Effect of Cu and Ag solute segregation on βSn grain boundary diffusivity

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We investigate the effect of various amounts of Ag and Cu solute atoms on the self-diffusivity of Sn in the (101) symmetric tilt βSn grain boundary. Using molecular dynamics simulations over a temperature range of 300 K to 450 K, we show that both Ag and Cu decrease the grain boundary self-diffusivity of Sn as the amount of solute in the interface increases. Additionally, the presence of Ag at the grain boundary interface causes a greater reduction in the self-diffusivity of Sn when compared to Cu. We also analyze the solute effect on the diffusive width of the interface and find that low concentrations of both Ag and Cu shrink the width relative to the pure βSn interface. However, adding Cu in excess density greater than $5 \times 10^{-3}$ atoms/Å$^2$ causes the interface to expand to values almost twice the original width, possibly caused by the larger cohesive energy of Cu-Sn versus Sn-Sn. © 2011 American Institute of Physics. [doi:10.1063/1.3606421]

I. INTRODUCTION

Characterizing the transport and structure of grain boundaries is an important part in modeling the large scale behavior of polycrystalline and nanocrystalline materials. At sufficiently low temperatures, diffusion in the bulk lattice can be “frozen out” and grain boundaries provide the only means of fast atomic and vacancy transport.\(^2\,3\) Labeled type-B and type-C kinetics, these regimes are exhibited by many types of micro- and nano-electronic interconnects. Understanding the role that grain boundaries play when the interconnects are under electric load will help improve the accuracy of current transport density damage evolution models as well as advance the potential for bottom-up interconnect design — both crucial for the realization of nano-electronics in everyday life.

Pb-free solder joints in particular can benefit from this closer look. So far, much work has been done in developing finite element models to determine the effect of high electric current density and calculate time-to-failure of the joints.\(^3\,5\) Yet accurate values of transport in the joint’s microstructure — atomic level processes that govern damage in the joint — are very few.\(^6\,7\) As one of the more promising Pb-free alternatives, understanding the diffusive properties of Sn grain boundaries in Sn-Ag-Cu solder alloy benefits the development of damage resistant electronics. To this end, experimental work investigating the effects of various amounts of Ag and Cu in Sn solder alloy under several cooling rates showed that each solute type and concentration results in the formation of very different polycrystalline microstructures.\(^8\,9\) The magnitude of diffusion in grain boundaries coupled with variations in solder microstructure underscores the importance of quantifying not only transport properties of the joint solvent material, Sn, but also the effects of dopants or solute additions on transport.

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A 1982 study by Bernardini, Gas, et al.\(^1\) investigates such solute effects on transport in polycrystalline Fe. They observe a decrease in the self-diffusivity of Fe as Sn solute atoms strongly segregate to the grain boundary. While thorough and informative, analysis of these types of experimental works must estimate quantities, such as grain boundary width, in order to compute the amount of solute segregation and estimate solute monolayer concentration using Gibbs adsorption theory.\(^12\,13\) Molecular simulation is well suited to complement this type of study. Preliminary work using simple model systems have shown the effects of substitutional dopant atoms on Cu grain boundaries and in Cu polycrystals.\(^14\,15\) Although these studies are also forced to approximate quantities, such as excess entropy, through the use of McLean’s model and extensions, atomistic model of concentrations and transport for particular structures can be measured.\(^1\) An example is found in our previous work, where molecular simulation was used to quantify self-diffusivities and grain boundary widths and investigate various structural anomalies for several different boundary types in βSn. Here, the self-diffusivity of a range of grain boundaries was computed and shown to agree well with experiment, while the diffusive and structural widths computed with simulation were larger than the value currently used in experiment.\(^17\)

Continuing the investigation into transport in polycrystalline βSn, with application to diffusion in Pb-free solder joints, in the present work, we measure the self-diffusivity of Sn in a (101) symmetric tilt βSn grain boundary containing various amounts of Ag and Cu solute. Using the modified embedded-atom method as an interatomic potential, we are able to quantify the effect that Ag and Cu have on the grain boundary self-diffusivity of Sn at typical solder operating temperatures. Additionally, we determine the effect solute has on the diffusive width of the grain boundary and offer insight into the unique characteristics of the grain boundary resulting from the two types of solute.

