Study by Atomistic Theory and High-Resolution Electron Microscopies of Cu Atoms at an Al Grain Boundary

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New insight into the atomic segregation of copper to an aluminum grain boundary has been obtained using atomic resolution electron microscopy techniques coupled with *ab-initio* electronic structure calculations. We find the copper segregation to be site specific, changing the structure of the boundary by unexpectedly occupying interstitial sites. The calculated energy for segregation was found to be sufficient for essentially all of the interstitial sites to be filled. Minor elemental constituents in materials can have profound effects on their engineering performance, often through segregation to grain boundaries in the host material. One important example is the great resistance to electromigration damage in microelectronics imparted by small additions of copper to aluminum interconnects.

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The phenomenon of segregation is of long–standing scientific and technological interest [5, 6]. An example of the importance of segregation has been the knowledge that only a few atomic percent of copper greatly reduces the rate of electromigration in polycrystalline Al films, a discovery that enabled the exponential growth of the computer industry [1, 2]. The improved performance of aluminum alloy interconnects in microelectronics under conditions of electromigration is associated with segregation of Cu atoms at Al grain boundaries (GB) and the resultant effect on the transport of Al atoms along the GB [3, 4]. While more fundamental understanding of electromigration is emerging [7], the details of how atomic transport proceeds in the presence of Cu are still speculative.

We have studied the site-specific segregation of Cu to a special GB in Al, the special character of which enables a coupled approach of model experiments and simulations to be applied. Theory predicted that segregation was not random, but occurred in a site-specific manner that could be verified using high-resolution transmission electron microscopies (HRTEM). We have therefore determined the atomic structure of a grain boundary that was fabricated to match the theory, the $\sum 5$ (310)/[001] symmetric tilt GB in aluminum doped with copper, by means of complementary transmission electron microscopy (TEM) based techniques, including focal series reconstruction [8] and Z-contrast imaging [9]. While copper in solution within aluminum normally resides at substitutional sites on the Al lattice, we report here the discovery of copper atoms occupying interstitial positions at this grain boundary. *Ab-initio* calculations within the local density approximation (LDA) demonstrate this to be a consequence of the small size of the Cu atoms relative to the host Al. These interstitial

sites remain empty in pure face centered cubic metals [10] and in alloys when the solute atoms are larger than the host atoms [11]. This change in atomic structure will slow mass transport by influencing the grain boundary diffusion for Al atoms and vacancies. The existence of this stable site may slow Cu depletion that leads to electromigration failure.

Electron microscopy is a powerful tool for the determination of atomic structures. Modern HRTEM microscopes have the ability to image individual atomic columns with sub–Ångström resolution [12-16]. This enables the determination of complex structures, such as crystal defects, precipitates, and interfaces, down to the atomic level. Analytical electron microscopy (AEM) gives us the possibility to distinguish among and quantify the amount of different elements in the analyzed volume of material [17]. Additionally, atomic resolution Z-contrast images combine the information of the atomic structure and the chemistry (Z = atomic number). *Ab-initio* electronic structure calculations can reliably predict structures and energetics of various postulated boundary structures. In this paper we will present results obtained with HRTEM and Z-contrast imaging and we will show the synergy in the combination of these two experimental techniques with atomistic simulations.

We have chosen the Σ5 (310)/[001] symmetric tilt grain boundary (STGB) in Al to investigate the potential for segregation of an impurity to distinct sites. The model grain boundary was fabricated by ultra-high vacuum (UHV) diffusion bonding of alloy single crystals (Al-1at%Cu). The UHV diffusion bonding enables us to fabricate well defined, precisely oriented interfaces under highly controlled environmental conditions [18] that allow us to exclude extraneous contamination, such as from the native oxide layer, by *in-situ* cleaning. The two single crystals of Al-1at%Cu were bonded in the solid state at a

temperature of 540 ºC with a constant applied pressure of 1.0 MPa for 8 hours. Afterwards the bicrystal was annealed for 100 hours at 200 ºC to encourage the copper segregation to the grain boundary.

