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in Al and Al-Cu

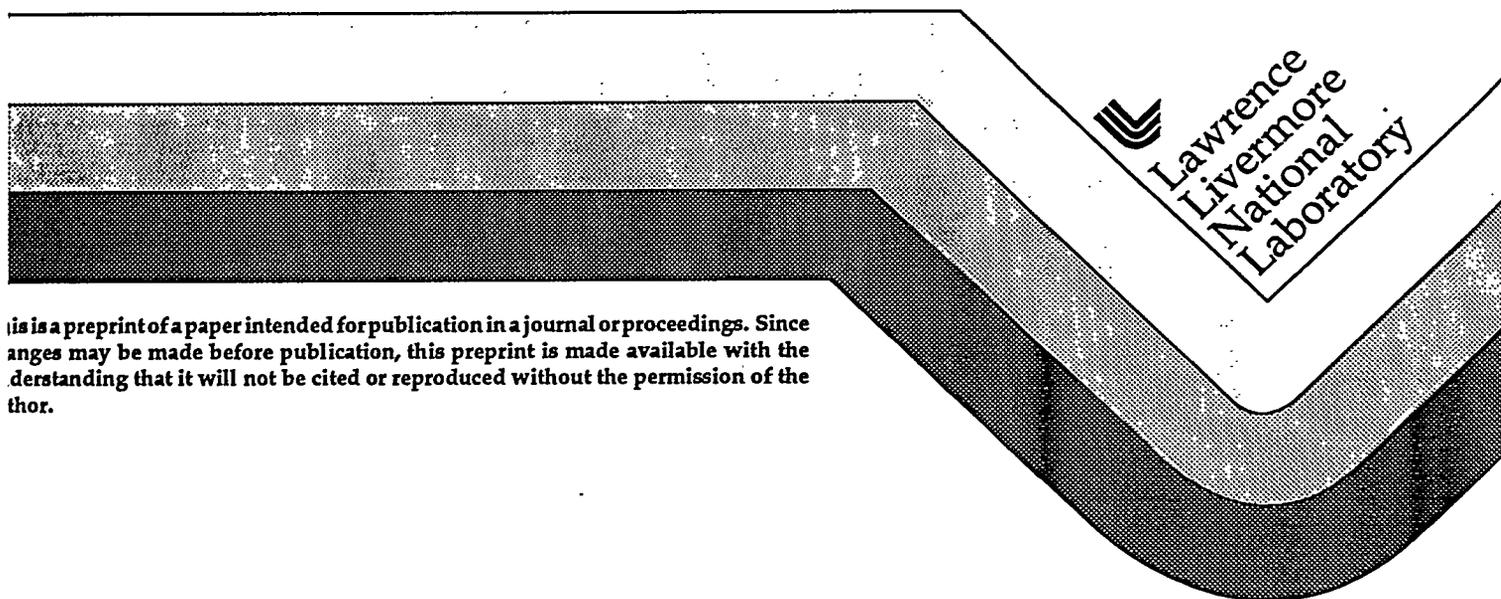
Hanchen Huang
T. Diaz de la Rubia
M.J. Fluss

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A Molecular Dynamics Study of the $\Sigma 11 \langle 1\bar{1}0 \rangle / (113)(113)$ Grain Boundary in Al and Al-Cu

Hanchen Huang, T. Diaz de la Rubia and M.J. Fluss
University of California
Lawrence Livermore National Laboratory
Livermore, CA 94550

We present results of molecular dynamics simulation studies of Cu segregation to the $\Sigma 11 \langle 1\bar{1}0 \rangle / (113)(113)$ grain boundary (GB) in Al. The simulations were performed with EAM potentials for Al and Al-Cu. The results predict that copper atoms tend to order along either side of the interface even in the pure symmetrical tilt boundary, forming alternating chains along the $\langle \bar{3}32 \rangle$ direction. The nucleation of the chains is driven by a change in the local atomic level stress induced by the pre-existing Cu atoms at the GB.

Copper is known to slow down electromigration in aluminum interconnects [1]. In particular, segregation of copper to the aluminum grain boundaries in polycrystalline or bamboo lines is expected to be a major factor [2]. Despite a large database of knowledge derived from experiment on the role that Cu atoms play in slowing down aluminum grain boundary diffusion, little is known about the details of where Cu atoms incorporate at the GBs, or about the atomistic mechanisms of how Cu atoms aid in slowing down grain boundary diffusion and electromigration. Such knowledge is important not only to help design new materials for Al interconnects, but also as input to rate-theory based continuum models of microstructure evolution and electromigration in such lines.

