In-Situ STM Studies of Strain Stabilized Thin Film Dislocation Networks Under Applied Stress.

Oliver Schaff, Andreas K. Schmid, Norm C. Bartelt, Juan de la Figuera and Robert Q. Hwang
Sandia National Laboratories, Livermore, California, USA

Abstract:

The effect of uniaxial applied stress on dislocation networks present in the atomic surface layer of Au(111) was studied. The measurements were made using a novel instrument combining ultrahigh vacuum scanned-probe microscopy with an in-situ stress-strain testing machine. The technique provides microscopic information, up to atomic resolution, about the large scale plasticity of surface layers under applied loads.
The herringbone reconstruction of the Au(111) surface is a classic example of a strain stabilized dislocation network. We find that under 0.5% uniaxially applied compressive strain a dramatic restructuring of the network takes place. The three-fold orientational degeneracy of the system is removed and threading edge dislocations are annihilated.

Keywords: Thin Films, Dislocations, Surface Dynamics, Surface Phase Transformation, Surface Elasticity, Gold Surfaces

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Introduction:

Well ordered dislocation networks, or reconstructions, are remarkably stable in many cases of heteroepitaxial metal thin films [1,2] as well as in many metal single crystal surfaces [3]. As a function of material combinations or layer thickness, a great variety of different structures can be observed. The scanning tunneling microscope (STM) images in figure 1 show two examples. The ubiquity of these dislocation networks and their potential usefulness in the fabrication of films with tailored mechanical, electronic, magnetic or chemical properties, motivates the search for a fundamental understanding of them.

Surface stress is generally invoked as the driving force for these reconstructions. In case of heteroepitaxy, the surface stress is qualitatively attributed to lattice mismatch between substrate and overlayer [4]. In the case of pure metals, the qualitative argument often given is that due to the reduced coordination of surface atoms, the preferred bond length of atoms in the surface layer is smaller than in the bulk [5,6]. Thus unreconstructed metal surfaces are under tensile stress and in many cases, relief of this stress is sufficient to stabilize a dislocation network. However, this simple argument does not explain the complexity of the spatial organization of the observed dislocation networks.

If the great variety of dislocation network structures found in different systems is so closely linked to the particular surface strain states, then one would expect a given surface dislocation network to be sensitive to any changes of the strain state of the surface. In this paper, we discuss how one can manipulate surface strain through the elastic deformation of crystals. We find that surface dislocation structures are indeed highly sensitive to externally applied stresses and how they respond provides quantitative information about the energy balance responsible for their structure.

Discussion:

The herringbone-reconstruction on the Au(111) surface (figure 2a), is an example of a strain-driven dislocation network. In essence, the top atomic layer on a Au(111) crystal contracts to form an anisotropic, periodic dislocation network consisting of parallel Shockley partial dislocations. Due to the three-fold symmetry of the underlying bulk crystal, the reconstruction can appear in any of three degenerate orientational domains. On clean and fully relaxed Au(111), one typically finds large regions where narrow stripe-shaped domains of two orientations alternate in a herringbone pattern with remarkable long range order, as in figure 2a. In the domain walls between these stripes, the Shockley partial dislocations are bent by approximately 60°. For topological reasons [7], every other Shockley partial has a threading edge dislocation at these bends, the positions of the threading segments are indicated in the inset in figure 2a.

The Au crystals shown in figure 2 are thick, Au(111) oriented films, grown under ultrahigh vacuum conditions on mica substrates (the preparation conditions were similar to recommendations published in the literature [8]). The great elasticity of mica allows us to impose controlled amounts of uniaxial, external strain onto the Au crystal by bending the mica substrate. In our experience, up to 0.5% strain can be achieved reliably without breaking the mica.

The bending apparatus is a specially desiged instrument for *in-situ* operation under ultrahigh vacuum conditions, installed in the same chamber where the Au films are grown. The instrument incorporates a STM and a sample heater, to facilitate measurements of dislocation dynamics under variable conditions of temperature and applied stress.

