Properties of dislocation half loops in Au(100): Structure, formation energy, and diffusion barrier

F. El Gabaly,* R. Miranda, and J. de la Figuera
Departamento de Física de la Materia Condensada, Universidad Autónoma de Madrid, 28049 Spain
(Received 20 February 2004; published 21 July 2004)

Dislocation half-loops intersecting the surface have been detected by Scanning Tunneling Microscopy after mild sputtering on Au(100). We determine their structure and formation energy by means of atomistic simulations. The Peierls barrier is also estimated from the simulations and found to be a few meV. This represents a very efficient way of moving mass parallel to the surface under applied stress, where a net movement of hundreds of atoms can take place with barriers smaller than that for the diffusion of a single adatom. Thermal diffusion is not observed.

DOI: 10.1103/PhysRevB.70.012102 PACS number(s): 61.72.Ff, 61.72.Bb, 68.37.Ef, 07.05.Tp

Dislocations located close to the surface of a crystalline solid are known to affect the mechanical properties of the surface, but dislocations can also give rise to enhanced reactivity at points where they emerge from the solid, and influence strongly epitaxial growth. Ordered dislocation networks have been used as templates for the growth of arrays of nanostructures. Certain dislocation configurations have also been proposed to act as a pathway for the net transport of atoms parallel to the surface with extremely low activation barriers.

Dislocations are usually treated within elastic theory introducing a cutoff length for atomic positions that are too far away from equilibrium positions. Such an approach has been extremely successful. Nevertheless there is an increasing number of experimental results related to the behavior of dislocations at the nanometer scale that require a fully atomistic modeling. Problems such as the estimate of the barriers for dislocation motion, the formation of compact dislocation networks in ultra-thin films, or the first steps of the nucleation of dislocations in nanoindentation experiments require atomic scale total energy calculations that nowadays can be based on semi-empirical potentials and simulations with thousands to millions of atoms. We present in this work an atomistic study of some of the properties of dissociated dislocation half-loops in Au(001) with a comparison to experimental observations of the half-loops obtained by both ion-beam irradiation and nanoindentation. The results will also be compared to studies based on simple dislocation geometries within the framework of dislocation theory in an isotropic elastic continuum. The simplest expected subsurface structure will be obtained, and possible complications in the experimental images will be addressed. Estimates for the formation energies of half-loops of different sizes will be presented, as will be the energy barrier for the glide of the dislocation structures.

The experiments were performed in a ultra-high-vacuum (UHV) Scanning Tunneling Microscope (STM) with a base pressure of better than \(2 \times 10^{-10}\) Torr. The Au sample was cleaned by cycles of Ar⁺ sputtering at 600 eV followed by annealing. Annealing to 900 K produced flat terraces with the well known 5 \(\times\) 20 "hex" reconstruction of Au(100). This reconstruction appears in STM images as fringes oriented along (110) directions. These fringes arise from a moiré-like effect between the topmost layer with an hexagonal arrangement and the lower bulk-like layer with square symmetry.

Annealing the Au(100) crystal at 600 K after sputtering produces structures on the surface as shown in Fig. 1, marked with black circles. These structures will be called mesas from now on. They are probably present right after the sputtering process, but the surface roughness at that stage makes it impossible to locate them. Annealing at 900 K makes them disappear from the surface. They are mostly rectangular protrusions 0.6 Å high with lateral sizes in the range of nanometers to tens of nanometers. The sides of the protrusions are aligned with the compact (110) directions. Two opposite edges of the mesas present an abrupt change in height when crossing them, and their separation will be called the "width" \(w\) of the structure. The other two decay smoothly, and their separation will called the "span" \(s\) of the structure.

FIG. 1. (a) STM image of the Au(100) surface after sputtering and gentle annealing, 116 nm \(\times\) 160 nm in size. Several mesas marked with black circles can be observed. The image has been differentiated to enhance the contrast on the terraces. (b) STM image of a single mesa. The width \(w\) and the span \(s\) as defined in the text are marked. The image size is 30.3 nm \(\times\) 30.3 nm.