Computer simulation studies of impurity segregation to grain boundaries have been carried out for many metal systems by Seidman and co-workers [3] and by Foiles et al. [4]. These authors have studied equilibrium segregation using constant chemical potential Monte Carlo techniques. In this paper we report a molecular dynamics computer simulation study of the energetics of Cu atoms at a $\Sigma 11$ $\langle 1\bar{1}0 \rangle / (113)(113)$ symmetrical Al tilt grain boundary (GB). Our results show that Cu atoms prefer to segregate at the planes adjacent to the GB plane itself. Furthermore, we show how pre-existing Cu atoms at a plane adjacent to the GB plane induce a change in the local atomic level stress that results in the formation of long Cu atom chains along that particular side of the interface.

The $\Sigma 11$ $\langle 1\bar{1}0 \rangle / (113)(113)$ symmetrical Al tilt grain boundary is a special coincidence site lattice (CSL) GB that has a lower energy cusp than most other CSL grain boundaries [5]. Our simulations employ computational cells 3 nm by 10 nm by 8 nm long along the $[1\bar{1}0]$, $[\bar{3}32]$, and $[113]$ directions, respectively containing 16,000 atoms. Periodic boundary conditions are used along $[1\bar{1}0]$ and $[\bar{3}32]$ directions, with fixed boundaries along the $[113]$ direction. To simulate a GB under constant pressure in a very large bulk material, in contrast to a nanocrystal, the lattice constants along the GB are fixed while that along $[113]$ is allowed to relax. The MD simulations were carried out with embedded atom method (EAM) potentials for Al [7], and for Cu impurities in Al [8,9].

These potentials give a reasonable representation of the properties of Al [7] and of dilute concentrations of Cu in Al [8,9]. In particular, the dilute limit of the heat of solution of Cu in Al was used in the fit and the atomic size mismatch and lattice expansion of Al upon Cu incorporation are predicted correctly [8,9]. Recent ab initio calculations on Al GBs showed that while classical MD simulations employing EAM potentials do not predict GB energies with great accuracy, the overall structures and forces are essentially predicted correctly [10].

We perform our simulations by first relaxing the $\Sigma 11$ GB structure using the force-matching potential for Al of Ercolessi and Adams (E-A potential) [7]. This potential predicts the melting point, latent heat of melting, and stacking fault energy of Al with much greater accuracy than any other pure Al potential in the literature. The E-A potential is therefore employed to equilibrate pure Al grain boundaries. To reach a global minimum, the system temperature is equilibrated at 800°K for 2 ps, and is then slowly cooled down to 0°K. Because no potential based on the force-matching method was available for Al-Cu, this configuration is further relaxed locally with the Rohrer potential for Al before adding impurities. Unfortunately, the small difference in the lattice parameter predicted by these two potentials results in small changes in the atomic arrangement at and near the GB. These changes can be quantified in terms of the atomic level stress as defined by Vitek and Egami [11]. In particular, the GB configuration obtained with the E-A potential predicts that the atoms in the GB plane will be under tensile stress and those in the plane immediately adjacent to the GB plane will be under compressive stress. However, upon relaxation of the configuration obtained with the E-A potential using the Rohrer potential at the appropriate lattice parameter, the atoms in the plane adjacent to the GB plane were found to be under a very small amount of tension (7GPa). The atomic level hydrostatic pressure and von Mises shear stress near the GB relaxed in this manner is mapped in Figure 1. The atoms on either side of the GB plane are found to be under less tensile stress than those on the GB plane itself. Therefore, from simple atomic size and stress considerations, since a

Cu atom is smaller than an Al atom, Cu will prefer regions of compressive as opposed to tensile stress. That is, for this particular type of tilt symmetric GB sites on either side of the GB are likely to be preferred for Cu segregation over those on the GB plane.