Dislocation climb in surface layers can be fast even at relatively low temperatures, because exchange of atoms between the surface layer and the adatom lattice gas covering the surfaces has a low barrier [9]. In the Au(111) surfaces we find that at approximately 80 °C, thermally activated dislocation motion of both climb and glide character becomes quite rapid [10], so it is plausible that the dislocation network can obtain its thermal equilibrium state. So, in this temperature range, restructuring of the dislocation networks we observe can be plausibly interpreted as changes in the equilibrium state of the surface.

We find that uniaxial, in-plane compression of a Au(111) surface lifts the degeneracy of the three possible orientational domains. Figure 2a-c shows a sequence of STM images of a Au(111) sample, annealed under applied strain ranging from 0 to 0.23 %. The dislocation structure changes dramatically from the typical Au(111) herringbone structure seen in figure 2a. Under small load of 0.17 % strain, figure 2b, domain wall motion results in the growth of domains with Shockley partials oriented along the [11-2] at the expense of the other type of domains. Under higher loads of 0.23 % strain, figure 2c, minority domains can be removed from the surface altogether, as indicated by the arrow. This trend continues for higher applied loads, figure 2d shows an area of a different sample after annealing under 0.4 % compression. Only one large domain has survived in this region, which implies that the total number of end-on perfect edge dislocations present in the network depends sensitively on a sample's stress state.

To study the mechanism by which the density of end-on edge dislocations in the network can change under load, we have conducted *in-situ* cyclical loading experiments. A sample was initially annealed under 0.5% tensile strain, to stabilize the majority domain of parallel Shockley partials shown in figure 3a. While keeping the sample at 80 °C, the externally applied strain was reversed. Comparing the structures seen in figures 3a and 3b, it is evident that the minority domain has grown towards the right by 20 nm. This domain wall motion resulted in the creation of 3 new dipoles of end-on perfect edge dislocations. Figure 3c shows schematically the creation of a dipole.

We point out that while the results described here are typical outcomes of our experiments, we have also observed inconsistencies. The application of external strain on the Au(111)/mica samples always leads to surface restructuring similar to the data shown, however, we have difficulty establishing the correlation between the orientation of majority domains in stressed samples and the precise direction of the applied strain. Tentatively, we attribute this difficulty to strain relief processes occuring in the bulk of the Au films or at the Au/mica interface which affect the orientation and value of the surface stress in an uncontrolled manner. Regarding the instrument used, we believe that while the stability of temperature and stress control is very good in the present setup, the precision of our calibrations could be improved. The values of strains we report here are simply deduced from the equation of curvature of the three-point bending arrangement. We estimate that the values of the strains applied to the mica substrates are within ± 20 % of the values given, and possible bulk relaxations of the Au films have been neglected.

These results are consistent with the idea that an array of parallel Shockley partial dislocations mainly relieves stress in a direction perpendicular to the dislocation lines. Parallel to the Shockley partials, the surface layer is still under high tensile stress. Partially relieving the tensile surface stress through the externally applied compression lowers the energy of stress domains. One might ask, how much energy does the surface energy change during the dislocation arrangements shown in figure 2? In particular, how much strain energy is needed to remove the threading edge dislocations of the herringbone reconstruction?

The answer to these questions is intimately associated with the anisotropy of the surface stress of the uniformly "striped" arrangement of parallel Shockley partial dislocations within one domain.

