Embedded-atom study of the spontaneous formation of misfit dislocations

C. M. Gilmore
U.S. Naval Research Laboratory, Washington, D.C. 20375-5000
and School of Engineering and Applied Science, The George Washington University, Washington, D.C. 20052
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Misfit dislocations were spontaneously formed at (111) interfaces of Pd-Cu bicrystals and monolayers simulated with the embedded-atom model of Daw and Baskes. The bicrystal model contained a total of 4417 atoms (2360 Pd and 2057 Cu) in a spherical configuration; the monolayer of Cu contained 294 atoms on a hemispherical substrate of 2360 Pd atoms. In all simulations the surfaces of the models were free of constraint. The simulation conducted was a 0-K energy minimization. This indicates that thermal activation was not necessary to produce the misfit dislocations. This is the first time that the spontaneous formation of misfit dislocations has been observed in computer simulations at these low misfits (6.7%) without thermal activation, and this is the first time that the displacements at the interface have been clearly demonstrated by computer simulation.

Misfit dislocations were first proposed by Frank and van der Merwe to occur at the interfaces between crystals of differing lattice parameter.[1] They utilized a model where the interaction potential of a one-dimensional monolayer on a substrate was represented as a sinusoidal function. They predicted that with misfits of 9% or more a monolayer on a crystal with misfit dislocations had a lower energy than the monolayer strained to coherency. They also concluded that at low temperatures the monolayer could be metastably strained to coherency for misfits up to 14%. In later work van der Merwe[2] extended the previous work to a two-dimensional grid of dislocations and found that this reduced the strains of 9% and 14% previously found to approximately 7% and 11%. Experimentally, misfit dislocations have been indicated with significantly smaller misfits such as 2.5% at Ni-Cu interfaces.[3] The mechanism of the loss of registry has not been identified, but Dodson[4] has suggested that the loss of registry is not due to the spontaneous formation of misfit dislocations. This conclusion was based upon a study by Dodson[4] of the stability of a strained interface with a Monte Carlo–simulation procedure utilizing pair potentials; it was found that the coherently strained interface was stable up to misfits of 15%. This was the largest misfit that was tested. The orientation of the interface was not reported. It has been suggested that misfit dislocations did not spontaneously appear because of a high activation energy,[5] or that the formation of misfit dislocations is related to the ultimate strength of a perfect crystal and that misfit dislocations at interfaces with misfit less than 15% are a result of improper processing procedures that could be improved to provide misfitting crystals with much higher strain than presently possible.[6] This disagreement between experiment and computer simulations led Bauer and van der Merwe to conclude that pairwise interaction potentials without *ad hoc* correction factors give no reliable quantitative information on surfaces, monolayers, and interfaces of metals.[7] More recently, the spontaneous formation of misfit dislocations has been reported by Grabow and Gilmer in a molecular-dynamics simulation of (001) interfaces with Lennard-Jones interatomic potentials.[8] The atomic configuration of the misfit dislocations was not observed; rather the misfit dislocations were indicated by the displacements produced at the surface of the solid. It was determined that for a single monolayer the critical misfit for the spontaneous generation of misfit dislocations was 11%, and for a 10-monolayer-thick overlayer the critical misfit was 6%. These molecular-dynamics simulations were conducted at a low, but unspecified, temperature. The authors[8] noted that their results were time and temperature dependent; so that at a higher temperature misfit dislocations would be more readily generated, and at a lower temperature the generation of misfit dislocations should be reduced. If the generation of misfit dislocations is a thermally activated process, then at 0 K there should not be any generation of misfit dislocations at low misfits.

It is the purpose of this paper to report the observation of the spontaneous formation of misfit dislocations at 0 K in systems with misfit as low as 6.7% with the embedded-atom model (EAM), and work is underway to investigate dislocations in systems with less misfit. In previous work we have already shown the presence of misfit dislocations in Ni-Au and Ni-Pt bicrystals[9] and monolayer clusters of Au on Ni,[10] but these were high-misfit systems with 14% (Ni-Au) and 10% (Ni-Pt) misfit and relatively small numbers of atoms. Dregia and coworkers have reported on the use of the EAM to study the segregation of gold at a copper-silver phase boundary. In transmission-electron-microscopy studies of the Cu-Ag phase boundary, misfit dislocations were observed, but there was no report of the use of the EAM to study the formation of misfit dislocations.[11]

