Electromigration of vacancies in copper

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The total current-induced force on atoms in a Cu wire containing a vacancy are calculated using the self-consistent one-electron density matrix in the presence of an electric current, without separation into electron-wind and direct forces. By integrating the total current-induced force, the change in vacancy migration energy due to the current is calculated. We use the change in migration energy with current to infer an effective electromigration driving force $\mathbf{F}_e$. Finally, we calculate the proportionality constant ρ^* between $\mathbf{F}_e$ and the current density in the wire.

The atomic flux caused by the passage of an electric current in a metal, known as electromigration (EM), has been investigated both theoretically[1] and experimentally[2] for decades. Since 1967 when Blech *et al.*[3] found that EM was one of the main failure mechanisms in Al conductors, a full understanding of EM mechanisms has been considered particularly important in the microelectronics industry, where reduced widths of wires increase the potential for EM damage.

Despite intensive study, meaningful and consistent measurements of quantities associated with EM processes, especially in polycrystalline wire, continue to be frustrated by variations in the microstructures of samples.[4–6] For example, it is common to measure experimentally the electromigration activation energy Q_{EM} and the effective valence Z^* for a given wire.[2,7] Q_{EM} determines the mobility μ of the migrating defects and Z^* characterizes the driving force for EM $\mathbf{F}_e$ via the equations

$$\mu = \frac{a^2 \nu}{kT} \exp(-Q_{\mathrm{EM}}/kT), \tag{1}$$

$$\mathbf{F}_e = Z^* e \mathbf{E}, \tag{2}$$

where a is the lattice parameter, ν is the attempt frequency for migration, and $\mathbf{E}$ is the externally applied field. However, Q_{EM} also reflects the mobility of the atoms before the current is applied, resulting in large discrepancies in the measured values of Q_{EM} depending on whether the migration path is through the bulk, along grain boundaries, or on the surface.[4–11] Similarly, Z^*, which is often presented as an intrinsic material property,[12] is actually dependent on complicated multiple electron scattering effects in the immediate vicinity of migrating defects,[13–18] as well as on scattering from all other defects in the wire.[14,15] As a result, measured values for Z^* in the same metal can vary by as much as 300%,[11,12,19] and Q_{EM} in pure Cu by as much as 250%.[5,8]

In theoretical studies, the driving force for EM is traditionally divided into two parts—the electron-wind force $\mathbf{F}_w$ and the direct force $\mathbf{F}_d$. $\mathbf{F}_w$ is the force on the defect due to the momentum transfer from the current-carrying electrons scattered by the defect. $\mathbf{F}_d$ is the force exerted on the partially screened charge on the defect by the externally applied field.[2] The separation of $\mathbf{F}_e$ into $\mathbf{F}_w$ and $\mathbf{F}_d$, and especially $\mathbf{F}_d$ itself, is highly controversial.[1,15,16,20–24] However, this separation of $\mathbf{F}_e$ has been deemed unnecessary in the first instance,[25] and it has been argued that the most satisfactory calculations of $\mathbf{F}_e$ to date have not used this separation *a priori*.[1,16,22,26]

In this report, we present a calculation of the *total* current-induced force on individual atoms in a Cu wire containing a single vacancy. In contrast with previous calculations[13,27–31] no separation into electron-wind and direct forces is made. Furthermore, the current-induced forces are calculated using the fully self-consistent one-electron density matrix in the presence of the current, rather than by merely repopulating the zero-current electron states near the Fermi level. We integrate the residual force, both with and without the current, for an atom as it migrates along the lowest-energy path into the vacancy, to determine the change in the energy barrier for migration with current ΔE. Using ΔE for each migration direction we obtain a vacancy drift velocity, and show that for typical experimental current densities, the activation energy for EM, Q_{EM}, is equal to Q—the energy barrier for migration in the absence of current—to within 10^{-5} eV. We also show that $\mathbf{F}_e$ can be written as $\hat{\mathbf{d}}\Delta E_T/d$, where ΔE_T is the difference between ΔE for migration with and against the current, $\hat{\mathbf{d}}$ is the unit vector in the direction of drift, and d is the migration distance in that direction.

Finally, we introduce ρ^*, the constant of proportionality between $\mathbf{F}_e$ and the current density. Unlike Z^*, which relates $\mathbf{F}_e$ to the externally applied field, ρ^* should be an intrinsic property of a given defect and its immediate surroundings that is nearly independent of the environment in which the defect is placed.