The surface stresses perpendicular and parallel to the Shockley partials, $\sigma_\perp$ and $\sigma_\parallel$, are defined in terms of derivatives of the surface free energy per unit area γ with respect to the lattice constants a perpendicular and parallel to the two directions [6]:

$$\sigma_\perp = \gamma + a_\perp \frac{\partial\gamma}{\partial a_\perp} \text{ and } \sigma_\parallel = \gamma + a_\parallel \frac{\partial\gamma}{\partial a_\parallel}.$$

Thus if the bulk strain ε is perpendicular to one of the Shockley partial directions, the difference in surface energy between this direction and one rotated by 120° from it is

$$\Delta\gamma = \left[\sigma_\perp - \left(\frac{1}{2}\sigma_\perp + \frac{\sqrt{3}}{2}\sigma_\parallel\right)\right]\varepsilon. \tag{1}$$

The strain energy involved with changing a herringbone phase to a uniformly striped phase is the energy required to convert half the unit cell from one stripe orientation to another:

$$\Delta E = \frac{A}{2}\Delta\gamma, \tag{2}$$

where A is the area of the herringbone unit cell ($\sim (15 \times \sqrt{3}a)(92a) = 2 \times 10^4\,\text{Å}^2$). Approximate theoretical estimates of $\sigma_\perp$ and $\sigma_\parallel$ are available from Narasimhan and Vanderbilt [11]: $\sigma_\perp \sim 0.3\text{eV/Å}^2$ and $\sigma_\parallel \sim 1.4\text{eV/Å}^2$ (Notice uniaxial compression of the dislocations has very effectively decreased the surface stress perpendicular to their length.) The compressive strain we applied in the experiment was 2×10^{-3}. Substituting these numbers into Equations (1) and (2) gives $\Delta E \sim -20\text{eV}$. Thus the elbows of the herringbone reconstruction must lower the energy of the system by less than 10eV to be removed by the types of strains we can apply to the system. This is consistent with calculations which suggest the elbows probably lower the energy by less than 1eV [10]. So the removal of the herringbone reconstruction by moderate strains, and the modification of such reconstructions generally by applied strains is not unexpected.

In summary, we have shown how the structure of the surface of an Au thin film can be changed by bending the substrate to which the film is attached. In principle monitoring such changes as a function of strain in thin films offers a precise experimental probe of the balance between the various forces that are responsible for the complicated dislocation networks that often occur on metal surfaces. For example, our preliminary results, which show that edge dislocations in the herringbone reconstruction of Au(111) are removed by surface strains of the order of 2×10^{-3}, can be easily understood in terms of the relatively small lowering in energy caused by the edge dislocations of the herringbone reconstruction.

This work was supported by the Office of Basic Energy Sciences of the U.S. DOE, Division of Materials Science under contract no. DE-AC04-94AL85000. One us (O. S.) gratefully acknowledges support from the Alexander von Humboldt foundation through a Feodor Lynen fellowship.

Figures:

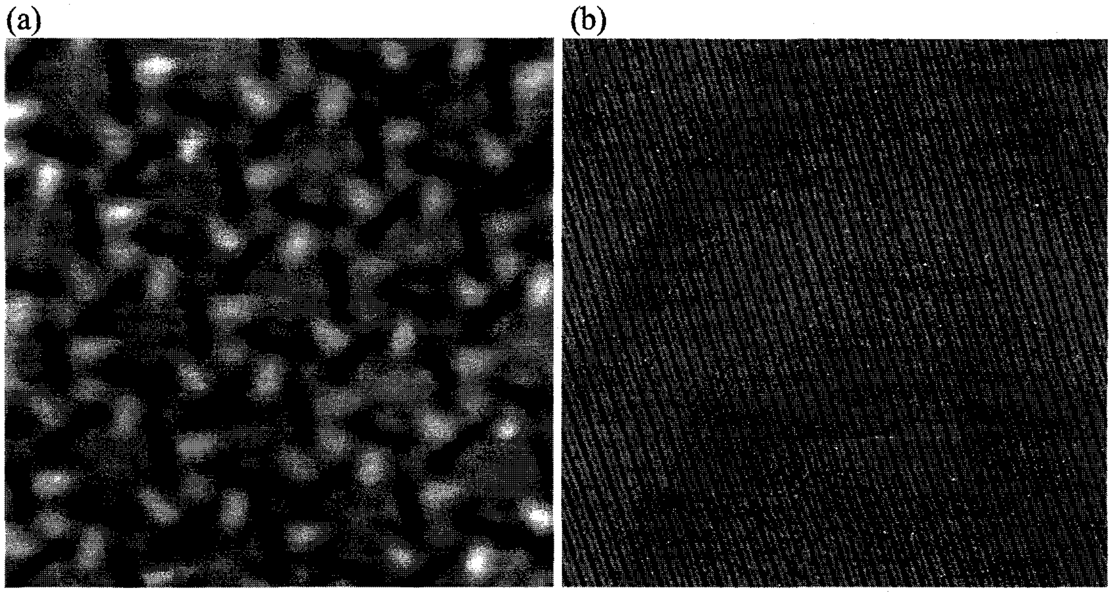

Figure 1:
STM images of dislocation networks in surface layers. (a) Two monolayer thick film of Ag on Ru(0001) (scan size 25 X 25 nm^2). (b) Two monolayer thick film of Cu on Ru(0001) (scan size 170 X 170 nm^2).