This work continues with the Methodology of diffusivity calculation and specifics of our molecular simulations in
Simulation Details. We then present and discuss our findings in Results and Discussion, and end with concluding remarks in Conclusions.

II. METHODOLOGY

Similar to experimental work,\(^1\,^{2}\,^{18}\) application of molecular simulation to calculate directly a solvent material’s self-diffusivity in a structurally heterogeneous solid, such as a grain boundary, is difficult. Instead, as in experiment, the measurable quantity is the group \(\delta_{GB} D_{GB} \) — a width-scaled diffusivity with units of volume/time. Lacking any other information, in experiments with polycrystalline metals, it is conventional to use an estimated average grain boundary width of \(d_{GB} = 5 \, \text{Å} \), a value defined according to Fisher’s model.\(^{19}\)

With molecular simulation, however, we can obtain this quantity in a more direct manner from the atomistic level, allowing us to investigate the validity of employing the average \(d_{GB}\) value in scenarios where its magnitude may come into question. In either case, the measured width-scaled diffusivity \(\delta_{GB} D_{GB}\) is normalized by \(\delta_{GB}\) to resolve the true diffusivity \(D_{GB}\) of the structure. This section provides detail on why and how \(\delta_{GB}\) is calculated for our grain boundary structures and how we quantify an interface width, \(\delta_{GB}\).

A. Diffusivity calculation

Self-diffusion of particles in a molecular dynamics (MD) simulation is typically measured via the Einstein or Green-Kubo relations, which involve tracking atomic displacements or velocities.\(^{20}\) Here, we follow the work of Keblinski et al.,\(^{21}\) wherein diffusion is measured with an adjusted form of the Einstein relation. This adjustment is performed because, in a particular MD run, atoms close to the grain boundary will exhibit a variety of displacement lengths. As one moves away in a direction perpendicular to the interface (\(z\)-direction, in our case) and into the defect-free bulk lattice, displacement begins to decrease to the order of atomic vibrations. Averaging the squared displacement over all atoms, as is normally done in a structurally homogeneous system, will wash out the true value of solvent self-diffusivity in the grain boundary. One could specify a region of the simulation box, within which the mean squared displacement would be calculated, but the dividing surface between fast and non-existent diffusivity regions for our systems is not known a priori. As a result, we compute the total squared displacement of solvent in our system (the displacement of all solvent atoms) and normalize this quantity by atomic volume per grain boundary area, shown in Eq. (1).

\[
\delta_{GB} D_{GB} = \frac{\Omega}{A} \times \frac{1}{4} \frac{d TSD}{dt}
\]  

(1)

Here, \(\Omega\) is the volume per Sn atom in our system, \(A\) is the interfacial area, and the factor of \(1/4\) is determined by the dimensionality of the total squared displacement (TSD). After this scaling, the quantity computed is likened to the interface width \(\delta_{GB}\) perpendicular to the plane of \(A\), multiplied by the true grain boundary diffusivity, \(D_{GB}\). Now, \(\delta_{GB}\) may be represented as shown in Eq. (2), where \(N_D\) is the number of diffusing atoms.

\[
\delta_{GB} = \frac{N_D \Omega}{A}
\]  

(2)

During a particular simulation run, the total squared displacement (TSD) is calculated and, with Eq. (1), yields the quantity \(\delta_{GB} D_{GB}\). Here, we assume that all diffusion takes place within the grain boundary. To finally resolve a value of \(D_{GB}\) for each system, we must determine \(\delta_{GB}\), the width of the interface, by means other than Eq. (2).

B. Interface width calculation

\(\delta_{GB}\) is evaluated post-MD run by examining the diffusive profiles of each \(\beta\)Sn grain boundary containing solute atoms and computing its value from these profiles via a full-width at half maximum analysis. The diffusive profiles are measured in addition to the simulation cell’s total diffusivity, outlined in Subsection II A. For a particular simulation run, we compute planar quantities of the diffusivity in directions parallel to the grain boundary interface and apply the analysis to establish a fixed value of \(\delta_{GB}\) at a given temperature. Planar diffusivity is calculated using a typical Einstein relation for atoms in a plane. We restrict the volume of space in which the mean squared displacement (MSD) is sampled to slices in successive \(z\)-planes of width \(\Delta z\), and \(D_{s\gamma}\) is evaluated as the slope of this quantity versus time. An example of this method is shown in Fig. 1. The background of this figure is a grain boundary, rotated from a typical viewing angle so that the simulation cell’s \(z\)-axis is parallel to the \(z\)-positions on the plot. Here, we see that planes in the \(z\)-direction close to the interface are areas of high diffusivity. The full-

