Brownian Motion of Dislocations in Thin Films

A. K. Schmid, N. C. Bartelt, J. C. Hamilton, C. B. Carter,* and R. Q. Hwang
Sandia National Laboratories, Livermore, California 94551-0969
(Received 17 January 1997)

The motion of edge dislocations in a single monolayer film of Cu on Ru(0001) was studied by time-resolved scanning tunneling microscopy. The dislocations were observed to make rapid 1D random walks in the film. This dislocation motion is attributed to the equilibrium thermal exchange of atoms between the solid film and the adatom gas covering the film. These results highlight a fundamental difference between the dynamics of dislocations in thin films and the bulk, which is in principle important in understanding the mechanical properties of thin films. [S0031-9007(97)03041-X]

PACS numbers: 68.35.Fx, 61.16.Ch, 61.72.Lk, 68.45.Da

It is a remarkable and well understood fact that surface diffusion is often many orders of magnitude faster than bulk diffusion. This fast diffusion is integral to our understanding of a wide range of surface phenomena, and it would obviously be unwise to extrapolate surface diffusion mechanisms from bulk processes. Here we show that dislocation motion near surfaces can also occur by fundamentally different processes than in the bulk, thereby increasing rates of dislocation motion in thin films. Since dislocation generation and motion are the means by which mechanical strain is relieved, our observation of fast dislocation motion has important implications for the mechanical behavior of thin films. The observed dislocation motion is sufficiently rapid that the thermally induced Brownian motion of a thin film dislocation can be directly measured, allowing the atomistic processes responsible for the high mobility to be quantified. We attribute the fast dislocation motion to rapid exchange of adatoms between the surface and the core of the dislocation.

Our observations consist of *in situ*, room temperature scanning tunneling microscopy (STM) measurements of the motion of edge dislocations in a single atomic layer of Cu deposited on the (0001) face of Ru. The Cu on Ru(0001) system is a benchmark system of how strain is accommodated in metal-on-metal epitaxy [1–4]. Because the lattice constant of Cu is 5.6% smaller than Ru, a sequence of strain relief structures occurs with increasing Cu film thickness. The first Cu layer is pseudomorphic (i.e., has the same structure as the underlying first layer). By the fourth layer, the in plane Cu lattice constant is close to the bulk Cu lattice constant, leading to a moiré structure on the Cu surface due to interference with the underlying Ru periodicity. At intermediate thicknesses, as we will discuss below, the films contain networks of dislocations. These dislocations are imaged by STM as buckled regions of the surface: The detailed structure of the various networks that occur in the Cu/Ru(0001) system has been investigated by Günther *et al.* [3]. All experiments discussed in this paper were performed in an UHV chamber with a base pressure of 3×10^{-11} torr. STM imaging used tunneling voltages ranging from -0.1 to -0.5 V applied to the sample and tunneling currents ranging from 0.1 to 2 nA.

Figure 1 displays an example of the dislocations (brighter stripes) that occur both in the first and second layers of Cu on Ru(0001). In the first layer, the dislocations form "U" shaped loops that emanate from the step edge. These dislocations are unexpectedly mobile: A sequence of STM images of these dislocations taken at 30 sec intervals is shown in Fig. 2. Within minutes, their lengths fluctuate by many lattice constants. However, the average length of all the dislocations does not change even after more than 11 hours (scanning at a rate of 2 images per min). Thus there is no indication that these fluctuations are part of a slow drift of the system to a configuration that is thermodynamically more favorable. The dislocations are evidently performing thermally induced equilibrium fluctuations.

In order to understand the origin of this motion, a better understanding of the structure of dislocations is

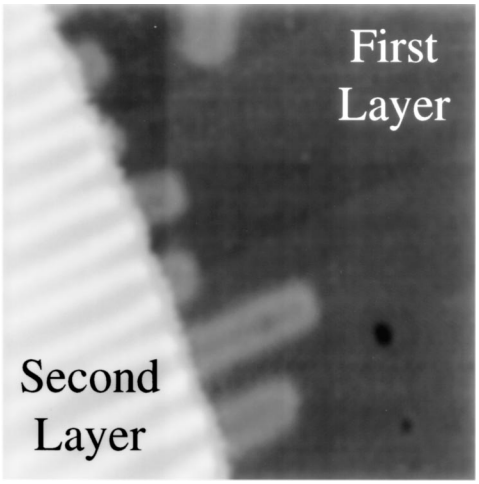

FIG. 1. Room temperature STM image (270 Å × 270 Å) of a Cu film exposing regions of one and two atomic layers. Partial dislocations are imaged as bright strips and form an ordered array in the second Cu layer. Partial dislocations in the first layer emerge where second-layer dislocations reach step edges.