The relation between grain boundary energy and impurity segregation to the interface has been calculated for the ∑5 (310)/[001] interface. Earlier work [19, 20] examined this boundary based on empirical potentials. Here using more reliable *ab-initio* methods extends that work. The calculations performed used the LDA predicted lattice constant for aluminum of a_0 = 0.398 nm, which is ~2% smaller than the experimental value of a_0 = 0.40494 nm. The computational supercells contain two oppositely oriented grain boundaries separated far enough to minimize any elastic interactions between the boundaries. We have considered a number of different positions for Cu substitution at the grain boundary and found a number of possible structures where the segregation energies are negative which denotes the preference for Cu to segregate to the grain boundary (Fig. 1). In Fig.1 the calculated atomic structures for the boundary are shown with the colors denoting the types of atoms. For the case where only substitutional sites are considered, the predicted structure of the ∑5 (310)/[001] symmetric tilt GB is shown in Fig. 1A. The energy of segregation for this structure is 0.46 eV per segregating Cu atom. When Cu is placed at interstitial sites in the GB the boundary assumes a different structure (Fig. 1B). The energy of segregation for this boundary is 0.67 eV per segregating atom, significantly more stable than the structure in Fig. 1A. This segregation energy suggests that at the equilibration temperature used, essentially all of the interstitial sites will be filled with Cu.

To experimentally determine the atomic structure of the Σ5 (310)/[001] symmetric tilt GB we used HRTEM with images acquired on the latest generation of transmission electron microscopes equipped with field emission guns (FEG). The advantage of using a FEG source over a thermionic source is the high brightness, a very coherent electron beam, and the reduction of the influence of chromatic aberrations on the image. These properties lead to an increased range of spatial frequencies transferred through the microscope to the image compared with less coherent electron sources. However, the influence of spherical aberration of the objective lens results in an image that is an encoded mixture of microscope properties and object structure [21, 22]. Additionally, the spatial delocalization of the electrons at boundaries and edges can also contribute to the observed image, resulting in beautiful (but not intuitively interpretable) moiré patterns. These properties of the FEG TEM interfere with the direct interpretation of HRTEM images.

To overcome these difficulties and decode the image we used focal-series reconstruction (FSR) of the exit wave function to remove the contrast transfer properties of the microscope and to validate the predictions of the theoretical grain boundary model [23]. High–resolution images (up to 40 images) of the grain boundary have to be recorded using equally spaced defocus values for a focal series, achieved only with automated control of the microscope. FSR not only corrects the lens aberrations resulting in directly interpretable phase images, but also it improves the image resolution [12].

The exit wave function FSR was carried out using the Philips focal series reconstruction package [24, 25]. We applied the software to retrieve the wave function at the exit-plane of the object. As the exit wave function is complex, it can be separated into

an amplitude image and a phase image. For very thin specimens, most of the relevant information is included in the phase. Therefore only the phase image will be discussed in the following. The main advantage of the phase image is that it can be directly interpreted and used for the determination of the position of the atomic columns in the image plane.

The final result of the reconstruction for the Σ5 (310)/[001] symmetric tilt GB in Al-1at%Cu is shown in Fig. 2. The image has nine identified units of boundary structure. The positions of the atomic columns appear bright in this phase image and we can directly deduce the atomic structure of the grain boundary. Most importantly the experimental phase image shows appreciable contrast at periodic interstitial sites in the GB.

We have performed complementary Z-contrast investigations using the VG HB603–U dedicated scanning transmission electron microscope (STEM) operated at 300kV equipped with a cold field emitter and a high resolution objective lens installed at Oak Ridge National Laboratory. Fig. 3 shows the Z-contrast image of the same grain boundary as imaged by HRTEM. Z-contrast images are obtained by scanning a finely focused electron probe (~0.13 nm) over the sample and synchronously detecting scattered electrons with a high angle annular dark field detector. Interference effects in the scattered electrons will be averaged over leading to an image with incoherent characteristics [26], therefore each atomic column can be directly located. Furthermore, at high scattering angles the electron scattering cross section approaches the Z^2 value for Rutherford scattering, which will give an image where the contrast is directly related to the atomic number Z [27].

