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RECONSTRUCTION OF TWIST GRAIN BOUNDARIES IN GOLD*

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ABSTRACT

The reconstruction of high-angle twist grain boundaries on the four densest atomic planes in gold are investigated using the recently developed method of grand-canonical simulated quenching. It is found that the grain boundaries on the two densest planes, (111) and (100), do not reconstruct, while those on the (110) and (113) planes do.

INTRODUCTION

Simulations of grain boundaries (GBs) are usually based on structures derived from the coincident-site lattice (CSL) construct. Often additional degrees of freedom associated with a volume expansion in the direction of the GB normal and a translation of the two halves of the bicrystal parallel to the grain boundary are included.[1,2] However, grain-boundary reconstruction in which atoms are added to, or removed from, the CSL structure is not usually taken into account.

Here we describe the results of simulations of twist grain boundaries on the four densest atomic planes of gold in which the number of atoms in the interfacial region is not fixed to that of the CSL structure. The recently developed method of grand-canonical simulated quenching (GCSQ)[3] is used in conjunction with an embedded-atom-method (EAM) potential[4].

Two questions will be addressed. First, do these grain boundaries reconstruct? Second, can the nature of the reconstruction be understood from an analysis of the unreconstructed GB?

GCSQ FOR EMBEDDED-ATOM-METHOD POTENTIALS

Before addressing these questions, we show how the previously derived GCSQ formalism[3] can be extended for use with EAM potentials.

For a single component system, the grand-canonical heat function, L, is:

$$L = E - \mu N \quad , \qquad (1)$$

where E is the internal energy and μ is the chemical potential of the N atoms in the system. The aim of a zero-temperature grand-canonical ensemble simulation is to minimize L by allowing the addition and removal of interstitials and vacancies in addition to structural relaxation. GCSQ overcomes the initially high energy barrier to the creation of a vacancy or an interstitial through two postulates:

(i) A solid of mobile atoms is considered as being formed from M mobile sites, each of which is characterized by the number of atoms occupying the site, x_i, its position, $\mathbf{r}_i$, and its momentum, $\mathbf{p}_i$.

(ii) The site occupancy, x_i, may take on any fractional value in the range 0 and 1 inclusive and may vary during the course of the simulation.

That the above two premises lead to physically meaningful structures will become apparent in the following discussion.

In analogy with the previous work involving pair potentials,[3] Eq. 1 may be rewritten for embedded-atom-method potentials as:

$$L = E_{pair} + E_m - \mu \sum_{i=1}^{M} x_i \quad , \tag{2}$$

where E_{pair} is the part of the interaction energy arising from pair interactions and E_m is the part of the interaction energy arising from the embedding term[4]. To impose the constraint that the site occupancy be limited to the range $0 \le x_i \le 1$ we make the change of variables

$$x_i = \frac{1}{2} (\cos \theta_i + 1) \quad , \tag{3}$$

where θ_i is now unconstrained.

In the embedding term, at every site i there is a local atomic density, ρ_i, which represents the total electronic density due to the other atoms. If the electron density contributed by atom k, distant r_{ik} from site i, is $\rho_k^a(r_{ik})$, then the local atomic density at site i may be written as:

$$\rho_i = \frac{1}{2} \sum_{k \neq i} (1 + \cos \theta_k) \, \rho_k^a(r_{ik}) \quad . \tag{4}$$

The embedding energy is then:

$$E_m = \frac{1}{2} \sum_{i} (1 + \cos \theta_i) \, F_i(\rho_i) \quad . \tag{5}$$

By including the kinetic energy associated with the movement of the sites in real space, the "kinetic energy" associated with the changes in occupancies of the sites, and the pair term in the potential energy, we obtain the Lagrangian:

$$\mathcal{L} = \frac{1}{2} Q \sum_{i=1}^{M} \dot{\theta}_i^2 + \frac{1}{2} m \sum_{i=1}^{M} \sum_{\alpha=1}^{3} \dot{r}_{i\alpha}^2 - \frac{1}{2} \sum_{i=1}^{M} (1 + \cos \theta_i) \, F_i(\rho_i) -$$

$$\frac{1}{8} \sum_{i=1}^{M} \sum_{\substack{k=1 \\ k \neq i}}^{M} (\cos \theta_i + 1)(\cos \theta_k + 1) \, U(r_{ik}) + \frac{1}{2} \mu \sum_{i=1}^{M} (\cos \theta_i + 1) \quad , \tag{6}$$

where m and Q are the masses associated with motion in real space and occupancy space respectively, and $\dot{\theta}$ is the time derivative of θ.

