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Dislocation mechanism of interface point defect migration

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Vacancies and interstitials absorbed at Cu-Nb interfaces are shown to migrate by a multistage process involving the thermally-activated formation, motion, and annihilation of kinks and jogs on interface misfit dislocations. This mechanism, including the energy along the entire migration path, can be described quantitatively within dislocation theory, suggesting that analysis of misfit dislocation networks may enable prediction of point defect behaviors at semicoherent heterointerfaces.

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In nanocomposites, interfaces between constituents account for a large fraction of the total volume and govern behaviors such as plastic deformation^{1,2} and mass transport.³ Thus, it may be possible to design nanocomposites with desired properties if their microstructures can be controlled (using microstructure engineering⁴) to yield interfaces with those properties. For example, interfaces that trap and accelerate the recombination of radiation-induced vacancies and interstitials make Cu-Nb layered nanocomposites far more resistant to radiation than pure Cu or Nb.⁵ Metal-insulator interfaces may make some composites superconducting—e.g., copper oxide bilayers—even though the constituent materials are not themselves superconducting.⁶

To enable design of nanocomposites via control of interfaces, frameworks relating the structure of arbitrary interfaces to their properties are essential and currently lacking. We present a physical basis upon which the structure of semicoherent interfaces may be related to their transport properties. Using atomistic modeling, we investigate the migration of isolated vacancies and interstitials at a well-studied Cu-Nb semicoherent heterophase interface^{5,7,8} and find that interface misfit dislocations play a governing role in interface point defect migration. The entire migration process can be described within dislocation theory, the key inputs to which are the interface misfit dislocation distribution, i.e., the interface structure, and the structure of the accommodated point defects. The ability of the dislocation theory to describe quantitatively the entire migration process suggests that analysis of the interface structure may help predict point defect behavior at other semicoherent interfaces. This finding brings closer the prospect of tailoring those properties that, in nanocomposites, are governed by point defect migration at interfaces, e.g., recombination of radiation-induced vacancies and interstitials,⁵ superplasticity,^{9,10} and impurity transport.¹¹

A simulation supercell containing a Cu-Nb interface is constructed by joining a block of Cu and Nb such that the interfacial $\{111\}_{\text{Cu}}$ and $\{110\}_{\text{Nb}}$ planes are parallel to each other. The Cu and Nb blocks are each 4 nm thick and in Kurdjumov-Sachs (KS) orientation: $\langle 110 \rangle_{\text{Cu}} \parallel \langle 111 \rangle_{\text{Nb}}$ in the interface plane. This construction corresponds to the experimentally observed crystallography of Cu-Nb interfaces in multilayer nanocomposites.⁷ The supercell, shown in Fig. 1(a), is periodic in the interface plane with free surfaces away from the interface. Interatomic interactions are modeled using an embedded atom method (EAM) potential.¹² This interface is semicoherent and contains two sets of misfit

dislocations, which form a network that spans the entire interface. Representative members of these two sets are illustrated in Fig. 1(b): set 1, with unit line vector $\hat{\xi}_1$, is predominantly screw and set 2 ($\hat{\xi}_2$) is mixed.⁸ Misfit dislocation intersections (MDIs) are discernible as periodic protrusions [indicated in Fig. 1(b)].

Cu-Nb interfaces were studied by molecular dynamics (MD) simulations at constant volume and at $T=800$ K (Langevin thermostat) using LAMMPS.¹³ Metastable atomic configurations were further investigated by conjugate gradient potential energy minimization (PEM) and saddle point configurations with the climbing image nudged elastic-band (CINEB) method.¹⁴ Unlike interfaces with a single low-energy configuration (coherent $\Sigma 3$ twin boundaries, for example), Cu-Nb interfaces have a rough potential energy landscape due to fluctuations in the positions of the atoms at MDIs. While some fluctuations are small and do not cause interface structural changes, others lead to formation of thermal kink pairs at MDIs in the Cu interface plane, as illustrated in Fig. 1(b). Thermal kink pairs are identified as clusters of four- and five-membered rings around which Burgers circuits reveal closure failures.⁸ The formation energies and activation barriers of thermal kink pairs are, $\Delta E_f = 0.27\text{--}0.35$ eV and $\Delta E_{act} \approx 0.45$ eV, respectively.

Vacancies (self-interstitials) are introduced into the Cu interface atomic plane by removing (inserting) a copper atom. Irrespective of their initial location, these defects migrate

FIG. 1. (Color online) (a) Three-dimensional view of the KS-oriented Cu-Nb bilayer supercell with interfacial Cu plane colored differently than other Cu atoms. (b) Plane-view of the interfacial Cu plane identifying the line and Burgers vectors of a few representative members of the two sets of misfit dislocations present in the interface. The periodic protrusions are misfit dislocation intersections. Differently colored atoms in (b) identify a thermal kink pair.