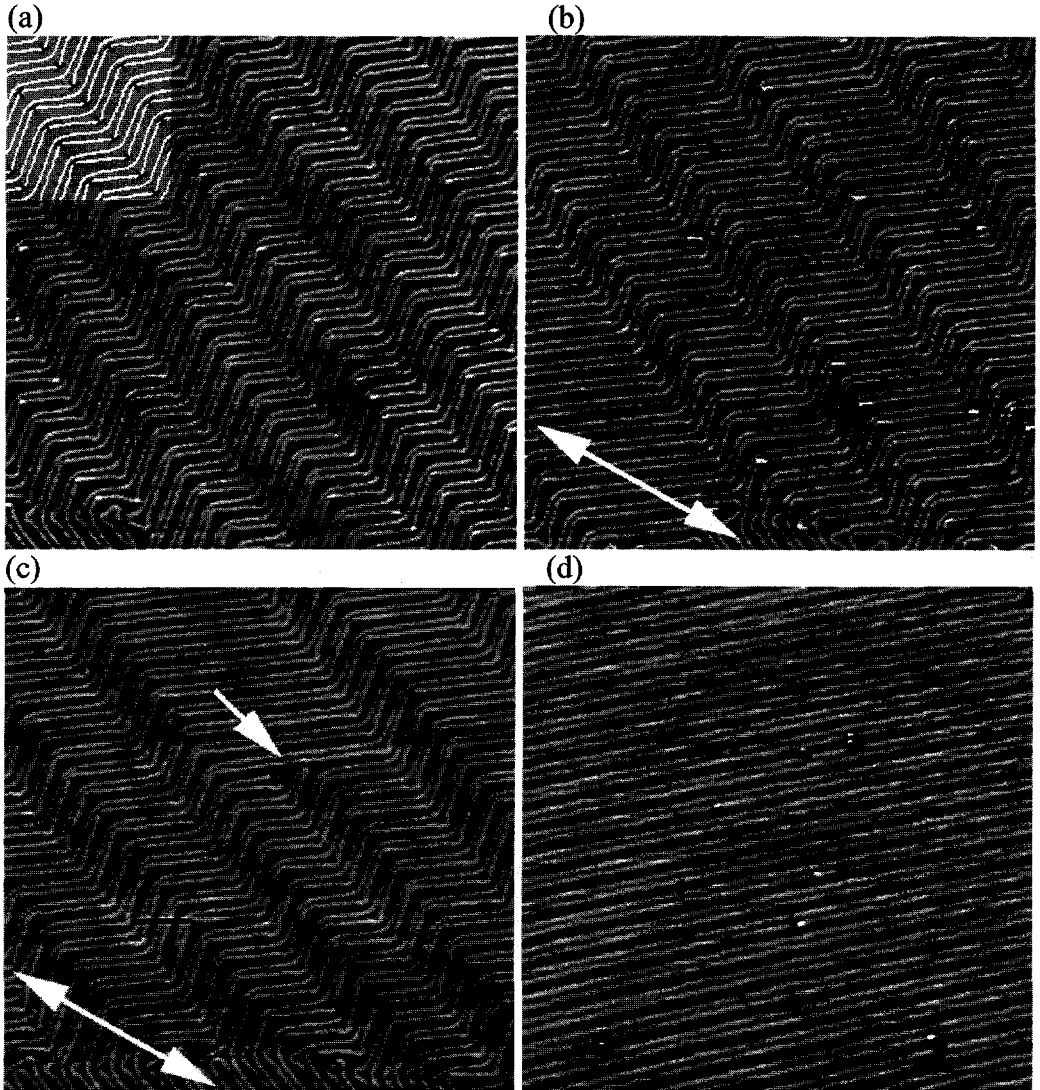

Figure 2: 170 X170 nm^2 STM images of Au(111) under various conditions of applied stress. Doubleheaded arrows in (b) and (c) indicate the direction in which the mica substrate surface was comressed.

(a) Well annealed surface before application of external stress. The inset highlights the dislocation structure. Narrow domains of parallel Shockley partial dislocations (white lines) running along the [11-2] direction alternate with narrow domains of Shockley partials running along [-211]. Black symbols in the inset mark the positions of end-on perfect edge dislocations in the domain walls.

(b) Uniaxial compressive stress of 0.17 % was applied. The same sample region as in (a) was imaged after briefly annealing above 80 °C. Relative coverage of one type of domain has increased by shifting domain walls.

(c) Upon increasing the stress to 0.23 % and annealing again, the relative coverage of the dominant domain increases further through the elimination of minority domains, an example is indicated by an arrow.

(d) Ultimately, the process often leads to the formation of large domains free of end-on edge dislocations. The image shows a different sample after annealing under 0.4 % uniaxial compression.