The equations of motion for r_i and θ_i may be evaluated in the usual way from the Euler-Lagrange equations:

$$Q \ddot{\theta}_i = \frac{1}{2} \sin \theta_i \left\{ F_i(\rho_i) - \mu + \frac{1}{2} \sum_{k \neq i} (\cos \theta_k + 1) \left[U(r_{ik}) + \rho_k^a(r_{ik}) \frac{\partial F_k}{\partial \rho_k} \right] \right\}, \tag{7}$$

$$m\ddot{r}_{i\alpha} = -\frac{1}{8}(\cos\theta_i + 1)\sum_{k\neq i}(\cos\theta_k + 1)\left\{\frac{\partial U(r_{ik})}{\partial r_{i\alpha}} + 2\frac{dF_i}{d\rho_i}\frac{d\rho_k^a(r_{ik})}{dr_{i\alpha}} + 2\frac{dF_k}{d\rho_k}\frac{d\rho_k^a(r_{ik})}{dr_{i\alpha}}\right\} \quad (8)$$

The zero-temperature solutions to Eqs. 7 and 8 can be found by looking for the stationary solutions $\ddot{\theta}_i = 0$ and $\ddot{r}_{i\alpha} = 0$. Equation 7 shows that $\ddot{\theta}_i=0$ is obtained for $\sin\theta_i = 0$. For $\sin\theta_i = 0$, $\cos\theta_i = \pm 1$, which means $x_i=0$ or $x_i=1$. That is, a stationary solution is obtained only if the site i is either occupied by one atom or is completely empty. Further, if site i is occupied, then Eq. 8 says that the force on site i due to the other occupied sites must be zero.

In this study, an embedded-atom-method potential parameterized to gold, cut off between the third and fourth nearest-neighbor shells was used[5]. The zero-temperature lattice parameter for this potential is a=4.0829Å. As initial model geometries we choose point-defect free high-angle GBs on the four densest atomic planes derived from the CSL rotation of two perfect semi-inifinite crystal lattices relative to each other about the plane normal. Thus, for example, the (110) θ=31.59° (Σ27) GB is obtained by rotating one perfect semi-crystal relative to another by an angle of 31.59° about the (110) plane normal. The system is oriented with the planar normals along the z-axis and, consequently, the x-y-plane is parallel to the GB plane. Because of the interface there is no periodicity in the z-direction; however, the structure is periodic in the x-y-plane. The (110) θ=31.59° (Σ27) GB has a rectangular planar repeat unit with an area which is Σ=27 that of the corresponding primitive planar unit cell (Σ=1) on the (110) plane in a perfect single crystal.

The zero-temperature structures and energies of the point-defect free GBs were determined by iterative energy minimization ("lattice statics") using a Region I-Region II scheme to simulate an isolated grain boundary. In this scheme, the computational cell is periodic in the x-y plane, but the GB region is embedded in the z-direction between two rigid block of atoms.[6,7] The number of atoms in the system remains fixed throughout the simulation, but the dimension of the unit cell in the z-direction are allowed to relax.

A Region I-Region II scheme similar to that used in the lattice-statics simulations was used for the GCSQ. Unrelaxed CSL grain boundaries with densities considerably greater than that of the point-defect free structures described above were chosen as initial geometries. Since, it may be expected that GCSQ will remove atoms from, rather than add atoms to, such systems,[3] the sites were initially arranged to be coincident with the locations of the atoms in the unrelaxed structures and no additional sites were added.

RECONSTRUCTION OF TWIST BOUNDARIES IN GOLD

The primary results for both the unreconstructed and reconstructed grain-boundaries are summarized in Table I. They are:

(1) The GBs on the two more dense planes, with the lower unreconstructed energies, do not reconstruct. The GBs on the two less dense planes, with the higher unreconstructed energies, do reconstruct.

(3) The reconstructions involve approximately one-fifth of the atoms in the planes on either side of the GB.

(4) Despite the large number of atoms involved in the reconstruction, the energy of the reconstructed GB is only slightly lower than that of the unreconstructed GB.