Atoms on the planes that are second adjacent to the GB plane are under slight compression (6GPa) according to the Rohrer potential, which may be an artificial factor because it is in contradiction with the more reliable E-A potential. On the other hand, the von Mises shear stress mapping, as shown in Figure 1.3, indicates that the GB core is limited to the three innermost planes. To confirm this, we also calculated the formation energy of one Cu atom on a plane that is second adjacent to the GB plane, and found it equal to that of one Cu atom at site B. Considering both the formation energy and the von Mises shear stress, we will focus on the GB core region (the three innermost atomic planes) in our GB segregation studies.

After generating the low energy equilibrium GB configuration using the Rohrer potential, various configurations of impurities near the GB are then studied. The formation energies of these configurations are tabulated in Table 1. A pure Al GB is taken as a reference system in calculating the energetics. Atoms are labeled as in Figure 2, where B, C, and T are abbreviations of Bottom, Center, and Top, respectively. Formation energy results, as listed in Table 1, show that site B is 0.09 eV more favorable than site C. This energy difference, although small, indicates that at room temperature the probability of a Cu segregation to site C is only 3% of that for segregation to site B. Therefore, when Cu atoms segregate to the GB they tend to be incorporated on the planes immediately adjacent to the GB plane rather than on the GB plane itself. These results confirm the argument made above based on the atomic level stress and indicate that size effects are clearly very important in determining the location of undersized Cu atoms at Al GBs.

To further study Cu atom clustering, we calculate the energy associated with adding a second Cu atom at various locations within the GB region. It is important to note that incorporating the first Cu atom on one side of the GB generates a local atomic level stress

that affects the incorporation of a second Cu atom. The atomic level hydrostatic pressure after incorporating a Cu atom is mapped in bottom of Figure 2. For neighbors of the first Cu atom, the sites on the same side of the GB become more compressive, while sites on the other side and one site on the GB plane become more tensile. However, one of the two neighboring sites on the GB plane is little perturbed. Following the same reasoning as above, a second Cu atom can only segregate to the same side of the GB as the first Cu atom or segregate to the unperturbed neighboring site on the GB plane. Energetics calculations indeed confirm this argument. Within 0.04 eV, there two most stable configurations are precisely formed by the two possible segregation paths described above. The next stable configuration is 0.11 eV higher than the most stable configuration.

It is impossible to draw any conclusion on the most stable structures of larger clusters solely from arguments based on two Cu atom clusters. The clusters of two Cu atoms along $[\bar{1}\bar{1}0]$ direction are at least 0.15 eV less preferred than the most stable configuration. Based on both energy calculations and atomic level stress analysis, Cu atoms do not prefer to cluster along $[\bar{1}\bar{1}0]$ direction. Therefore, to investigate larger Cu atom clusters we will focus on clusters within one unit cell along $[\bar{1}\bar{1}0]$ direction extending along $[\bar{3}\bar{3}2]$ direction. For clusters containing three Cu atoms, there are two low energy configurations that are within 0.05 eV of each other. They are clearly extensions along the $[\bar{3}\bar{3}2]$ direction on the same side as pre-existing Cu atoms. The next stable configuration is 0.10 eV higher than the most stable configuration. In terms of the atomic level stress analysis, we find that for configuration B4B5, as shown at top of Figure 2, the first two Cu atoms make the opposite side of the GB more tensile and one end of the GB plane more tensile as well. Therefore, a possible segregation site for the third Cu atom is either on the same side as the pre-existing Cu atoms or on the GB plane. This is in perfect agreement with the energetics calculations. Based on results for clusters of up to three Cu atoms, we expect that Cu atoms will segregate along one side of the GB, with the possibility of having

alternating chains along two sides of the GB or along one side of the GB and the GB plane itself.

To further understand which of these three possibilities prevails, we have also studied the energetics of clusters of four Cu atoms. As the number of atoms in a cluster increases, the number of possible configurations increases very fast. Therefore, for clusters of four Cu atoms, we focus only on possible extensions of the two most stable clusters of three Cu atoms. The two lowest energy configurations, within 0.04 eV, are extensions of three Cu atom clusters along the same side of the GB as the pre-existing Cu atoms. Five other configurations, within 0.10 eV, correspond to extension along the same side of the GB, along the GB plane, or across the GB plane, respectively. Clearly, Cu atom segregation along two parallel sides of the GB (configuration 4(i) in Table 1) is unfavorable.