FIG. 2. (Color online) A delocalized vacancy migrates from (a) one MDI to (c) a neighboring one through (b) an intermediate state; atom coloring is the same as in Fig. 1(b). Dislocation models for states (a)–(c) are depicted in (d)–(f), respectively.

with low activation energy to a nearby MDI. Unlike point defects in perfect crystals, which remain compact, interface point defects delocalize at MDIs into kink-jog pairs.⁸ A delocalized vacancy is shown in Fig. 2(a). The migration mechanisms of these defects are directly observed in MD simulations of an isolated interface vacancy or interstitial. In both cases, migration occurs from one MDI to a neighboring one by a two-stage, one-dimensional process along a set 1 misfit dislocation, as illustrated in Fig. 2. First a defect delocalized at one MDI extends over two MDIs [Fig. 2(b)]. Next, it collapses back onto a neighboring MDI [Fig. 2(c)]. The energy difference between the extended and collapsed states is $\Delta E_{a \rightarrow b} = 0.06\text{--}0.12$ eV.

Transitions between the successive states in Fig. 2 are thermally activated and involve the nucleation of kink pairs, like the one shown in Fig. 1(b). Figure 3(a) shows an intermediate state—termed **I**—between the configuration in Fig. 2(a) and the extended state in Fig. 2(b). It contains a thermal kink pair that nucleated at an MDI adjacent to the delocalized vacancy. One member of the pair, labeled “KJ3,” annihilates with a member of the delocalized vacancy, labeled “KJ2.” Afterward, only “KJ1” and “KJ4” remain, corresponding to the extended state of Fig. 2(b).

The transition from the extended state in Fig. 2(b) to the collapsed state in Fig. 2(c) is also mediated by a thermal kink pair. Figure 3(b) shows a configuration where the indicated kink pair “KJ2’”–“KJ3’” forms between the two MDIs on which the point defect “KJ1”–“KJ4” is delocalized. The kink pair “KJ1”–“KJ2’,” which is structurally equivalent to thermal kink pair in Fig. 1(b), then annihilates leading to the formation of the configuration in Fig. 2(c). The state in Fig. 3(b) is also termed **I** as it is structurally equivalent to the one in Fig. 3(a). The formation energy of a thermal kink pair in an **I**-type state is $\Delta E_{a \rightarrow I} = 0.25\text{--}0.35$ eV: identical to the formation energy of an isolated thermal kink, like that in Fig. 1(b).

All the configurations in Fig. 2 and 3 are metastable and can be found by PEM. We used CINEB method¹⁴ with multiple climbing images to determine the unstable, saddle point

FIG. 3. (Color online) Formation of a thermal kink pair (a) at an MDI adjacent to a delocalized vacancy [Fig. 2(a)] and (b) between the kink-jogs of a vacancy extended over two MDIs [Fig. 2(b)]; atom coloring is the same as in Fig. 1(b). Dislocation models for states (a) and (b) are depicted in (c) and (d), respectively, with the thermal kink pairs boxed.

transition states **t** that separate them. For convergence, we require that the maximum elastic-band force on any atom in the band is less than 9 pN. The chain of states for the CINEB calculation was initialized by linear interpolation between the metastable configurations in Figs. 2 and 3. Note that the combined path thereby obtained between the first and last states in Fig. 2 is extremely tortuous and could not have been found by direct linear interpolation between these two states.

The energies along representative minimum energy paths (MEPs), one for the migration of a delocalized vacancy and the other for an interstitial, are shown in Fig. 4. States **a**, **b**, and **c** in the MEP for the vacancy correspond to the configurations in Figs. 2(a)–2(c), respectively, and the intermediate states **I** are shown in Fig. 3. A complete migration path for the first stage is given by **a** → **t** → **I** → **t** → **b**. States **t** are ones with maximum Peierls energy—the energy required to overcome the lattice resistance to shear of adjacent close-packed planes during kink motion.¹⁵ Typical transition barriers, which depend on the area of the shearing region, obtained

FIG. 4. Energies along representative MEPs for point defect migration at a Cu-Nb interface. Dashed lines indicate energy values from linear elastic dislocation theory (see text).

from CINEB method are $\Delta E^{act}=0.35\text{--}0.45$ eV and are identical to the activation energy for formation of isolated thermal kink pairs, like that in Fig. 1(b).