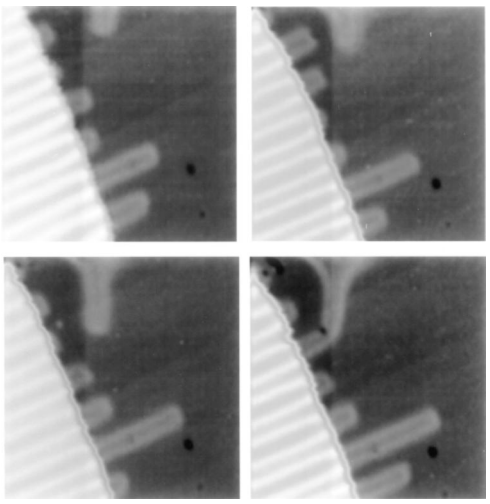

FIG. 2. Time sequence of first-layer dislocations emanating from second-layer step edges (clockwise from upper left). Images were acquired 30 sec apart. Length changes can be referenced by the stationary impurity (black dot) in the lower right of each image Each image has size 270 Å × 270 Å.

necessary. Dislocations form in thin films to relieve strain because they allow the film to have a different atomic density than the substrate. The structure of dislocations is largely determined by the crystallography of the film and substrate. On triangular close-packed surfaces, such as hcp(0001) and fcc(111), changing the atomic density of a layer naturally results in the formation of stacking faults. That is, atoms in each close-packed layer that would normally prefer to be in either fcc or hcp sites can, with relatively little cost in energy, shift to the other type of site. As shown in Fig. 3, shifting a region of the surface from fcc to hcp stacking or vice versa, changes the surface atomic density at the boundary between the two

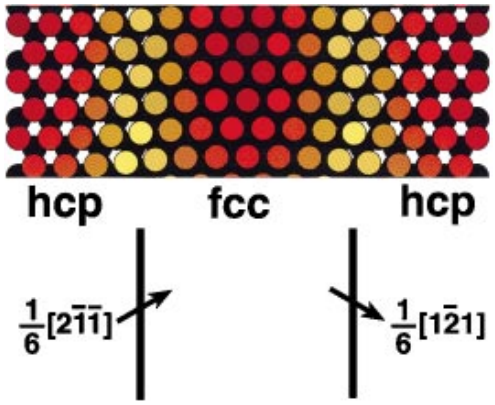

FIG. 3(color). Schematic illustration of the atomic structure at partial dislocations between fcc and hcp stacking regions. The line diagram marks the position of the underlying dislocation lines and their associated Burgers vectors. Atomistic calculations [4] indicate that atoms at the dislocations tend to be raised relative to those in the ideal stacking sites, as shown by their brighter color in the figure.

regions, thereby partially relieving strain. This boundary is a dislocation characterized by the vector of the shift from one type of stacking to the other (this is the Burgers vector [5] of this dislocation). Since the shift between fcc and hcp stacking is not a full lattice vector, these domain boundaries are partial dislocations. Partial dislocations are the building blocks for the large variety of dislocation networks found on close-packed surfaces and general models for such dislocation arrays have been constructed [6]. The reconstructions of the clean Pt(111) and Au(111) surfaces [7–11] are composed of them.