To further study relative prevalence of extension along one side of the GB, formation of alternating chains between two sides of the GB, and formation of alternating chains between one side of the GB and GB plane itself, we study clusters of seven Cu atoms so that the Cu atom at the center is not much affected by those at the ends of the cluster. The most stable configuration is the one with all Cu atoms on one side of the GB. Alternating chains between two sides of the GB are only 0.04 eV higher, making them also highly possible. Extension along the GB plane is clearly unfavorable, at least 0.15 eV higher than the lowest energy configuration.

In summary, constant pressure and temperature MD simulations indicate that equilibrium segregation of undersized Cu impurities to the $\Sigma 11$ GB in Al will result in the formation of long Cu chains along one particular side of the interface. The chains can alternate between the two sides of the GB. While this appears to be somewhat counterintuitive, our results show that these chains can indeed nucleate and grow during segregation of Cu atoms from random locations in the bulk of the bicrystal. The critical step in the process is the change in local atomic level stress induced by the presence of the pre-

existing Cu atom(s) on a plane adjacent to the GB plane itself. Since a migration barrier must exist for Cu atoms at the GB, formation of the chains must be associated with the ability of Cu atoms to surpass the kinetic barrier for diffusion across the GB interface. Therefore, these chains will only be expected to appear in cases where the interface is kept at sufficiently high temperature during the segregation process so that the kinetic barrier to the formation of the final equilibrium configuration can be surpassed.

From these results, it may be expected that segregation of other undersized impurities to this particular GB would also exhibit the same behavior [6]. At present, we are investigating this possibility as well as segregation phenomena to other Al GBs.

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Table 1
Energetics of Cu Impurities at a $\Sigma 11$ $\langle 1\bar{1}0 \rangle / (113)(113)$ Tilt Al GB

Configuration	E, eV	Configuration	E, eV
One Cu Impurity:			
1(a) B4	-0.22	1(b) C4	-0.13
Two Cu Impurities			
2(a) B4C3	-0.47	2(f) C3C4	-0.27
2(b) B4B5	-0.43	2(g) C4C $\bar{4}$ *	-0.16
2(c) B4C4	-0.36	2(d) B4T4	-0.16
2(e) B4B $\bar{4}$ *	-0.31		
Three Cu Impurities			
3(a) C3B4B5	-0.70	3(g) C3B4C4	-0.53
3(b) B4B5B6	-0.65	3(h) B4C4C5	-0.50
3(c) B4B5C5	-0.60	3(i) C3C4C5	-0.41
3(d) B4C4B5	-0.57	3(j) C4B5T5	-0.34
3(e) C4T4B5	-0.56	3(k) B4T4B5	-0.33
3(f) C3C4B5	-0.54	3(l) B4C4T4	+0.19
Four Cu Impurities			
4(a) C3B4B5B6	-0.92	4(f) C3T3B4B5	-0.85
4(b) B3B4B5B6	-0.88	4(g) B3B4B5C5	-0.83
4(c) B4B5C5B6	-0.87	4(h) C3B4C4B5	-0.77
4(d) B3C3B4B5	-0.86	4(i) C3B4T4B5	-0.54
4(e) C2C3B4B5	-0.85		
Seven Cu impurities:			
7(a) B1B2B3B4B5B6B7	-1.51	7(d) B1B2B3B4C4C5C6	-1.32
7(b) B1B2B3C3T4T5T6	-1.47	7(e) B1B2B3C3C4C5C6	-1.25
7(c) B1B2B3B4C3C4C5	-1.36	7(f) B1B2B3C2C3C4C5	-1.25

* the bar represents a site one period away along $[1\bar{1}0]$ direction from that without a bar.

Figure Caption:

Figure 1: Atomic level stress mapping of the relaxed Σ_{11} $\langle 1\bar{1}0 \rangle / (113)(113)$ Al tilt GB. Hydrostatic pressure obtained with the E-A potential is mapped in 1(a) where the gray scale ranges from 67 GPa tension (white) to 37 GPa compression (black). Hydrostatic pressure obtained with the Rohrer potential is mapped in 1(b) where the gray scales ranges from 33 GPa tension to 6 GPa compression, and the von Mises shear stress from the Rohrer potential is mapped in 1(c) where the gray scale ranges from 0 to 4 GPa.