The Z-contrast image in Fig. 3 clearly shows increased brightness in selected columns directly at the GB. Results from AEM confirm that Cu is enriched at the GB. Since the Z-contrast image is collected serially with a rastered beam, instabilities in the microscope will lead to distortions in the final image. These distortions must be removed for the proper interpretation of atomic structure [28]. When the distortions are removed, the position of the high intensity features in the image correlate perfectly with the interstitial position, which was determined in the phase image of the focal series reconstruction.

We find that the Cu atoms assume interstitial sites at this Al GB. This structure is quite stable and diffusion of Cu is considered to be more difficult than if the Cu was substitutional. Likewise, the presence of Cu is expected to influence Al and vacancy diffusion at the GB. For the related case of self-diffusion of Cu in the $\sum 5$ (310)/[001] symmetric tilt GB, the mechanisms of self-diffusion have been reported in detail [29]. This study by atomistic simulation indicated that the dominant diffusion mechanism for this elemental boundary involved an interstitialcy mechanism involving the interstitial site identified here. One would expect the behavior of the elemental Al boundary to be qualitatively similar to that observed for Cu due to their common crystal structure. The occupation of the interstitial site by the impurity will thus modify the diffusion behavior of the boundary. In particular, it should shut off the dominant diffusion mechanism for the elemental version of this boundary and so retard diffusion. Since structural holes are expected to be a common feature of grain boundaries, one would expect that the segregation of a smaller impurity, such as Cu in Al, will frequently fill those locations in other GBs as well. This structural change of general GBs will remove potential interstitial

based diffusion mechanisms and so retard GB diffusion overall in the polycrystal. This picture provides a detailed mechanistic understanding of the role that Cu additions to Al play in the enhanced resistance to electromigration.

We conclude that the combination of atomistic theory with high-resolution microscopies of a model boundary provides important information on site-specific segregation of Cu to Al grain boundaries. However, even with current electron microscope resolution, we are limited to observing only a handful of specially oriented grain boundaries. For the foreseeable future, information on more general boundaries will come from theory that has been benchmarked at these very special boundaries. It appears that this approach offers the possibility to extend this study to other grain boundaries, which could add substantially to the understanding of electromigration mechanisms.

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References and Notes

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Figure Captions

Figure 1 – Predicted atomic structures of the ∑5 (310)/[001] symmetric tilt GB in Al–1at%Cu alloy calculated by atomistic simulations using electronic structure methods. The models are viewed along the common [001] directions in the crystals on either side of the GB. (A) The expected structure for Cu (blue) segregated to the Al (pink) GB if only substitutional sites are considered. The three sites illustrated are inequivalent, however they have similar segregation energies, with the greatest being 0.46 eV/atom. The occupation of the sites in the first planes on either side of the boundary is expected to be random. (B) The expected structure for Cu segregated to the Al GB when interstitial sites are also considered. The Cu atoms sit in what is an interstitial hole in the elemental boundary. Note that there are three atomic columns in the central plane for each unit cell, seen to be in agreement with the experimental images. The segregation energy per atom is 0.64 eV, which is more energetically favorable than the substitutional sites.