These concepts can be directly applied to the structure of the Cu/Ru(0001) film of Fig. 1. The partial dislocations appear in the second Cu layer (left of Fig. 1) as lighter stripes separating regions of fcc and hcp stacked Cu [3,4]. In contrast, most of the first layer Cu (right of Fig. 1) shows no long periodic corrugations, consistent with the pseudomorphic structure observed in earlier studies [2]. However, dislocations in the first layer are found at the step edge of the second layer. These dislocations are stabilized by the presence of second layer islands and their associated dislocation patterns. Note that the first-layer dislocations form loops that originate from the point where the second-layer dislocation lines intersect second-layer step edges. Where the two partial dislocations meet at the end of the loops in the first layer, the partial Burgers vectors sum to form a dislocation with a full lattice constant Burgers vector, i.e., as a perfect edge dislocation. Since the layer is only one atomic layer thick, this edge dislocation is only one atomic unit long and threads from the interface to the surface. These pairs of threading dislocations can be visualized using an embedded atom (EAM) calculation of their static structure, as shown in Fig. 4. Each pair of lines is comprised of two partial dislocations running along the $\sqrt{3}$ or $[\bar{2}11]$ direction separating regions of hcp and fcc stacking [12]. Where the partial dislocations meet, a perfect edge dislocation is formed [11].

If partial dislocations move on the plane containing the dislocation line and the Burgers vector, the density of the layer is preserved, and the dislocation is said to glide [5]. Threading edge dislocations of unit length, as in our case, can only glide parallel to their Burgers vector. In order to move in any other direction, atoms must be added to or removed from the crystal. This can be readily seen from Fig. 4. For the dislocation pairs to change in length in the manner we observe, atoms must be added or removed from the extra row evident in Fig. 4. This process, dislocation climb, is controlled by the availability and mobility of vacancies and/or interstitials to change the length of the extra row. Because of the typically slow diffusion of bulk vacancies and interstitials, bulk dislocations climb slowly.

On a surface, however, there is the possibility of another source of atoms for dislocation climb. There always exists a 2D gas of atoms, i.e., adatoms, on the surface in equilibrium with the solid. The existence of these adatoms leads

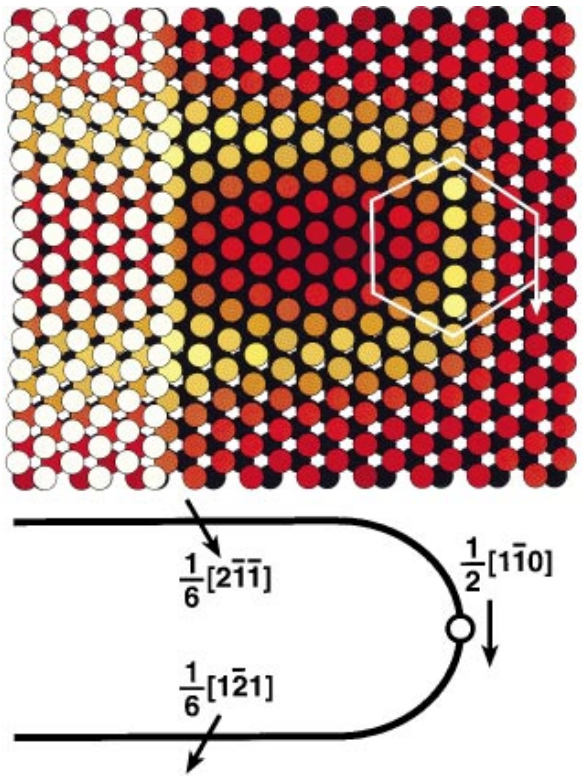

FIG. 4(color). EAM calculated dislocation structure at a second-layer step edge. A perfect edge threading dislocation is formed at the intersection of the two partial dislocations. A Burgers circuit is superimposed on the image indicating the presence of the threading dislocation at the intersection of the two partial dislocations. The line diagram shows the orientation of the dislocations and their Burgers vectors. The small circle at the intersection of the partials indicates the threading dislocation oriented perpendicular to the page.

to enhanced surface self diffusion. Under equilibrium thermodynamic conditions, the adatom density is determined by balancing the chemical potentials of the solid and the adatom gas. To maintain this balance, the solid and the gas must constantly exchange atoms. This is usually thought to occur at surface steps, via continuous condensation and evaporation of adatoms. The random component of this exchange leads to observable fluctuations in step position. However, past experiments have shown that other paths for the solid to exchange atoms with the adatom gas are possible. For example, a high density reconstructed Pt(111) surface can be produced *metastably* by providing a supersaturated Pt gas-phase environment through a deposition flux [10]. In response to the increase in the supersaturation, the Pt(111) surface reconstructs by atoms being directly incorporated into the first layer. The same effect occurs upon room temperature deposition of Cu on the first monolayer of Cu on Ru(0001) [2], as shown in Fig. 5. Annealing this metastable film completely removes the dislocation network and returns the film to the pseudomorphic phase [2]. These results establish that the substrate-adatom exchange can occur in the terraces under