In the work reported here, misfit dislocations were studied in bicrystals of Pd-Cu and monolayers of Cu on Pd with a misfit of 6.7%; thus this system had a misfit significantly less than 15%, and the misfit was close to

the limits defined by van der Merwe[2] and Grabow and Gilmer.[8] In this study of Pd-Cu, 4417 total atoms (2360 Pd and 2057 Cu) were utilized in the spherical bicrystal arrangement, with the outer surface of the sphere being free of constraint. The interface between the two crystals was along a (111) plane; the (111) surface of the Pd crystal passed through the center of the sphere. The Cu monolayer contained 294 atoms placed on a hemisphere of Pd with 2360 atoms; in all other respects the analysis of the monolayer was the same as the bicrystal. All atoms were initially placed in atomic positions corresponding to a Pd lattice, and then the atoms were relaxed to equilibrium positions at 0 K with a conjugate-gradient energy-minimization technique.[12] The interactions between atoms were modeled with the EAM of Daw and Baskes[13] and the potentials utilized were those of Foiles, Baskes, and Daw.[14] The EAM includes a pairwise potential ϕ_{ij} and a many-bodied interaction term $E_i(\rho_i)$ which is the energy to embed the atom i into site i that has local electron density (ρ_i). The total cohesive energy is then the sum

$$E_{\text{tot}} = \sum_i E_i(\rho_i) + \tfrac{1}{2} \sum_{\substack{i,j \\ (i \neq j)}} \phi_{ij}(R_{ij}) \ . \tag{1}$$

The results of the relaxation are shown in Fig. 1, where the Pd and Cu atoms on both sides of the (111) interface plane are plotted as a function of position; the positions normal to the (111) plane are not shown. The Pd atoms are the solid circles and the Cu atoms are the open circles. The locations of the atoms parallel to the (111) planes for the bicrystal and the monolayer were essentially identical. The obvious triangular shape in Fig. 1 corresponds to the positions where the atoms in one of the planes lie at the saddle-point positions of the other plane as shown in Fig. 2(b). In a perfect face-centered-cubic (fcc) crystal (the initial positions in this study), the layering of the (111) close-packed planes is *ABCABC*. This is the layering inside the triangular shape shown in Fig. 1, and it is the layering shown in Fig. 2(a), where only two layers, *A* and *B*, are shown. However, outside of the triangular shape the atoms have been displaced to "*C*"-type positions shown in Fig. 2(c). The *C*-type positions are stacking-fault positions; thus the atoms outside the triangular shape were displaced into stacking-fault positions by displacements of the type $(a/6)[11\bar{2}]$ and the layering sequence would be *ACABC*. This displacement corresponds to a partial misfit dislocation. The three sides of the triangle in Fig. 1 correspond to atoms displaced to the saddle points in the three directions $[11\bar{2}]$, $[1\bar{2}1]$, and $[\bar{2}11]$, and the triangle resulting from the displacements reflects the threefold symmetry of the (111) surface. In Fig. 1 the Pd crystal was the substrate and it has the larger lattice parameter (3.89 Å) in comparison to Cu (3.62 Å). The Cu atoms were originally located at positions corresponding to a lattice parameter of 3.89 Å, but after the relaxation the Cu atoms contracted back towards their natural lattice parameter, and the Cu atoms were pulled up to and over the saddle points between the Pd atoms in the substrate. The Cu atoms farthest from the center were displaced the most. As was noted by Dodson and Taylor,[6] the spontaneous formation of the misfit dislocation is a surface phenomenon. The misfit dislocations would not have formed if periodic boundary conditions had been utilized; a real crystal with surfaces cannot be modeled with periodic boundary conditions in three dimensions. If the simulation was initiated with atoms of two crystals in registry and periodic boundary conditions were imposed in two directions within the interface plane, the two crystals remained in registry. These computer simulations with a free surface are in agreement with the experimental observations of Pd thin films deposited on Cu (111)-oriented single crystals by Chao *et al.*[15] They observed partial misfit dislocations when the Pd layer was 1 Å in average thickness; the Pd layer was thus not continuous.

Utilizing small clusters of atoms with a free surface to study the spontaneous formation of the dislocations in

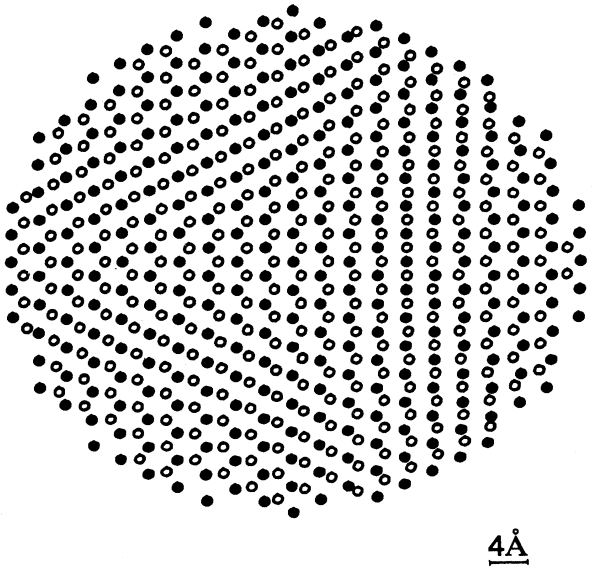

FIG. 1. The (111) interface of a Pd (solid circles) -Cu (open circles) bicrystal. The layers shown are the Pd and Cu layers adjacent to the interface.