\[ \text{FIG. 1. (Color online) Planar diffusivity vs \(z\)-coordinate in the simulation cell. [h] is the maximum of the diffusion profile and [\(\delta\)] is the width at [h]/2. Background is grain boundary rotated with \(z\)-axis parallel to planar diffusivity plot abscissa. Points on plot correspond to lattice planes in background separated by \(\Delta z\).} \]
width at half maximum of such profiles is used to quantify an interface width, as indicated in the figure. In addition to the width, the shapes of these profiles are useful in comparing and contrasting the effects of the two solutes studied in this work.

Many works employ other measures of the interface structure and mobility to investigate thermodynamic phase and interface width.\textsuperscript{21–24} The use of a potential energy profile per plane, as well as the square of the planar structure factor, has been used to determine \( \delta_{GB} \).\textsuperscript{21,22} For our work, the diffusive width provides information about how the grain boundary interfaces evolve with increasing solute and simulation temperature, and we use the diffusive width in the calculation of \( D_{GB} \), given the quantity \( \delta_{GB}D_{GB} \) measured in simulation. Values of \( \delta_{GB} \) calculated from a planar diffusion measurement are more closely related to the totally squared displacement we are measuring in simulation. Therefore, we believe the most meaningful grain boundary diffusivity, \( D_{GB} \), is computed using the diffusive width measurements.

III. SIMULATION DETAILS

In our simulations, we are modeling the (101) symmetric tilt grain boundary of \( \beta \)Sn with varying amounts of solute particles randomly placed in interstitial positions along the interface. The (101) distinction indicates that two grains of \( \beta \)Sn are rotated opposite to one another until they both share a common (101) Miller plane, equivalent to a 180° twist boundary.\textsuperscript{3} The grain boundaries and randomly inserted solute configurations are constructed with the Etomica Molecular Simulation API, and, for solute species, we are using Ag and Cu.\textsuperscript{25} Interactions between Sn and Ag and Sn and Cu are modeled with the modified embedded-atom method (MEAM) in the LAMMPS Molecular Simulator.\textsuperscript{26–28} Details of the potential and of our simulation setup and conditions are continued below.

A. Interatomic potential

The development of the MEAM potential is outlined below and details are given in Refs. 29 and 30. The potential was parameterized for Sn and the Sn-Ag and Sn-Cu systems in Refs. 31, 32, and 33, respectively. In the model, the total energy \( E \) is given as a sum of atom energies \( E_i \), as follows:

\[
E = \sum_i \left[ F_i \left( \frac{\rho_i}{Z_i} \right) + \frac{1}{2} \sum_{j \neq i} \phi(r_{ij}) \right]. \tag{3}
\]

Here, \( F \) is the embedding function or the energy required to embed an atom of type \( i \) into the background electron density \( \rho_i \). This factor is normalized by \( Z_i \), the number of nearest neighbors in the reference structure. The second term, \( \phi(r_{ij}) \), is the pair interaction between atom \( i \) and its neighbors, \( j \). Sn, Ag, Cu, and the cross-potential parameters are listed in Table I.\textsuperscript{31–33}

These parameters are determined by fitting experimental values of a material’s bulk modulus, average atomic volume, cohesive energy, and equilibrium nearest-neighbor distance of a reference lattice structure. The \( \beta \)Sn phase simulated in this work, one of two allotropes of Sn, is metallic and stable at temperatures above 286 K to Sn’s experimental melting point of 505 K. Using the MEAM potential, the equilibrium lattice constants are \( a = 5.92 \text{ Å} \) and \( c = 3.23 \text{ Å} \), preserving the 0.546 \( c/a \) ratio observed experimentally, while the melting temperature is lowered in comparison to experiment to 453 K. As reported in Ref. 31, the potential for Sn has successfully reproduced experimental values of the heat capacity for Sn’s \( \alpha \) and \( \beta \) phases, as well as the phase transition temperature between liquid and \( \beta \)Sn and \( \beta \) and \( \alpha \) Sn. The alloy forms of the potential reflect input from experiment as well. Cu-Sn interactions reproduce a theoretical bulk diffusion activation energy of Cu in the c-direction of \( \beta \)Sn lattice that is equivalent to experimental work, as well as a vacancy formation energy that is very close to experiment.\textsuperscript{33} Similarly, for Ag-Sn interactions, the atomic volume, bulk modulus, and polycrystalline shear modulus for Ag-Sn are reproduced almost exactly.\textsuperscript{32} Details on MEAM’s implementation in LAMMPS are available elsewhere.\textsuperscript{26}