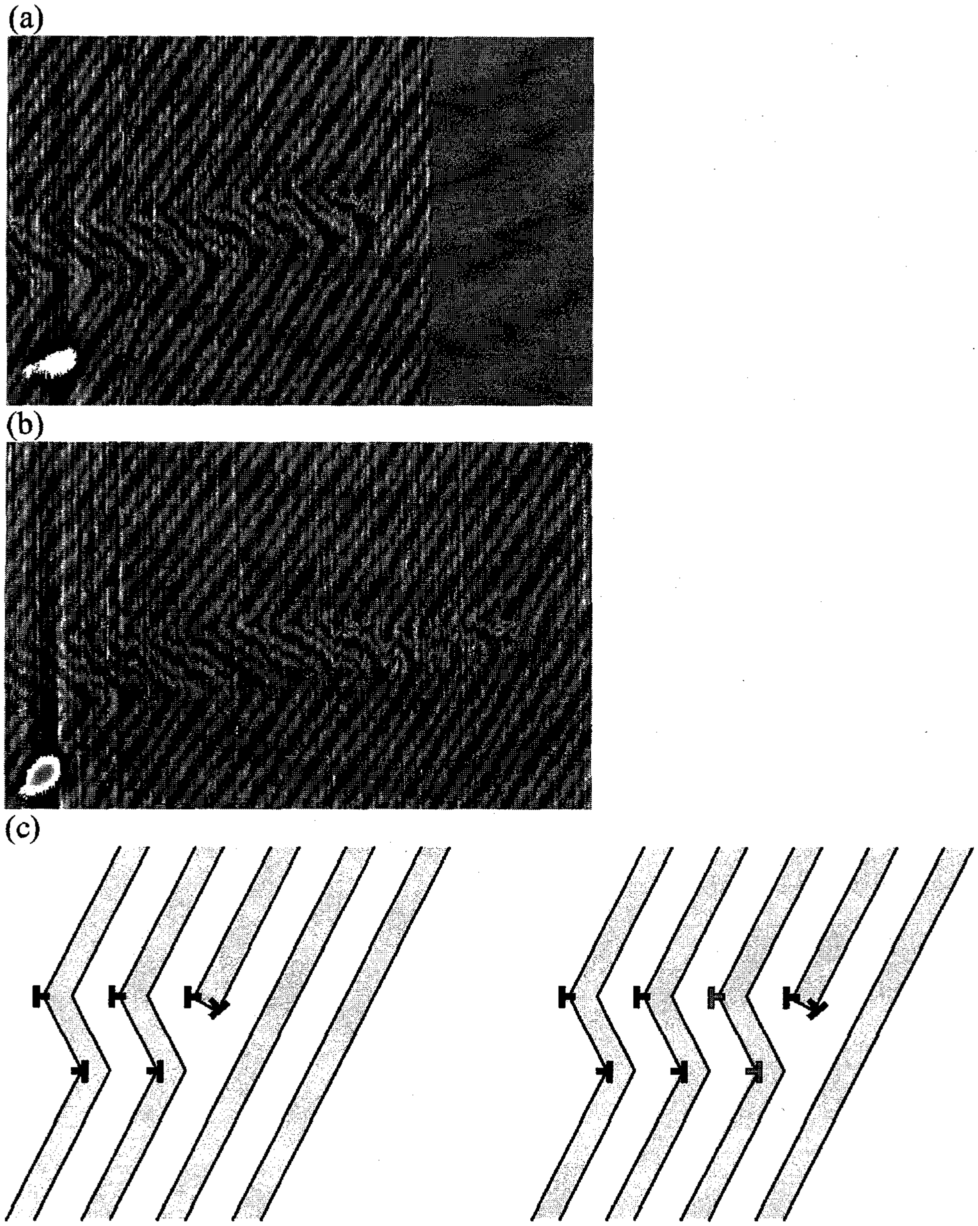

Figure 3:
Reversing the externally applied stress, the conversion of domains from one orientation to another was observed. Initially the Au(111) sample was annealed under 0.5 % applied tensile stress to stabilize the dominant domain orientation. Then the applied stress was reversed to 0.5 % compression and the STM images (a) and (b) were acquired at 80 °C sample temperature (size of panels (a) and (b) is 125 nm X 75 nm). Using the bright defect at the left side as a guide to the eye, a narrow domain near the image center can be observed to grow towards the right. The dislocation reaction involved in the domain wall motion is shown schematically in (c).

References:

[1] C. Günther, J. Vrijmoeth, R.Q. Hwang, and R.J. Behm, Phys. Rev. Lett. **74**, 1 (1995)

[2] H. Brune, H. Röder, C. Boragno, and K. Kern, Phys. Rev. B **49**, 2997 (1994)

[3] J.V. Barth, H. Brune, G. Ertl, and R.J. Behm, Phys. Rev. B **42**, 9307 (1990)

[4] Epitaxial Growth, Ed. J.W. Matthews, New York: Academic Press (1975)

[5] A.R. Sandy, S.G.J. Mochrie, D.M.Zehner, G. Grübel, K.G. Huang, and D. Gibbs, Phys. Rev. Lett. **68**, 2192 (1992)

[6] H. Ibach, Surface Science Reports **29**, 193 (1997)

[7] C.B. Carter and R.Q. Hwang, Phys. Rev. B51, 1 (1995)

[8] J.A. DeRose, T. Thundat, L.A. Nagahara, and S.M. Lindsay, Surf. Sci. 256, 102 (1991)

[9] A.K. Schmid, N.C. Bartelt, J.C. Hamilton, C.B. Carter, and R.Q. Hwang, Phys. Rev. Lett. **78**, 3507 (1997)

[10] To be published

[11] S. Narasimhan and D. Vanderbilt, Phys. Rev. Lett. **69**, 1564 (1992)