Figure 2: Mapping of local atomic level hydrostatic pressure near the first Cu atom at the Σ_{11} GB. The gray scale ranges from 66 GPa tension to 36 GPa compression at the bottom, and from 76 GPa tension to 23 GPa compression at the top. The coordinates correspond to atoms at the middle when three atoms along $[1\bar{1}0]$ are shown, and those in the front when two atoms are shown along $[1\bar{1}0]$.

Figure 1

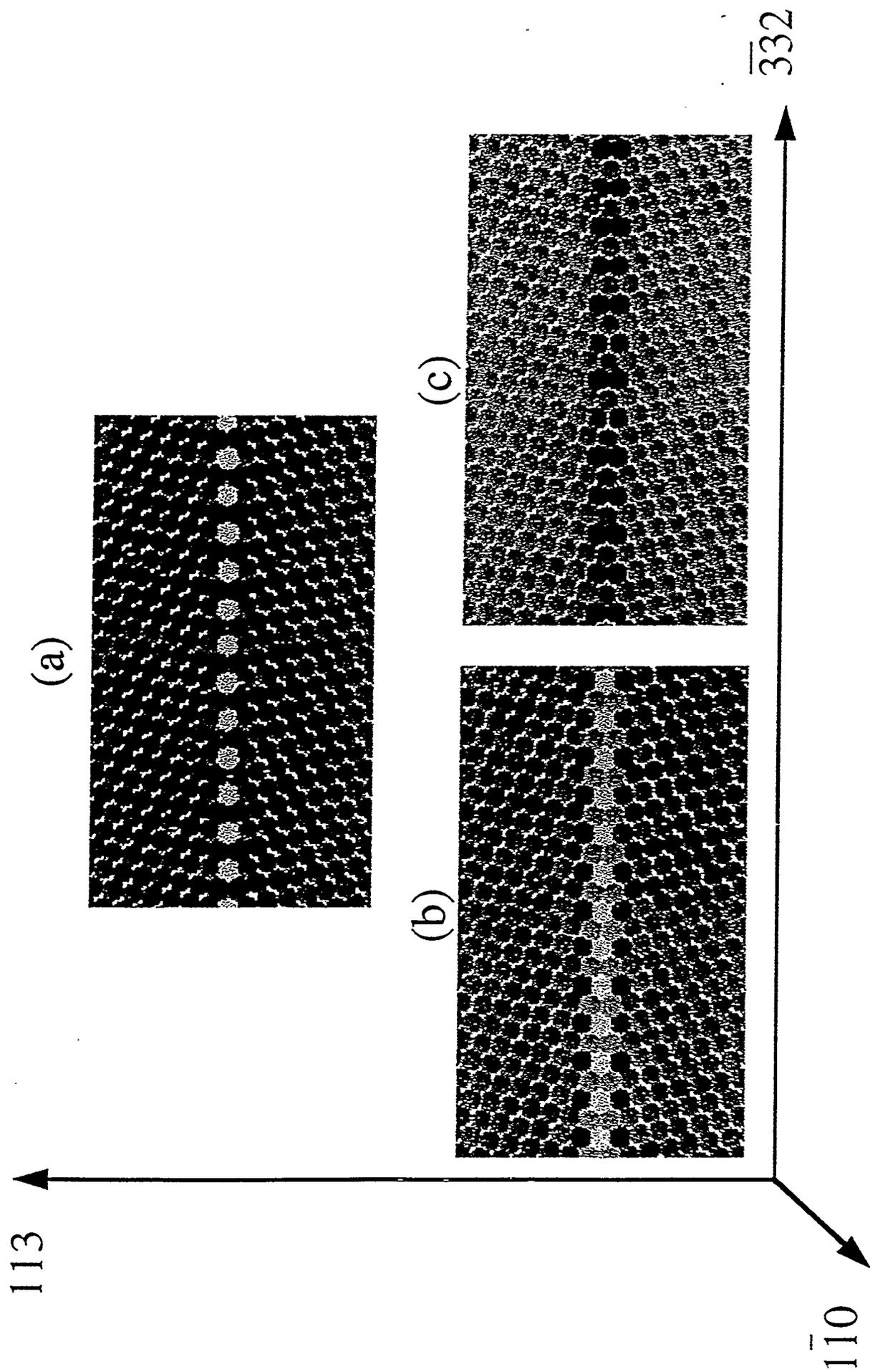


Figure 2