The method for the present calculations has been described in detail elsewhere.[32] Our system consists of two semi-infinite perfect fcc leads with (111) surfaces, connected by an atomic-scale wire. The electronic structure of the system is described by an empirical single-orbital tight-binding model, fit to the bulk cohesive and elastic properties of Cu. The electron eigenstates for this system may be divided into two classes. The first, $\{|\Psi_1\rangle\}$, consists of an incident electron wave in the left lead, partially reflected back into the same lead and partially transmitted through the connecting wire, and conversely for $\{|\Psi_2\rangle\}$. The states $\{|\Psi_1\rangle\}$ and $\{|\Psi_2\rangle\}$ are populated up to electrochemical potentials E_F+eW and E_F, respectively, where E_F is the position of the Fermi level in the absence of current flow. The two electrodes are rigidly shifted relative to each other in energy by an amount equal to the applied bias eW so as to preserve atomic charge neutrality in the bulk of each electrode. Self-consistency is maintained by adjusting the onsite energies on all lead atoms bonded to wire atoms, as well as on all wire atoms, until all these atoms are charge neutral.

The system is described by the one-electron density matrix

$$\rho_{nm}(W)=\frac{1}{2\pi i}\oint_C G_{nm}(z)dz+\int_{E_F}^{E_F+eW}(d_1)_{nm}dE. \quad (3)$$

Here $G(z)$ is the Green function for the system, defined by $G(z)(z-H)=(z-H)G(z)=1$, where H is the tight-binding Hamiltonian, and $d_1=\Sigma_1|\Psi_1\rangle\delta(E-E_1)\langle\Psi_1|$, where E_1 is the eigenenergy of $|\Psi_1\rangle$. All electron operators are expressed as matrices in the tight-binding positional basis, in which indices n and m refer to atomic sites n and m respectively. The closed contour C cuts the real energy axis at E_F and at a second point well below the lower band edge.

The total force on atom n at position $\mathbf{R}_n$ is expressed as

$$\mathbf{F}_n=-4\sum_{m\neq n}(\nabla_n H_{mn})\mathrm{Re}[\rho_{nm}(W)]-\sum_{m\neq n}\nabla_n\phi_{nm}, \quad (4)$$

where $\nabla_n=\partial/\partial\mathbf{R}_n$, H_{nm} is the Hamiltonian matrix element between atoms n and m, and ϕ_{nm} is a repulsive pair potential. If R_{nm} is the distance between atoms n and m, then $\phi_{nm}=\epsilon(a_f/R_{nm})^p$ and $H_{nm}=-(\epsilon c/2)(a_f/R_{nm})^q$, where a_f is the fcc lattice parameter. ϕ_{nm} and H_{nm} are truncated just beyond the second nearest-neighbor distance in fcc. The model is fitted to the lattice parameter, bulk modulus and cohesive energy of bulk Cu. We choose a band filling of 0.24304 electrons per atom, excluding spin degeneracy, and set $a_f=3.61$ Å, $p=9$, $q=3$, $\epsilon=0.012611$ eV, and $c=112.35$. The details of the fitting procedure and of the calculation of $G(z)$ and d_1 are given elsewhere.[32]

The current-induced force on atom n and the local electron bond current from atom m into atom n are then given, respectively, by

$$\Delta\mathbf{F}_n=-4\sum_{m\neq n}(\nabla_n H_{mn})\mathrm{Re}[\Delta\rho_{nm}] \quad (5)$$

and

$$I_{nm}=-\frac{4e}{\hbar}H_{mn}\,\mathrm{Im}[\Delta\rho_{nm}], \quad (6)$$

where $\Delta\rho_{nm}=\rho_{nm}(W)-\rho_{nm}(0)$.[32]

Importantly, while the bond current depends on the imaginary part of $\Delta\rho_{nm}$, which arises only from the partially populated electron states with energies between E_F and E_F+eW, the current-induced force depends on the real part of $\Delta\rho_{nm}$, which contains contributions from *all* occupied states, not merely the states near E_F. For this reason a fully self-consistent density matrix in the presence of the current is needed to calculate current-induced forces.