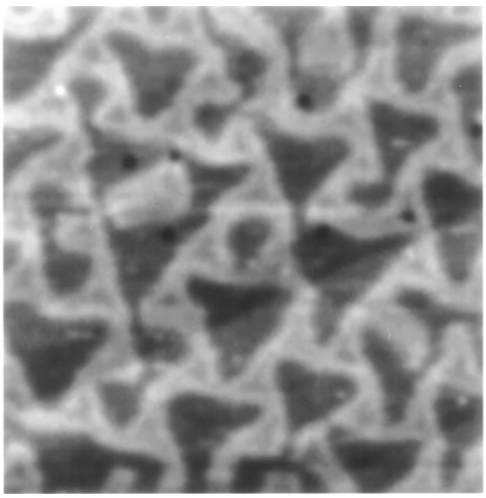

FIG. 5. Dislocation network of first-layer Cu created by a supersaturated Cu gas phase that results from room temperature deposition (685 Å $\times$ 685 Å).

suitable conditions. We will now argue that there is also a direct random *equilibrium* thermal exchange between the adatom sea and the first layer.

That depositing even small numbers of adatoms on the first layer causes the creation of metastable dislocations (Fig. 5) strongly suggests that the source and sink of atoms causing dislocation climb is the surface adatom gas. Another possible source is an equilibrium density of vacancies in the first layer Cu. The relative importance between adatoms and vacancies can be appraised by estimating the equilibrium ratio of the number of second layer Cu adatoms to first layer Cu vacancies. In the presence of a partially completed second layer, the equilibrium ratio of the adatom to vacancy concentration in the first layer is given by $\rho_a/\rho_v = \exp(\varepsilon_b/kT)$, where ε_b is the difference between the binding energy of Cu on Ru and Cu on Cu. (This result assumes a nearest neighbor pairwise interaction between Cu atoms which is the same in the first and second Cu layers.) From measurements of the thermally induced desorption of Cu films from Ru, ε_b has been estimated to be 130 meV [1], giving $\rho_a/\rho_v \approx 200$ at room temperature, suggesting again that adatom exchange is the dominant process for the fluctuations.

Intuitively, the most likely position for this exchange to take place is at the core of the dislocation since that is the area of largest lattice distortion. This is also suggested by our inability to resolve atomically the core of the dislocation in this case, while the core structure of other nonfluctuating dislocations have been imaged [10]. Furthermore, the EAM calculation mentioned above shows that there is no energy barrier to the incorporation of an adatom into the edge dislocation core, while other sites have an energy barrier.

To probe the nature of the fluctuations in detail, the lengths of many dislocations were followed as a function of time. Figure 6(a) shows the time dependence of the

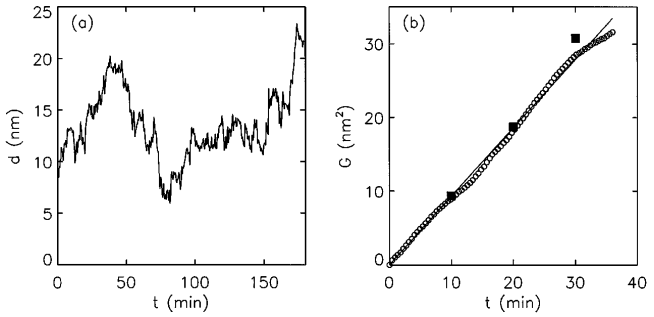

FIG. 6. (a) Time dependent trajectory of an edge dislocation in the first layer of Cu/Ru(0001). Data were taken from 270 Å × 270Å images acquired every 27 s. The circles in pane (b) show the mean-square displacement as a function of time for the trajectory shown in (a), while the other squares were obtained from 350 nm^2 images acquired every 10 min for several hours.