B. Structure development and simulation procedure

We construct the (101) symmetric tilt grain boundary of \( \beta \)Sn, which can be thought of as twist grain boundaries with 180° rotation. Our simulation cell is periodic in the directions parallel to the grain boundary interface and fixes atoms at the top of grain 1 and at the bottom of grain 2, mimicking a bulk structure and creating a “sandwich” of movable atoms.\textsuperscript{31} Various quantities of solute are then randomly inserted into interstitial positions at the grain boundary interface. The final structure is shown in Fig. 2 as a normal and expanded view. In this type of setup, it is important to equilibrate the system correctly in order to obtain a grain boundary interface of minimum energy and to simulate at an average pressure of zero.

The process of minimization of the grain boundary is done in three steps. First, near 0 K the two grains move independently in \( x \), \( y \), and \( z \)-directions via molecular dynamics, their respective atoms all having the same average force each time step. This step is shown in Fig. 3 (minimization). Next, solute atoms are randomly inserted at interstitial

<table>
<thead>
<tr>
<th>Material</th>
<th>( E_C ) (eV)</th>
<th>( r_0 ) (Å)</th>
<th>( x )</th>
<th>( A )</th>
<th>( \beta^{(0)} )</th>
<th>( \beta^{(1)} )</th>
<th>( \beta^{(2)} )</th>
<th>( \beta^{(3)} )</th>
<th>( \epsilon^{(1)} )</th>
<th>( \epsilon^{(2)} )</th>
<th>( \epsilon^{(3)} )</th>
<th>( \rho_0 )</th>
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<tbody>
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<td>Sn</td>
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<td>3.44</td>
<td>6.20</td>
<td>1.0</td>
<td>6.2</td>
<td>6.0</td>
<td>6.0</td>
<td>6.0</td>
<td>4.5</td>
<td>6.5</td>
<td>–0.183</td>
<td>1.0</td>
</tr>
<tr>
<td>Cu</td>
<td>3.62</td>
<td>2.50</td>
<td>5.106</td>
<td>1.07</td>
<td>3.62</td>
<td>2.2</td>
<td>6.0</td>
<td>2.2</td>
<td>3.14</td>
<td>2.49</td>
<td>2.95</td>
<td>1.0</td>
</tr>
<tr>
<td>Ag</td>
<td>2.85</td>
<td>2.89</td>
<td>5.89</td>
<td>1.06</td>
<td>4.46</td>
<td>2.2</td>
<td>6.0</td>
<td>2.2</td>
<td>5.54</td>
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</tr>
<tr>
<td>Cu,Sn</td>
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<td>5.38</td>
<td>5.92</td>
<td>5.89</td>
<td>2.2</td>
<td>6.0</td>
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<td>5.54</td>
<td>2.45</td>
<td>1.29</td>
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<td>Ag,Sn</td>
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<td>2.96</td>
<td>6.07</td>
<td>0.7</td>
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<td>2.2</td>
<td>5.54</td>
<td>2.45</td>
<td>1.29</td>
<td>0.7</td>
</tr>
</tbody>
</table>

Table I. Parameters for the MEAM potential.
positions in the grain boundary interface. Shown in Table II are the specific amounts of solute inserted and their corresponding interfacial excess density. The positions of the solute atoms are then adjusted via a conjugate gradient energy minimization while holding the Sn atoms fixed. Finally, once a minimum energy structure is found, the system is then equilibrated using molecular dynamics (MD) at the desired production run temperature (Fig. 3 - equilibration). Here, atoms in the bottom grain within twice the potential cutoff distance of the bottom edge of the structure are fixed, and atoms in the top grain within twice the potential cutoff distance of the top edge of the structure are given an average force in the x, y, and z-directions. This creates a floating boundary at the top of the box and allows the system to reach an average pressure of zero over 100 picoseconds. Following these steps, the floating boundary is fixed and the grain boundaries are simulated with MD between 9 and 15 ns (Fig. 3 - production). All molecular dynamics are carried out with a Nose-Hoover thermostat (NVT) and a time-step of 0.001 picoseconds.