For calculating the vacancy migration energy in the presence of a current, the following system was used. The wire was composed of 4 (111) planes, containing 31 atoms each. One atom from near the center of the wire was removed to create a vacancy in such a way that the atomic geometries before and after migration in the [111] direction were equivalent by symmetry. Then the atoms in the wire were allowed to relax to establish the starting geometry for the simulation.

Migration of the vacancy was accomplished by choosing one of its neighboring atoms and moving it into the vacancy in a stepwise fashion. All other atoms in the wire were relaxed at each step until the forces on each was less than 10^{-5} eV/Å. The migrating atom was relaxed to the same precision in the plane perpendicular to the diffusion direction. This ensured that the migration was carried out along the lowest energy path. The residual force on the chosen atom was then calculated at each step and integrated along the entire path to determine the energy barrier for migration.

Using our potential for Cu,[32] Q for vacancy migration in the forward [111] direction was found to be $Q_f=0.641$ eV, and $Q_b=0.646$ eV for migration in the opposite direction. For migration within the (111) plane, Q was given by $Q_p=0.600$ eV. The experimental value for the migration energy of a vacancy in Cu is 0.76 eV.[33] The small difference between Q_f and Q_b arises from the accumulation of errors in the residual force on the migrating atom, stemming from small but finite errors in the relaxed positions of other atoms. Q_p differs from Q_f and Q_b because the wire has a finite width. But here we are concerned only with the change of the barrier height due to the current. The errors we have identified cancel when the current-induced changes in the barrier heights along different migration directions are calculated. This has been confirmed by repeating the calculations for a smaller system, where the current-induced change in the barrier height remained the same fraction of the total barrier height.

With the application of a bias of 0.2 V, a total current of 2.1×10^{-4} A was produced. Assigning to each atom in the cross-section of the wire the area per atom in the perfect fcc (111) plane gives a corresponding current density of 1.2×10^{10} A cm^{-2}. The change in Q for vacancy migration along the direction of the electron current, ΔE_f, was $+0.0079$ eV or $+1.23\%$ of Q_f, while for migration in the opposite direction, the change in Q, ΔE_b, was -0.0085 eV or -1.32% of Q_b. As one might expect, the barrier for migration perpendicular to the current was little affected by the current, with a change in barrier height, ΔE_p, of only $+0.18\%$ of Q_p. These results indicate a vacancy drift in the direction opposite the electron current, which agrees with

experimental observations.[34] It is this bias in the barrier heights that causes a net drift of the vacancies within the metal.

A point of interest that should be mentioned here is that ΔE_f and ΔE_b are not equal in magnitude, not even as a fraction of their respective values of Q. One would expect $\mathbf{F}_e$ to be the same at each point along the migration path in the [111] direction whether traveling forward or backward, and indeed that is the case. However, before any migration takes place, the atoms within our wire undergo an additional relaxation due to the current, changing the initial state of the system. Therefore, ΔE_f and ΔE_b differ because they are measured relative to the zero-current state, and not the additionally relaxed current-carrying state.

The current density in our calculations exceeds that in typical EM experiments by more than four orders of magnitude. We have confirmed that at a bias of 0.2 V the relationship between the current-induced forces and the current is linear by observing that (i) the forces are halved when the bias is reduced to 0.1 V and (ii) the I-V relation is linear. For typical experimental current densities of 10^6 A cm^{-2}, the current-induced changes in barrier heights take on values of order $\Delta E = 10^{-6}$ eV. However, these values for ΔE are about five orders of magnitude smaller than the discrepancies in the various experimental values of the EM activation energy Q_{EM}, which can differ by as much as several tenths of an eV in different experiments.[5] Therefore, it is essentially the intrinsic, zero-current migration energies of the vacancies in various microstructural environments that are measured in experiment.

Once ΔE has been calculated, a vacancy drift velocity $\mathbf{v}_D$, can be obtained by adding up the migration rates in each direction. Assuming only nearest-neighbor hopping $\mathbf{v}_D$ becomes[35]

$$\mathbf{v}_D = \sum_{i=1}^{12} \mathbf{r}_i \nu \exp[-(Q+\Delta E_i)/kT], \tag{7}$$