The interpreted character of those half-loops which have the span aligned with the reconstruction fringes (not shown) can be tested by observing whether on top of the mesa there is a missing/extra reconstruction fringe with re-
interstitials corresponds to either extrinsic stacking fault positions or exact on-top positions they do not relax to a regular dislocation half-loop. Instead, some of the extra atoms are ejected to the surface. Likewise, vacancies in a triangular plane give rise to vacancies in the surface layer. When relaxing statically the interstitial plane in the previously described position, a perfect edge dislocation half-loop is first generated [see Fig. 2(b)]. Each perfect edge dislocation continues the relaxation by dissociating within a \((111)\) plane into a stacking fault bounded by Shockley partial dislocations\(^6\) as shown in Fig. 2(c). The precise shape of the stacking fault region and the length of the stair-rod dislocation depends on the depth of the dislocation half-loop. The top layer of the EAM simulation is very similar in shape to the experimentally observed mesa, reproducing its 0.6 Å height [compare Fig. 2(d) to Fig. 1(b)]. The length of the topside of the original triangle of interstitials is the final span of the mesa.

The precise structure of the dislocations underneath the surface cannot be determined from the STM images alone as these only show the uppermost atomic layer. The simplest structure proposed corresponds to the V-shaped half-loop shown in Fig. 2. A test of such a model is the experimentally observed width-to-span relationship for mesas reported in Ref. 9. For small spans, the width and span are proportional. At larger spans, there is a saturation in the width with a typical value of 7 nm. In the V-shaped model, the depth of the structure and the span are proportional because the stacking faults are located on intersecting \(\{111\}\) planes. The saturation of the width at large spans (which means also deep half-loops) is due to the equilibrium width of a long dislocation dissociated into a stacking fault ribbon.\(^6\) The EAM simulations of simple V-shaped half-loops, as shown in Fig. 3(a), fall in the proportional part of the width-to-span curve. The results are in excellent agreement with the experiments reported for nanointerdenetration mesas.\(^9\) The smaller half-loops present stacking faults of a triangular shape [see Fig. 3(b)], with the Shockley partial dislocations aligned to close-packed directions. The larger half-loop of Fig. 3(c) shows a tendency to have parallel Shockley partial dislocations close to the surface.

So far it has been assumed that the dislocation structure underneath the surface is the result of the dissociation of V-shaped dislocation half-loops. Such structures are clearly inadequate to explain experimental observations of non-symmetric mesas as shown in Fig. 4(a). We propose that the subsurface structure in these cases is an irregular, W-shaped dislocation half-loop [see Figs. 4(b) and 4(c)]. A regular W-shaped structure could originate symmetric mesas, but would give rise to half-loops with a different width-to-span relationship relative to the simple V-shaped half-loops [see Fig. 3(a)]. The EAM simulations prove that such structures are higher in total energy than the simple V-shaped half-loops. We calculate that a W-shaped symmetric structure (similar to the one shown in Fig. 4(c) with both sides of equal length) is 1.5 eV higher in energy than a simple V-shaped half-loop made of a similar number of interstitials.

The dislocation half-loops should move easily if there is a common glide direction for all the dislocations that comprise the structure. The Shockley partials that form the edges of the structure can move in each of the \(\{111\}\) planes in which
each stacking fault resides. The intersection of both planes defines a line along the axis of the stair-rod dislocation. Such a direction is the common glide direction for the half-loop. The movement of the half-loop in this direction will be hampered by the Peierls barrier of the dislocations involved. The energy barrier for glide of the dislocation half-loops was calculated on a smaller slab of 13600 atoms using a modified version of the DYNAMO code which implements the Nudged Elastic Band Method (NEB)\(^\text{18}\). The results are presented in Fig. 5. All the barriers obtained are extremely small. Even for the 13 atoms-wide half-loop, corresponding to the net movement of 91 atoms, the barrier for displacing the half-loop by one lattice distance is only 10.9 meV. Experimentally, the mesas have been observed to move under applied stress.\(^\text{11}\) They have been assumed to move in the nanoindentation experiments as they are detected far away from the point of nanoindentation. In fact they have been observed to slide along the stair-rod axis in molecular dynamics simulations of nanoindentation under applied stress. Nevertheless, we have not detected any thermal motion of dislocation half-loops a few times larger than those simulated here. This is the case for both the sputtering experiments (up to a temperature of 400 K) and the nanoindentation experiments. The most likely explanation lies in the diffusion prefactor: we expect the diffusion prefactor to be very low for large half-loops given the concerted motion involved in moving the full structure. The number of atoms in this systems makes the direct estimate of the diffusion prefactor from the simulations quite difficult. The experimental data provides a rough estimate: given that no movement is detected at 300 K in times of the order of hours and assuming a diffusion barrier of the order of 25 meV for these slightly larger half-loops, a prefactor of the order of $10^{-2} \text{s}^{-1}$ is obtained. This has to be compared to the typical prefactor for adatom diffusion of $10^{13} \text{s}^{-1}$.