IV. RESULTS AND DISCUSSION

Using MD over a range of temperatures, we simulate the (101) symmetric tilt grain boundary of $\beta$Sn. At each temperature, specific quantities of solute atoms of Ag and Cu are randomly inserted at the grain boundary interface and the width-scaled Sn self-diffusivity is calculated. We also analyze the planar self-diffusivity profiles in the direction perpendicular to the grain boundary interface. From this, we can quantify the interface’s diffusive width $\delta_{GB}$ and characterize the effect that Ag and Cu have on the interface structure of $\beta$Sn.

A. Width-scaled self-diffusivity ($\delta_{GB}D_{GB}$) of Sn

We compute the mean-squared displacement of Sn for multiple MD runs at a given temperature and specific solute concentration. By employing Eq. (1), we plot the width-scaled diffusivity versus temperature in Fig. 4 for each type of solute over a range of quantities and temperatures. For Ag and at low temperatures, the diffusivity of Sn does not exhibit any type of clear trend with increasing solute concentration. Statistically, the points at 300 K and 350 K are very close in magnitude. However, as the temperature increases, we see the Sn diffusivities for specific solute amounts begin to deviate. At 450 K, the diffusivity for a system with 50 solute atoms is decreased by an order of magnitude when compared to the 5 solute atom system and by about one-third when compared to the 25 solute atom system. With the addition of Cu instead of Ag, the trends are similar but less pronounced. We see a smaller deviation in the diffusivity of Sn at higher temperatures with respect to solute concentration — about twice the diffusivity at 5 atoms than at 50 atoms. In contrasting the two solute types, the addition of 25 and 50 atoms of Ag lowers the diffusivity of Sn more than similar quantities of Cu. For small numbers of solute, the effect of Ag and Cu are statistically similar on this width-scaled diffusivity plot.

B. Planar self-diffusivity profiles and interface width

For a closer look at the diffusive properties of Sn and an opportunity to investigate its interface structure, we plot the planar self-diffusivity in planes parallel to the grain boundary interface. For clarity in the plots in Fig. 5 and Fig. 6, only profiles from a single run are plotted; however, the single run chosen was the one with a diffusivity closest to the average. Also, note the change in scale on the plots’ y-axes. The profiles for varying Ag amounts at temperatures of 300

<table>
<thead>
<tr>
<th>$\Gamma_s$ ($10^{-3}$ atoms/Å$^2$)</th>
<th>2.085</th>
<th>4.171</th>
<th>10.43</th>
<th>20.85</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>$N_s$ (atoms)</th>
<th>5</th>
<th>10</th>
<th>25</th>
<th>50</th>
</tr>
</thead>
</table>

FIG. 3. (Color online) LEFT minimization (near 0 K), CENTER equilibration, and RIGHT production structures. Black arrows indicate direction of motion of the block portion. Free atoms are movable in x, y, and z directions. Actual simulation cells are 3-dimensional and periodic in x and y directions.

FIG. 2. (Color online) Typical configuration of grain boundary with its interface loaded with smaller solute atoms (off-shade, orange in color). LEFT is a simulation snapshot after equilibration, and RIGHT is the same snapshot with the interface exposed for clarity.
K, 350 K, 400 K, and 450 K are shown in Fig. 5. Similar to Fig. 4, at temperatures of 300 K and 350 K, the authors are unable to discern any trend in diffusivity when increasing solute amount. Although, at 300 K, the profiles show a decrease in diffusivity when increasing solute amount from 5 atoms to 10 and from 5 atoms to 50; the same does not hold true for profiles at 350 K. At 400 K and 450 K, the effect of solute on Sn self-diffusivity is clearly evident and is amplified as temperature increases. Widths of the profiles remain relatively stable as temperature increases and as solute increases.