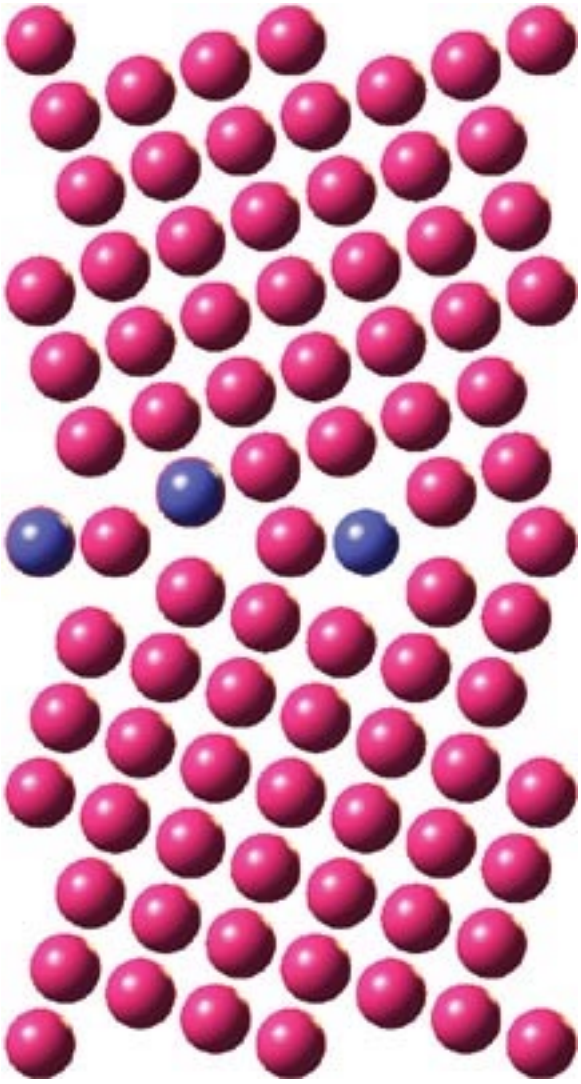
Figure 2 – The phase part of the FSR exit wavefunction from HRTEM images of the ∑5 (310)/[001] symmetric tilt GB in Al–1 at.% Cu as viewed parallel to the tilt axis, with the atomic model of Fig.1B overlaid. The arrow marks one of the positions of the periodically spaced interstitial sites in the image. By comparison of the individual HRTEM images with image simulations we have determined a sample thickness of 6 nm.

Figure 3 – Z-contrast image of the ∑5 (310)/[001] symmetric tilt GB in Al–1 at.% Cu in the same specimen and orientation as in Fig. 2. The periodic bright columns at the boundary, one of which is marked by the arrow, correspond to the Cu filled interstitial

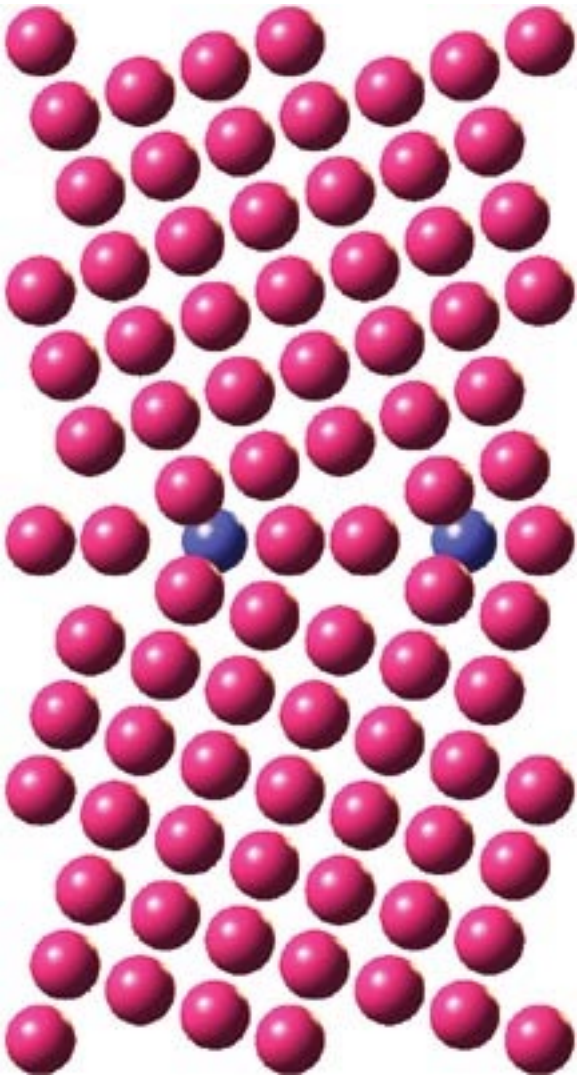
sites discovered in the exit wavefunction reconstruction. The high intensity of these columns indicates that they are filled with a high Z element, which AEM has identified as Cu.