(5) The size of the GB volume expansion is similar for the unreconstructed and reconstructed GBs, with one showing a small positive difference and the other a small negative difference.

TABLE I

Interplanar spacing, d/a, in units of the lattice parameter; Number of atoms, N_d, removed from the planes of atoms on either side of the GB during reconstruction; GB energy, E_{gb}, in mJ m^{-2}; and GB volume expansion, $\delta V/a$, in units of the lattice parameter. (In the unreconstructed GB, the number of atoms in each atomic plane is equal to the sigma value.) The results for the unreconstructed GBs are consistent with those of Wolf.[1,2]

	d/a	N_d	E_{gb} (unrec.)	E_{gb} (recon.)	$\delta V/a$ (unrec.)	$\delta V/a$ (recon.)
(111) θ=47.9° (Σ31)	0.577	-	198	-	0.018	-
(100) θ=43.9° (Σ29)	0.5	-	531	-	0.057	-
(110) θ=31.6° (Σ27)	0.354	11 (20%)	698	675 (-3.3%)	0.053	0.052
(113) θ=53.4° (Σ31)	0.302	11 (18%)	667	645 (-4.5%)	0.049	0.053

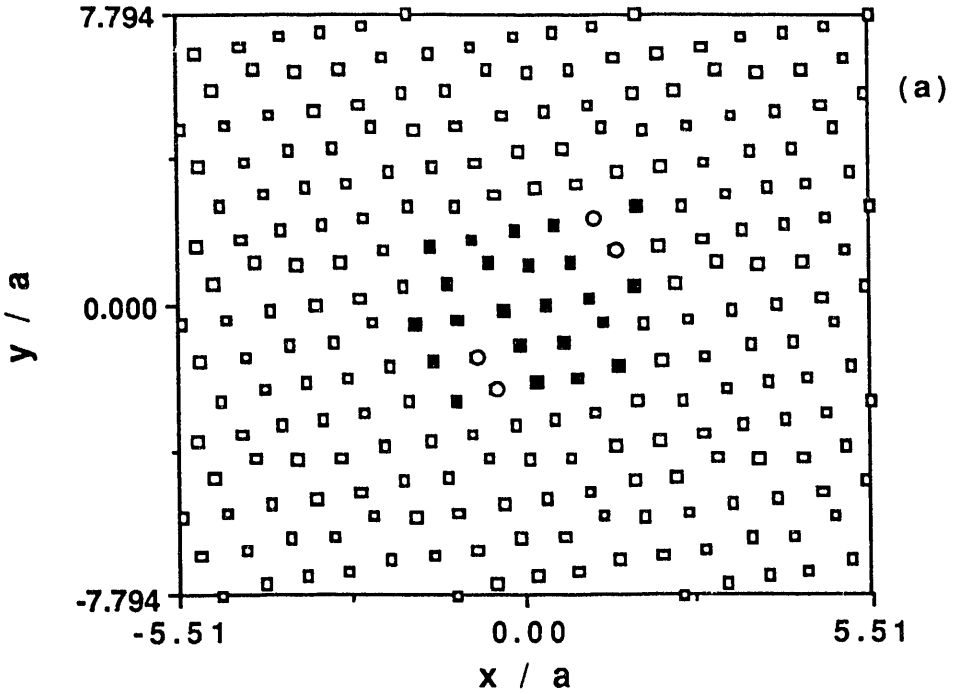
To explore the structural nature of the reconstruction, Figures 1(a) and 1(b) show plan views of one of the planes of atoms adjacent to the unreconstructed and reconstructed (110) θ=31.6° (Σ27) GB. For clarity a 3×3 square array of unit cells is shown, with the atoms in the central unit cell denoted by squares. An analysis of the energy of each individual atom shows that the 4 atoms denoted in Fig. 1(a) by circles have significantly higher energies than the other atoms in the plane. One might, therefore suppose, that they would be most likely to be involved in the reconstruction. Figure 1(b) shows, however, that the structure of the reconstructed GB is not that simple.

To see directly the effect of removing these 8 highest energy atoms, (the 4 atoms shown in Fig. 1(a) and the 4 corresponding atoms in the plane on the other side of the GB) a lattice-statics simulation was performed with them removed. The energy of the resulting GB was 1950 mJ m^{-2}, which is approximately 3 times larger than that of the unreconstructed and reconstructed GB respectively.