A similar analysis is completed for Cu solute in the βSn grain boundary and illustrated in Fig. 6. Again, the scales of the plots’ y-axes vary with temperature, but are equivalent to those in Fig. 5 at specific temperatures for the sake of comparison. In Fig. 6, the effect of Cu solute on the self-diffusivity of Sn with increasing solute amount occurs at 350 K and continues to high temperature. The effect of specific solute concentrations on diffusivity becomes more distinct as temperature increases. As solute concentration is increased, we see an increase in diffusive width at all temperatures, with the increase at 450 K being the least prominent. Additionally and perhaps most importantly, the interface diffusivity profiles exhibit a change from a single peak at 5 and 10 atoms of Cu to double peaks at 25 and 50 atoms of Cu.

Further evidenced by the planar diffusivity profiles in Fig. 5 and Fig. 6 is the effect of solute on Sn self diffusivity. Both Ag and Cu decrease the planar diffusivity in the (101) grain boundary at temperatures at 400 K and above, although the effect of Cu is seen at 350 K. It is shown here, however, that Ag plays a larger role. At 350 K and 400 K, peaks in the diffusivity of the Ag system are significantly lower than systems with Cu for corresponding temperatures. In the comparison of βSn’s structure for different solute types, we see no qualitative difference in interface width with temperature for Ag as solute, but for Cu, it is apparent that the interface width grows with increased solute amount and the diffusive profile changes shape at large solute amounts. The center of the βSn grain boundary interface containing Cu exhibits slower diffusion than at the edges of the interface containing no Cu. To further characterize this behavior, we quantify the interface

![Image](image-url)
width at a range of temperatures for various solute concentrations as well as inspect simulation snapshots and trajectories.

An analysis of the full-width at half maximum of the planar self-diffusivity profiles in Figs. 5 and 6 is shown in Fig. 7. Here, we quantify the diffusive width of the (101) grain boundary interface with varying solute amount at a range of temperatures. It is important to mention that the analysis assumes a profile that is Gaussian-like, yet width measurements from our profiles of the βSn interface with large amounts of Cu solute deviate from this. In our analysis of these profiles, the maximum is taken as the highest peak of the two. This introduces the possibility to skew or induce spurious width measurements for very high peak and very low “trough” regions. However, the profiles in our case exhibit only moderate dips in diffusivity over the range of x-y planes, and it is unlikely that this affects the width measurements in such a manner.

At Fig. 7 - LEFT, it is shown that diffusive widths for the (101) interface containing Ag increase very little with solute concentration and temperature. In comparison to a pure βSn interface (shown as black circles), the width has decreased by at most 1 Å with the addition of Ag solute. As Cu is inserted at the interface (Fig. 7 - RIGHT), an increase in interface width with temperature is more obvious, as is the increase in width with solute amount. At 25 and 50 Cu atoms in the interface, the width of the (101) grain boundary exceeds the pure boundary width for temperatures above 300 K. There is also a marked difference in widths between Ag and Cu at solute amounts of 50 atoms. The amount of Ag solute seems to have no effect on the width, while the addition of Cu causes a distinct increase in width.

We have shown thus far that the addition of both Cu and Ag decrease Sn self-diffusivity in the (101) βSn grain boundary. Separately, Ag reduces the diffusivity more than Cu and promotes a smaller diffusive width of the grain boundary. With Cu addition, small amounts of solute give the same effect on diffusivity as Ag addition, but as the Cu amount is increased to 25 and 50, the grain boundary width grows larger than that of pure βSn. Evidence of this is shown in the planar diffusivity profiles for βSn with Cu added. At values of 25 and 50 atoms of Cu, we see wide profiles with two peaks in diffusivity, indicating a slower diffusing plane of the interface sandwiched by two fast diffusing planes. We attempt to describe this behavior through the visual analysis.
of rendered simulation trajectories of both Ag in βSn and Cu in βSn. In Fig. 8 we show a rendered snapshot of Ag in the (101) grain boundary (LEFT) and Cu in the boundary (RIGHT). These shots are taken from a simulation run at 450 K, both containing 50 atoms of respective solute. It is evident that the amount of disorder in the system containing Ag is less than in the system containing Cu. This observation can explain the difference in diffusive widths of the two systems. A more ordered interface will be less mobile and exhibit a lower value of diffusivity.