Remarkably, a migrating defect need not pass through all possible metastable transition states, as is evident from Fig. 4. For example, the migration pathway $\mathbf{a} \rightarrow \mathbf{t} \rightarrow \mathbf{b}$ is also observed frequently. In this pathway, the nucleating thermal kink pair interacts with a kink-jog of the point defect even before the former fully localizes. Such a path bypasses the metastable state **I** but has the same saddle point energy as one that does not. The migration of delocalized point defects, therefore, can occur through multiple MEPs but the rate-limiting step in every MEP remains the same. This multiplicity of available transition paths may increase the activation entropy for migration.

The foregoing investigation shows that formation and migration of point defects at Cu-Nb interfaces is fundamentally a process involving formation, interaction, and annihilation of kinks and jogs along set 1 (screw character) interface misfit dislocations, on which point defects delocalize, and can be described within the theory of dislocations. Building on this insight, we construct dislocation models for successive stages of vacancy migration. Figures 2(d) and 2(f) model the initial and final configurations of a delocalized vacancy, respectively, while Fig. 2(e) corresponds to the extended state in Fig. 2(b). Figures 3(c) and 3(d) model the structurally equivalent intermediate states in Figs. 3(a) and 3(b), respec-

tively. The isolated thermal kink pair in Fig. 1(b) is structurally equivalent to the boxed dislocation configuration in Fig. 3(c). All jogs and kinks in our model are perpendicular to the set 1 dislocation line on which they reside.

To rigorously calculate the energies of these dislocation configurations, the anisotropy and heterogeneity of the Cu-Nb bilayer as well as the elastic nonlinearity arising from the small dislocation spacings should be considered, as should the interaction of the kinks and jogs with the remainder of the misfit dislocation network. We can, however, account quantitatively for the entire MEP shown in Fig. 4 even if we restrict our analysis to uniform isotropic, linear elastic solutions for dislocation interactions among the kinks and jogs along a single set 1 misfit dislocation. The energy of a kink pair on a screw dislocation is then given by Eq. (1).¹⁵ The first term on the right-hand side of Eq. (1) is the change in the elastic interaction energy upon climb of a segment of length “ L ” of a straight screw dislocation by a distance “ a ” due to the formation of a kink pair and is given explicitly by Eq. (2). The second term is the total (negative) elastic interaction energy, given by Eq. (3), between all pairs of parallel dislocation segments created during nucleation of a kink-jog pair, each of length “ a_i ” and separated by “ L'_i .” The third term is the sum of self-energies of kinks and jogs. Energy expressions for all the states in Figs. 2(d)–2(f), 3(c), and 3(d) are readily obtained as a combination of Eqs. (2) and (3) with appropriate values for the variables L , L'_i , and a_i .

$$W(L, a, \{L'_i\}, \{a_i\}) = 2\Delta W_{inter}^{dis}(L, \infty, a) + \sum_i W_{inter}^{jog}(L'_i, a_i) + \sum_i 2 \frac{\mu b^2 a_i}{4\pi(1-\nu)} \ln\left(\frac{a_i}{\alpha b}\right), \quad (1)$$

$$\Delta W_{inter}^{dis}(L, \infty, a) = \frac{\mu b^2}{4\pi} \left[\sqrt{L^2 + a^2} - L - a + L \ln\left(\frac{2L}{\sqrt{L^2 + a^2} + L}\right) \right], \quad (2)$$

$$W_{inter}^{jog}(L, a) = - \frac{\mu b^2}{4\pi(1-\nu)} \left[2L - 2\sqrt{L^2 + a^2} - 2a \ln\left(\frac{L}{\sqrt{L^2 + a^2} + a}\right) \right]. \quad (3)$$

We evaluate Eqs. (2) and (3) using the Reuss average of elastic constants for cubic materials;¹⁵ for Cu, $\mu=43.6$ GPa and $\nu=0.361$ (appropriate for $T=0$ K).¹⁶ As shown in a previous study,⁸ set 1 misfit dislocations in the Cu-Nb interface have the same Burgers vectors as glide dislocations in fcc Cu, so we take $b=\frac{a_{Cu}}{\sqrt{2}}$ with $a_{Cu}=3.615$ Å ($T=0$ K). From our MD simulations, we obtain $a_1=\frac{a_{Cu}}{\sqrt{3}}$, $a_2=\frac{a_{Cu}}{\sqrt{2}}$, and $L=\frac{3a_{Cu}}{\sqrt{2}}$.