CONCLUDING REMARKS

It has been shown that high-angle twist GBs on the (110) and (113) planes in Au reconstruct by the removal of approximately one-fifth of the atoms in the grain-boundary region. Moreover for the GB on the (110) plane the reconstruction was shown to be structurally complicated and not related to the structure or energy of the unreconstructed GB in any obvious way.

That these results are rather general and not merely specific to this potential is evidenced by rather similar results obtained for simulations on the same boundaries using a Lennard-Jones (LJ) potential parameterized to Cu.[3,8] The most significant differences for the LJ potential were that the grain-boundary volume expansions were substantially smaller for the reconstructed GBs than for the unreconstructed GBs, and that the energies of the reconstructed GBs were significantly lower than those of the unreconstructed GBs: 6% and 19% for the GBs on the (110) and (113) planes respectively.



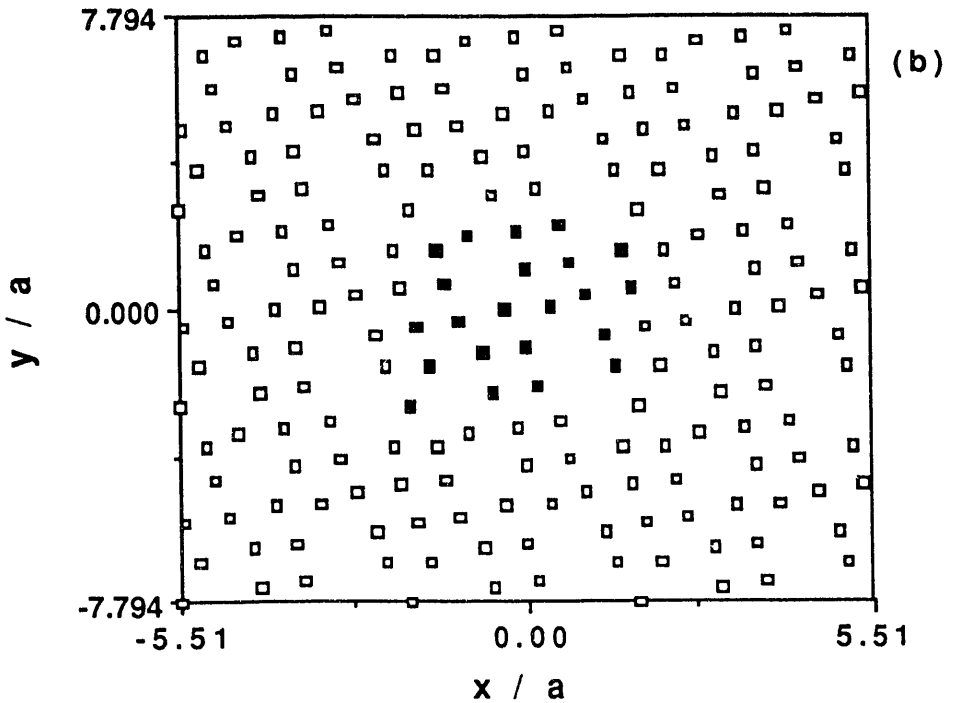


Figure 1

Plan view of the plane closest to the interface in (a) the unreconstructed and (b) the reconstructed (110) θ=31.59° (Σ27) GB. For clarity, nine unit cells in a 3×3 arrangement are shown. Atoms in the central unit cell are denoted by closed squares. In the unreconstructed GB the four highest-energy atoms in the central unit cell are denoted by open circ es.

There is little experimental information on the reconstruction of these GBs However, the absence of any reconstruction for the (100) θ=43.9° (Σ29) GB is consistent with experimental results on the closely related (100) θ=36.9° (Σ5) and (100) θ=22.6° (Σ13) GBs in gold, which show no reconstruction.[9-11]

These results have important implications for other GB studies. For example, before calculating activation and migration energies for GB migration, great effort must be taken to ensure that the thermodynamic ground state is found. As another example, the elastic properties of reconstructed GBs can be considerably different from those of unreconstructed GBs.[8]

Finally, grand-canonical simulated quenching has been extended to multi-component systems,[8] and, thus, may be used to investigate other interfacial phenomena such as surface reconstruction, segregation and epitaxy.

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