C. Effect of atomic size and cohesive energy

With a focus on the system with Cu added, the full trajectory (of which Fig. 8 is a snapshot) shows that the Cu atoms maintain their z-axis position at the center x-y plane of the interface. This plane corresponds to the “troughs” seen in Fig. 8 profiles at higher solute concentration. Yet only part of the interface behavior is described by Cu’s z-axis position, and still unexplained are the highly mobile regions of βSn in planes above and below the Cu solute. For this, further analysis of the trajectory was necessary. In observing the Cu solute atom’s subtle motion in the central z-plane of the interface, we notice a preferred coordination of Sn around the Cu atom. Motion of the Cu atom is actually a concerted motion of a Cu and 4-Sn cluster.

Coordination similar to that of Cu is not seen for the other solute, Ag. This preference is described in a fairly straightforward manner by comparing the cohesive energies used in the MEAM potential, listed in Table I. Sn-Sn interactions carry a cohesive energy of 3.08 eV, Ag-Sn is lower at 2.83 eV, and Cu-Sn is higher at 3.5 eV. At the interface, Sn-Sn interactions are preferred over Ag-Sn, while Cu-Sn interactions are favored over Sn-Sn. The larger cohesive energy of the Cu-Sn system is shown in the simulation trajectories to induce local ordering in the interface, which at larger distances creates disordering when in contact with the βSn lattice. For an interstitial Cu in the bulk βSn lattice, the quality of the surrounding βSn structure may keep the preference for Cu-Sn ordering at bay. Conversely, when Cu is present at the grain boundary, the already low-coordinated Sn atoms are free to rearrange and form clusters with Cu. It appears that these clusters are not structurally compatible with the βSn lattice and create more disorder at the grain boundary. As such, the cohesive energy of Cu-Sn interactions actually increases diffusivity with respect to a Ag solute through the secondary effect of structural disruption at the interface.

Further comparison of the MEAM properties of Ag, Cu, and Sn reveal that equilibrium values of the reference structure lattice constants $r_0$ vary as well. For analysis in this work, values of $r_0$ can be thought of as corresponding to relative atomic size — here, Cu is smaller than Ag and both are smaller than Sn. Because there is variation in both cohesive energy and size of the solutes, we cannot say definitively what effect the larger size of Ag has on the decreased mobility of Sn in the (101) interface. Nevertheless, other works have investigated the separate effects of atomic size and cohesive energy mismatch. We highlight the work carried out over the past several years by Millett, et al.,14,15 on the role dopant atoms play in grain boundary energetics and overall stability of nanocrystals. In a 2005 investigation, they examined the effect of Lennard-Jones dopant particles — over a range of sizes and cohesive energies ($\sigma$ and $\varepsilon$) — on grain boundary energy. They demonstrated that, while the overall contribution of a dopant atom’s cohesive energy does not play a significant role in decreasing the energy of the solvent grain boundary, the size of the dopant atom as compared to the host atom is influential in affecting the energy. This is explained by a reduction of tensile stress at the grain boundary through the insertion of a dopant atom. Furthermore, for sizes of the dopant ranging from smaller than the host atom to larger than the host atom, the larger the dopant, the greater the decrease in grain boundary energy. In our case, one can equate grain boundary energy with grain boundary diffusivity by referring to both empirical relationships and trends observed in simulation.1,17,18 Accordingly, we can say that the size of Ag plays an important role in the reduction of the self-diffusivity of Sn as a result of a reduction in grain boundary energy.

A final comparison of the two solutes at high concentration is made in Fig. 9, where, for 50 atoms of corresponding solute, we show planar diffusivity profiles at a range of temperatures. Noting the different scales on the plots’ y-axes, it is shown that, at temperatures of 400 K and 450 K, diffusivity is exceptionally hindered by Ag when compared to Cu. Again, we see evidence of Ag’s greater reduction in Sn self-diffusivity at the grain boundary versus Cu, here at similar concentrations. Still, whether this an effect of atomic size or decreased cohesive energy, we cannot state conclusively.

