the typical precipitate spacing S,
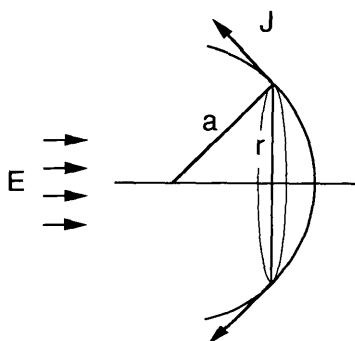
$$R_I \propto Z_i E e \frac{\delta_I D_I}{S a} \qquad (8)$$

A possible alternative mechanism for the coarsening of precipitates in the interior of grains is the lattice diffusion controlled Ostwald ripening. The rate of this process is governed by the interface tension driving force ($\sim \gamma_I \Omega_\theta / a^2$), the lattice diffusivity D_L and the diffusion distance ($\sim a$), i.e.,

$$R_L \propto \frac{\gamma_I \Omega_\theta D_L}{a^3} \qquad (9)$$

Using $\gamma_I \sim 0.5$ J/m^2, $\Omega_\theta \sim 10^{-29}$ m^3, S $\sim 5\times10^{-7}$ m, $Z_i \sim 10$, E ~ 500 V/m, $\delta_I \sim 10^{-9}$ m, a $\sim 10^{-7}$ m and $D_L/D_I < 10^{-4}$ (T/T$_m$ < 0.5), one obtains that the speed ratio of the lattice diffusion controlled kinetics over the interface diffusion controlled kinetics $R_L/R_I < 3\times10^{-2}$ at temperatures below half of the melting point, indicating the precipitates drifting and agglomerating mechanism dominates inside grains.

Precipitates are assumed to migrate in a perfect lattice in the previous discussion. In bamboo-like interconnects, grain boundaries may trap the precipitates to reduce surface area. The precipitate then participate in Ostwald ripening on the grain boundary, by a combination of grain boundary and interface diffusion, driven by the interface tension. The precipitate can also break away from the boundary if the applied field is sufficiently strong.

The force due to the electron wind can be derived using virtual work method. The grain boundary trapping force is calculated by the Zener's method. The balance between the electron wind and the grain boundary tension yields [8]

$$E a^2 = \text{constant} \qquad (10)$$

The constant is material specific. 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 big ones will escape. For the special case $\lambda = 0$, the above condition becomes

$$E a^2 = \frac{3}{2} \frac{\Omega_{Al} \gamma_B}{\beta e Z_{Cu}} \qquad (11)$$

Using $\Omega_{Al} = 1.66\times10^{-29}$ m^3, $\gamma_B = 0.5$ J/m^2, $Z_{Cu} = 10$, $\beta = 1.5$, and e $= 1.6\times10^{-19}$ C, one obtains that

$$E a^2 = 5.2 \times 10^{-12} \text{ Vm} \qquad (12)$$

For example, the field needed for a particle of radius a $= 0.1$ μm to penetrate a grain boundary is E $= 520$ V/m. This field is of the same order of magnitude typically used in electromigration tests.

CONCLUDING REMARKS

Subjected to an electric field, a θ-phase particle moves in an α-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 is important at temperatures of practical significance (T < 450 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 TEM observations. If both the marker and the interface velocity can be measured, the Al and Cu mobilities on the precipitate-matrix interface can be determined.

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