length of one such dislocation pair over several hours. The length fluctuations appear to be random, with no apparent tendency towards either growth or shrinkage. If the threading dislocations are, in fact, performing random walks, the mean-square change in dislocation length, d, at different times, t' and $t + t'$ should be proportional to the time difference, $G(t) = \langle [d(t') - d(t' + t)]^2 \rangle = 2D|t|$, where D is the diffusion coefficient of the random walk. As shown in Fig. 6(b), the mean-square displacement, $G(t)$, computed from the data is completely consistent with this predicted linearity (a tendency towards growth or shrinkage of the dislocation length would cause the mean-square displacement increase as the square of the time difference). The diffusion coefficient computed from the slope of the mean-square displacement plots is 0.008 nm^2/s. In order to evaluate the effect of imaging on these observations, we have monitored the length of the dislocations using different scan sizes and rates. As seen in Fig. 6(b), the mean-square displacements derived from images acquired at a rate of 1 frame every 10 min are completely consistent with the mean-square displacements from the frames acquired every 27 s. We conclude that there is no appreciable influence of the scanning STM tip on the dislocation motion.

The measurement of D provides quantitative insight about the atomic events responsible for dislocation motion. If the exchange occurs by uncorrelated incorporations of single atoms of size a into the edge dislocation, then this causes changes in d of length $\sqrt{3}\,a$, and so D is $D = 3a^2/\tau$, where τ is the time between uncorrelated incorporation events. Using $a = 0.27$ nm for pseudomorphic Cu on Ru(0001), this yields $\tau \approx 30$ s.

To appreciate how remarkably large the corresponding exchange rate is, consider what the rate would be if this dislocation were deep inside the bulk. In Cu, the primary mechanism of self diffusion is vacancy diffusion [13]. The rate of vacancies exchanging with the dislocation per second (assuming no barrier for vacancy incorporation into the core) is approximately given by the bulk self diffusion constant divided by the square of the lattice constant. From measurements of Cu self diffusion rates, a vacancy-dislocation exchange rate of $1/30$ s would require a temperature of approximately 400 °C above the temperature at which these experiments were performed [13].

In conclusion, we have observed equilibrium Brownian fluctuations of edge dislocation in the first layer of Cu on Ru(0001). We estimate there is 1 atomic exchange with each threading edge dislocation every 30 sec at room temperature. The mass exchange required for these fluctuations is provided by the equilibrium adatom gas on the surface, rather than by vacancies within the top layer. The consequent easy motion of dislocations is an important factor to consider in defining the evolution and response of thin films to further growth and external forces.

This work was supported by the Office of Basic Energy Science, Division of Materials Science, of the U.S. Dept. of Energy under Contract No. DE-AC04-94AL85000.

*Permanent address: Department of Chemical Engineering and Materials Science, Amundson Hall, University of Minnesota, Minneapolis, MN 55455.

[1] K. Christmann, G. Ertl, and H. Shimizu, J. Catal. **61**, 397 (1980).
[2] G. O. Pötschke and R. J. Behm, Phys. Rev. B **44**, 1442 (1991).
[3] C. Günther *et al.*, Phys. Rev. Lett. **74**, 754 (1995).
[4] J. C. Hamilton and S. M. Foiles, Phys. Rev. Lett. **75**, 882 (1995).
[5] J. P. Hirth and J. Lothe, *Theory of Dislocations* (Krieger, Malabar, Florida, 1982).
[6] C. B. Carter and R. Q. Hwang, Phys. Rev. B **51**, 4730 (1995).
[7] U. Harten *et al.*, Phys. Rev. Lett. **54**, 2619 (1985).
[8] A. R. Sandy *et al.*, Phys. Rev. B **43**, 4667 (1991).
[9] A. R. Sandy *et al.*, Phys. Rev. Lett. **68**, 2192 (1992).
[10] M. Bott *et al.*, Phys. Rev. Lett. **70**, 1489 (1993).
[11] J. V. Barth *et al.*, Phys. Rev. B **42**, 9307 (1990).
[12] P. J. Feibelman *et al.*, Surf. Sci. **302**, 81 (1994).
[13] N. L. Peterson in *Diffusion in Solids: Recent Developments*, edited by A. S. Nowick and J. J. Burton (Academic Press, New York, 1975), p. 126.