The parameter α in the last term of Eq. (1) is related to the dislocation core radius and cannot be estimated within the linear elastic theory of dislocations. We obtain $\alpha=0.458$ by fitting the formation energy, $\Delta E_f=0.27$ eV, of the thermal kink pair in Fig. 1(b). Then, the calculated change in energy between states **a** and **I** obtained from the theory, $\Delta W_{a \rightarrow I}=0.232$ eV, is in good agreement with the results from atomic-scale simulations ($\Delta E_{a \rightarrow I}=0.25\text{--}0.35$ eV). The change in energy between states **a** and **b**, $\Delta W_{a \rightarrow b}=W(3L, a, \{L'_i\}, \{a_i\}) - W(L, a, \{L'_i\}, \{a_i\})$, is indepen-

dent of α as the number of dislocations segments in both states is equal and, therefore, requires no input from the simulations. The calculated value, $\Delta W_{a \rightarrow b}=0.130$ eV, is on the higher end of the range obtained from atomistic simulations, $\Delta E_{a \rightarrow b}=0.06\text{--}0.12$ eV, but still remarkably accurate considering the number of simplifying assumptions made. The higher values predicted by the theory are likely due to an overestimate of the shear modulus, which is thought to have a lower value at the interface than in the neighboring crystalline layers.¹⁷

The above model accounts for the energies of all metastable states in the migration path of interface point defects. When further augmented with a generalized stacking fault energy (GSF) function, $\gamma^{GSF}(s)$, the model accounts for the energy along the entire defect migration MEP. Within the Peierls-Nabarro framework,¹⁵ kink-pair nucleation is viewed as a continuous change in the Burgers vectors of incipient kinks from 0 to $b=|\vec{b}|$, where $\vec{b}$ is the final Burgers vector of

each kink.¹⁸ Kink pair annihilation is viewed as a continuous change in the Burgers vectors of adjacent opposite-sign kinks from b to 0. An expression for the energy along the minimum energy path between two states **A** and **B** in terms of sb , $\forall s \in [0, 1]$, is given by Eq. (4).

$$\Delta W_{\mathbf{A} \rightarrow \mathbf{B}}^{\text{MEP}}(L, a, s) = \Delta W_{\mathbf{A} \rightarrow \mathbf{B}}(L, a, s) + A \gamma^{\text{GSF}}(s). \quad (4)$$

We consider a sinusoidal function $\gamma^{\text{GSF}}(s) = U_o \sin^2(\pi s)$, where $U_o = 0.175 \text{ J m}^{-2}$ is the unstable stacking fault energy along a $\langle 112 \rangle$ direction in bulk Cu for the EAM potential used in our simulations.¹² Like the shear modulus, unstable stacking fault energies are thought to be lower near the interface than in the crystalline layers.¹⁹ Therefore, the energies along the migration path obtained from the model are expected to be greater than those obtained from simulations. The area A swept by an incipient kink pair is obtained from simulations and assumed constant during nucleation and annihilation. We also assume that the core radius of the incipient kinks is proportional to the Burgers vector and that α remains constant during the process. For typical A , the activation barriers $\Delta W_{\mathbf{a} \rightarrow \mathbf{I}}^{\text{MEP}}|_{\text{max}} = 0.512 \text{ eV}$ and $\Delta W_{\mathbf{I} \rightarrow \mathbf{b}}^{\text{MEP}}|_{\text{max}} = 0.233 \text{ eV}$ are, as expected, greater than, but still in good agreement with those obtained from the simulations (Fig. 4). Our simulations were performed at zero applied stress but the energy barrier for nucleation and motion of kink pairs may be expected to change with the resolved shear components of applied stress. This effect can be incorporated readily into Eqs. (2)–(4) (Ref. 18) and—along with the previously discussed diffusion anisotropy—could be accessible to experimental verification.

Previous atomistic modeling studies have shown that point defects may also delocalize and migrate through col-

lective displacements of clusters of atoms, in addition to single-atom jumps, at high angle tilt boundaries in fcc metals.²⁰ The migration barriers determined in these studies ranged from 0.3 to 1.0 eV.^{21–25} For the model interface we studied, the migration barrier $\sim 0.4 \text{ eV}$ is on the lower end of this range. Additionally, our findings demonstrate a definite migration mechanism of delocalized interface point defects. The fact that this mechanism can be modeled quantitatively by dislocation mechanics suggests that it may be possible to predict point defect migration mechanisms in other semicoherent interfaces based on their misfit dislocation networks. For example, this mechanism may not operate at interfaces where MDIs are far apart because a thermal kink pair nucleating at one MDI may have too high an energy penalty to become sufficiently extended to bridge to a neighboring MDI.

Insight into the structure of these networks may in turn be obtained by analyzing the total dislocation content as expressed by the Frank-Bilby equation.²⁶ Detailed calculations for arbitrary semicoherent interfaces taking into account dislocation core radius α , the kink pair nucleation area A , the GSF function $\gamma^{\text{GSF}}(s)$, as well as interaction between all members of the misfit dislocation network may be performed using mesoscale dislocation dynamics^{27–29} or phase field models.³⁰ These findings may in turn serve as the basis for predicting interface diffusion-controlled properties in nanocomposite materials.

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