Figures

Figure 1



(A)



(B)

Figure 2

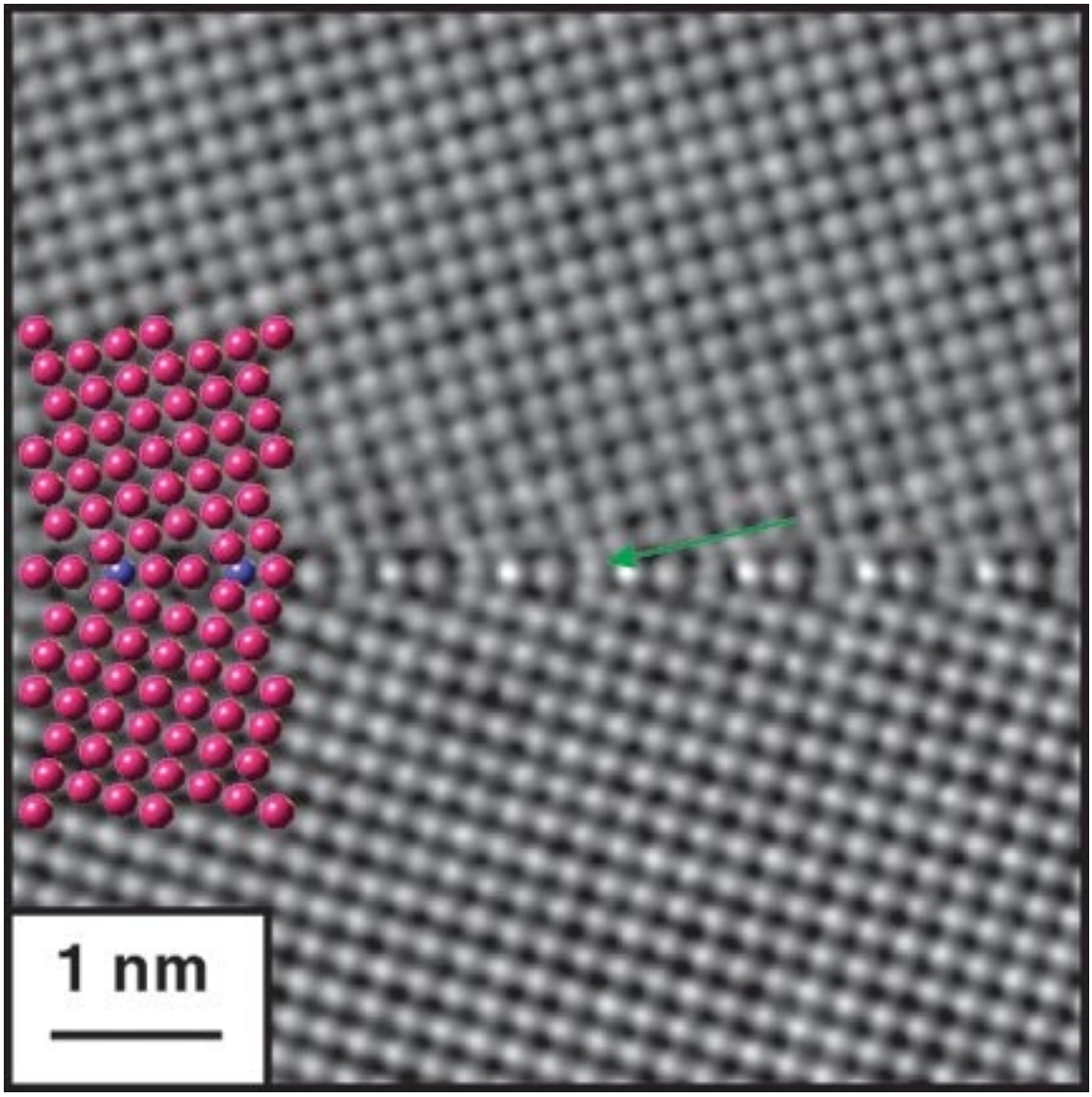


Figure 3