D. Grain boundary self-diffusivity ($D_{GB}$) of Sn

After the direct calculation of grain boundary widths from plots in Figs. 5 and 6, we can resolve the true grain boundary self-diffusivity of Sn, namely, $D_{GB}$ in units of length$^2$/time. In doing so, we have removed the effect of the interface width on the magnitude of the diffusivity. Specifically, we have normalized the quantity $\delta_{GB}D_{GB}$ at various temperatures and solute amounts by the corresponding grain boundary width $\delta_{GB}$ at the same conditions. This is shown in...
Fig. 10. In comparison to Fig. 4, low temperature values of $D_{GB}$ for the system with Ag added show very little change relative to $d_{GB}$, and at higher temperatures, the relative magnitudes of $D_{GB}$ are separated by a slightly larger amount. For Cu, low temperature diffusivities have collapsed to a smaller range of values for varying solute concentration. At temperatures of 400 K and 450 K, solute amounts of 25 and 50 show a greater deviation from amounts of 5 and 10.

Removing any variation of grain boundary width with temperature or solute concentration allows us now to speak definitively about possible changes in diffusion rates or mechanisms of Sn. While there is a reduction in the magnitude of diffusivity with increased solute concentration, there is not a clear change in slope in these Arrhenius style plots. Therefore, we can say that the addition of Ag and Cu in low amounts influences the number of diffusive events, but does not affect the mechanisms of diffusion. For a mobile boundary, like the (101) in $\beta$Sn, this is not surprising, and the interface may require larger solute concentrations or precipitation effects for it to exhibit a change in mechanism style.

V. CONCLUSIONS

This work investigated the effect of solute atoms of Ag and Cu on the self-diffusivity of Sn in the (101) symmetric tilt $\beta$Sn grain boundary. Through molecular dynamics simulations of various solute amounts, and over a temperature range of 300 K to 450 K, we show that both Ag and Cu decrease the grain boundary self-diffusivity of Sn as solute amount in the interface increases. The magnitude of these reductions and secondary effects from each solute were also explored.

From the primary quantity of self-diffusion measurement in grain boundaries, $\delta_{GB} D_{GB}$, the effect of solute was shown in an Arrhenius style plot. For increasing solute amounts, the width-scaled diffusivity decreased at temperatures above 350 K. There was also a greater decrease in this value for the Ag solute when compared to the Cu solute. Magnitudes at temperatures of 300 K and 350 K for both solute types were inconclusive regarding the effect of solute amount.

To quantify the width of the (101) grain boundary interface, planar diffusion profiles were plotted at various solute amounts and temperatures. For Ag, we saw again that an increase in the solute amount leads to a decrease in the self-diffusivity of Sn, and over the range of temperatures, the relative shape and width of the profiles remains constant. Profiles of Cu exhibit similar behavior in reducing the diffusivity in the interface, albeit by a smaller amount. In contrast to Ag, diffusion profiles for large amounts of Cu develop a double peak structure with a slower diffusive “trough” at the center plane of the interface and an increased diffusive width. After visual analysis of simulation trajectories, we state that the cohesive energy of the Cu-Sn interactions creates highly coordinated clusters of Sn around single Cu atoms. This essentially induces a local order at the center of the interface and structural disorder at the longer distances.

The diffusive widths of the planar profiles are also quantified using a full-width at half maximum analysis. From this, we see no increase in the width of the (101) boundary upon addition of Ag or increase in temperature — in fact, the width is less than that of the pure (101) boundary. However, with the addition of Cu to the (101) grain boundary interface, there is an increase in width, and at solute amounts of 25 and 50 atoms, the width surpasses that of the pure (101) boundary. Also, with 50 Cu atoms in the interface, the diffusive width increases significantly with temperature to a value almost twice that of the pure interface. This is the effect of the large cohesive energy of Cu-Sn presenting itself.

Finally, using the calculated diffusive widths $\delta_{GB}$ at each temperature and solute amount, we normalized the measured...
The \( \delta_{\text{GB}} D_{\text{GB}} \) quantity to resolve a grain boundary diffusivity independent of width. This also allows us to comment on possible shifts in diffusion mechanisms at the interface. An Arrhenius plot of \( D_{\text{GB}} \) versus \( T \) exhibited similar trends in the magnitude of diffusivity for each solute type and amount, as compared to the plot of \( \delta_{\text{GB}} D_{\text{GB}} \) versus \( T \). It is also evident that the slope of the diffusivity at a specific solute amount does not change significantly, indicating a common diffusion mechanism throughout the range of solute amounts studied.

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26. See [http://www.etomica.org](http://www.etomica.org) for more information about the Etomica Simulation API.