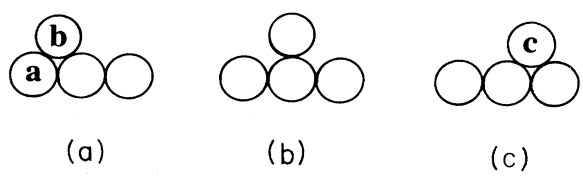

FIG. 2. (a) shows an "*A*"-type layer of a fcc crystal with one atom placed in a *B*-type position in the layer above. (b) shows the atom in the "*B*"-type layer being pushed to a saddle-point position; this corresponds to the configuration of atoms in the triangular shape shown in Fig. 1. (c) shows the atom in the upper "*B*"-type layer being pushed into a stacking-faulted "*C*"-type position.

thin films is appropriate, since the misfit dislocations would most likely form during the initial stages of growth of the new thin film phase when the new phase was in the form of discontinuous clusters of atoms on the substrate. The film would not form instantly as one continuous, uniformly strained sheet. In all forms of crystal growth, including monolayer epitaxial growth, the growth occurs on an atom-by-atom basis, with the new phase forming initially as a small cluster with free surfaces at all edges. It is possible for the clusters to be only a monolayer thick, or it is possible for the clusters to have multiple layers. This research does not, however, address any particular mode of growth because the system was not allowed to evolve in a dynamic way, as would happen in real crystal growth. The use of free surfaces on the boundary more closely simulates the clusters of new phases (either monolayer or island types) than those that would occur with periodic boundary conditions.

In this study an energy minimization was utilized, so that the total energy of the crystal could only be decreased. This implies that there was sufficient strain energy in the coherently strained crystal to form the misfit dislocations, and that if a local activation barrier was present the crystal strain energy was sufficient to provide the energy to overcome the barrier, and that thermal activation was not necessary for Pd-Cu. For systems of fcc metals with larger misfit than Pd-Cu, there should also be sufficient strain energy to overcome any activation barriers to dislocation formation on the (111) plane. Systems of less misfit, non-fcc metals, or other crystallographic orientations must still be studied. In the analysis of the Pd-Cu bicrystal the total energy of the coherently strained crystal was -2.46×10^{-15} J (-1.54×10^{4} eV), and this decreased to -2.54×10^{-15} J (-1.59×10^{4} eV) in the relaxed crystal.

This study indicates that the extent of the stable and metastable states of strained interfaces should be examined with more realistic models than the continuum models[2] or computer simulations with pair potentials.[4,8] The spontaneous generation of misfit dislocations was observed at 0 K in both a bicrystal of Pd-Cu and a monolayer of Cu on Pd with misfits of only 6.7%, and computer simulations in progress indicate the spontaneous generation of misfit dislocations at even smaller misfits (5% in Pd-Ag). These misfits of 6.7% are well below the 15% misfit where Dodson[4] observed metastable crystals strained to coherency. The observation of the spontaneous formation of misfit dislocations in a monolayer of Cu on a Pd substrate at 0 K with 6.7% misfit is well below the metastable limit of 11% observed by Grabow and Gilmer.[8] The observation of the spontaneous formation of misfit dislocations at 0 K in the Pd-Cu bicrystal with 6.7% misfit is approximately at the 6% metastable limit observed by Grabow and Gilmer, but, as stated above, misfit dislocations have been indicated in systems under study with even less misfit than reported here. The results of Grabow and Gilmer indicated that misfit dislocations were thermally activated; the results for Pd-Cu indicate that, for this magnitude of misfit, thermal activation was not necessary. One significant difference between this work and that of Dodson[4] and Grabow and Gilmer[8] may be that this work was on the (111) interface, whereas the previous work of Grabow and Gilmer was with the (001) interface. This difference should be further investigated.

Although we had previously demonstrated the character of misfit dislocations for systems with a large misfit and a relatively small number of atoms,[9,10] this is the first time that the atom arrangement around a misfit dislocation has been demonstrated in a computer simulation in a system with a small misfit and a large number of atoms.

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