where i labels the hopping direction, $\mathbf{r}_i$ is the change in the position of the vacancy for the respective hop, ν is the attempt frequency for the hop, and ΔE_i is the current-induced change in barrier height for the hop. Putting $Q=(Q_f+Q_b)/2$, setting[35] $\nu = 2.1\times 10^{12}$ s^{-1} and using the perfect fcc lattice parameter for Cu of 3.61 Å, at 1000 K and at a current density of 1.2×10^6 A cm^{-2}, we find a vacancy drift velocity of 14.4 μm s^{-1} against the electron current. Relating this to an edge displacement as measured in experiment is difficult, but with the assumption of noninteracting vacancies in an otherwise perfect crystal, the edge displacement is $C\mathbf{v}_D$, where C is the fractional vacancy concentration. Assuming a thermal equilibrium vacancy concentration and a vacancy formation energy of 1.31 eV (Ref. 33) gives an edge displacement of 0.32 μm day^{-1}, which agrees reasonably with experimental values.[34]

It is common to use a Nernst-Einstein type relationship for $\mathbf{v}_D$ in which $\mathbf{v}_D$ is expressed as a mobility times a driving force, $\mathbf{v}_D = \mu \mathbf{F}_e$. Expanding Eq. (7) to first order in ΔE_i, the mobility can be written as $\mu = (a^2\nu/kT)\exp(-Q/kT)$,[36] and the effective driving force for electromigration as

$$\mathbf{F}_e = \frac{\Delta E_T}{d}\,\hat{\mathbf{d}}, \tag{8}$$

where $\Delta E_T = \Delta E_f - \Delta E_b$, d is the (111) interplanar distance, and $\hat{\mathbf{d}}$ is the unit vector in the negative [111] direction.

In order to predict the electromigration of a given defect, one must know the intrinsic, zero-current energy barrier for migration Q for that defect. Furthermore, one would like to be able to express the EM driving force $\mathbf{F}_e$ on the defect in terms of a suitably defined intrinsic property of the defect. Towards this goal we introduce a quantity, which we call the EM susceptibility ρ^* that relates the EM driving force to the current density in the specimen. We consider a macroscopic wire carrying an average electron current density $\mathbf{j}$ and define ρ^* by

$$\mathbf{F}_e = \frac{\Delta E_T}{d}\,\hat{\mathbf{d}} = \rho^* \mathbf{j}. \tag{9}$$

Recalling the definition of Z^* in Eq. (2), we see that ρ^* is related to Z^* by $\rho^* = -\rho e Z^*$, where ρ is the bulk resistivity of the wire. In spirit, ρ^* is analogous to the constant K used by Dekker *et al.*,[37,28,29] but it differs from K in that K is related to the electron-wind force, whereas ρ^* is related to the total force.

There are two important points about ρ^*. The first is that $\mathbf{F}_e$ is related not to the externally applied field, but to the current density within the wire. The second is that the quantity ρ^* should be an intrinsic characteristic of the defect and its immediate surroundings, and nearly independent of any other defects that may be present.

This may be understood in the following way. The self-consistent potential and density matrix in the neighborhood of a defect immersed in a given current density are determined by the electron scattering caused by that defect. The self-consistent density matrix determines the current-induced forces on atoms in the vicinity of the defect, via Eq. (5). Therefore, once we know the local current density in which a defect is immersed, the current-induced forces in the vicinity of the defect are also known. In the limit of small concentrations of defects the local current density in which a defect is immersed will be virtually the same as the experimentally measured average current density $\mathbf{j}$. Then, ρ^*—the constant of proportionality between the EM force on a defect and the electron current density in the specimen—should be an intrinsic property of the defect and its immediate surroundings. For a vacancy in Cu we find $\rho^* = -6.6\times 10^{-5}$ eV cm A^{-1}. This agrees within an order of magnitude with the value of K for Cu in Ref. 28 although a quantitative comparison is difficult because of the difference in the definition of K and ρ^*, and in the method of their calculation.

In summary, we have calculated the current-induced forces on atoms around a vacancy in a Cu wire using the self-consistent, current-carrying density matrix. By integrating these forces we have calculated the changes in the activation energy for migration of a vacancy in a Cu wire due to an electric current. We have shown that for current densities typical of electromigration experiments, the current-induced changes in the activation energy for migration are 5 orders of magnitude smaller than the activation energy in the absence

of a current. Therefore the measured activation energies for electromigration are experimentally indistinguishable from the activation energies for defect migration in the absence of a current. Finally, we have proposed that the constant of proportionality, ρ^*, between the EM driving force $\mathbf{F}_e$ and the current density should be an intrinsic property of a given defect and its immediate surroundings.

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