The prefactor is expected to depend strongly on the number of atoms of the half-loop. Although the (large) observed half-loops do not move, the smaller ones could potentially have an important role in the thermal mass-transport on the surface. Unusual mechanisms, such as a single interstitial in the surface layer of strained Cu\(_{100}\) (a surface crowd ion)\(^\text{19}\) or subsurface diffusion below surfactant layers\(^\text{20}\) have been recently proposed as efficient surface diffusion pathways. The physical reason for the easy diffusion in the former case is analogous to the one that facilitates glide of the dislocation

![Image 3](image3.png)

**FIG. 3.** (Color online) (a) Width-to-span relationship for V-shaped simulated half-loops (empty diamonds) and for experimentally generated mesas (filled circles, from Ref. 9). The star marks the width and the span of a W-shaped simulated half-loop. Also shown are the perspective view of (b) a 7 atoms wide half-loop and (c) a 23 atoms wide half-loop.

![Image 4](image4.png)

**FIG. 4.** (Color online) (a) STM image of a nonrectangular mesa. The image size is 30 nm $\times$ 30 nm. (b)–(c) EAM simulation of a possible dislocation structure that can give rise to such a top view image. (b) Top view; (c) perspective view.

![Image 5](image5.png)

**FIG. 5.** Peierls barrier for the displacement of V-shaped half-loops of different sizes, as estimated by the NEB method.

![Image 6](image6.png)

**FIG. 6.** Calculated formation energy of dissociated V-shaped half-loops as a function of span.
half-loops: the spread of the distortion caused by the defect in the moving direction. In our case, the key process would be the formation of dislocation half-loops. In order to estimate whether this surface diffusion pathway is relevant the formation energies of half-loops of different sizes were calculated and they are shown in Fig. 6. Even the smallest loop, three atoms deep, has a formation energy of 3.08 eV. For bigger half-loops, the formation energy increases with the size of the mesa. The formation energy per interstitial atom decreases from 0.51 eV (3 atoms wide half-loop) to 0.174 eV (23 atoms wide half-loop). Based on this formation energies, we rule out a significant contribution of half-loops to thermal mass transport at surfaces.

In summary, dislocation half-loops have been observed by STM after mild sputtering and annealing of a Au(100) crystal. The behavior of dissociated half-loops has been studied by atomistic simulations employing EAM potentials. The starting configuration to simulate a half-loop is a flat triangular plane of interstitials. Relaxing statically the configuration goes through the expected dislocation reactions giving rise to a dissociated dislocation half-loop. The formation energies for half-loops of different sizes has been estimated, ruling out a significant contribution to thermal mass transport at the surface. The diffusion barrier for the half-loops has been estimated by the NEB method, giving an extremely low value of 5–12 meV. This small barrier explains how the half-loops could be observed in nanoindentation experiments quite far from the nanoindentation point, and provides an efficient nonthermal mass-transport mechanism under applied stress along compact directions.

The authors thank John C. Hamilton and Juan M. Rojo for useful discussions. This research was partly supported by the Office of Basic Energy Sciences, Division of Materials Sciences, U. S. Department of Energy, by the Comunidad Autónoma de Madrid through Project No. 07N/0041/2002, and by the Spanish Ministry of Science and Technology through Projects No. BMF 2001-0174 and MAT2003-08627-C02-02. J.d.I.F gratefully acknowledges as well support through a “Ramón y Cajal” contract from the Spanish Ministry of Science and Technology.

---

8Electronic address: farid.elgabaly@uam.es; http://hobbes.fmc.uam.es