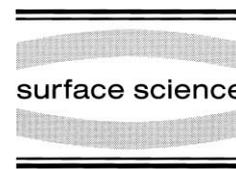




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Multiplication of threading dislocations in strained metal films under sulfur exposure

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Abstract

Strained thin films often contain ordered networks of misfit dislocations which can determine their chemical and mechanical properties. We consider the reaction of sulfur with two-monolayer films of Cu on Ru(0001). These films contain a network of parallel partial dislocations, separating regions of fcc and hcp stacking, with threading edge dislocations where partial dislocations meet. Sulfur reacts with the threading dislocations and dissociates them. The increase in the threading dislocation density is accommodated by modifying the dislocation network. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Copper; Dislocation multiplication; Ruthenium; Scanning tunneling microscopy; Strained metal films; Sulfur; Threading dislocations

1. Introduction

Since the advent of microscopies that permit the imaging of individual dislocations in materials, a recurrent issue, and the goal of a considerable number of studies, has been the multiplication mechanisms involved in the proliferation of dislocations in real samples. In metals, the density of dislocations can easily reach 10^{10} cm^{-2} . Several mechanisms involving reactions between existing dislocations have been proposed, and experimentally verified [1]. In thin film systems, however, the presence of the surface alters the behavior of dislocations in fundamental ways. The lower symmetry can give rise to new dislocation reactions forbidden for bulk dislocations. The scanning tun-

neling microscope (STM) provides a unique probe of these processes and has been applied in several cases to investigate the behavior of bulk dislocations emerging at surfaces [2,3]. In this work, we present STM observations of how adsorbates can multiply the number of dislocations by mechanisms unique to thin films.

Strained metal films can exhibit well-ordered dislocation networks that relieve the misfit between substrate and film [4]. In three-fold symmetry substrates such as hcp(0001) or fcc(111), the possibility of either fcc or hcp stacking relative to the substrate gives rise to a specific class of dislocation networks [5]. The building blocks are Shockley partial dislocations that bound areas of different stacking.

A prototypical system exhibiting this type of dislocation pattern is Cu on Ru(0001). Depending on the film thickness, different ordered dislocation networks are formed in equilibrium [6]. A detailed analysis of these structures can be found in

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Ref. [7]. Here, we concentrate on the interactions of sulfur with the well-ordered two-monolayer film of Cu on Ru(0001). At this thickness, Cu exhibits a pattern of Shockley partial dislocations, oriented parallel to the $\langle 112 \rangle$ directions. At the partial dislocations, the atoms sit near bridge positions relative to the substrate, and their buckled position is typically imaged brighter by STM. The lattice misfit with the substrate is mostly relieved in the direction perpendicular to the partial dislocations, since the lattice spacing parallel to the dislocation lines is that of Ru. At the points where partial dislocations with different Burgers vectors meet, threading edge dislocations form.

The threading dislocations are expected to be the most reactive sites on the film [8]. The adsorption of a reactive gas, such as sulfur, onto this film can, in theory, change the dislocation pattern not only by pulling atoms from the dislocations thus producing climb, but also by decorating the exposed cores of the dislocations. This decoration could in principle change the cost of creating a threading dislocation and even make it negative, causing their proliferation. As discussed below, we will argue that this is indeed the case for the adsorption of sulfur on Cu/Ru.

It is instructive to compare the interaction of sulfur and the Cu/Ru(0001) film with the interaction of sulfur and pure copper surfaces. Copper is very reactive toward sulfur and produces reconstructions on the low index Cu faces: on Cu(100) a $p(2 \times 2)$ structure [9] and a more complex $\sqrt{14} \times \sqrt{14}R14^\circ$ structure [10], on Cu(111) a $\sqrt{7} \times \sqrt{7}R19.1^\circ$ reconstruction forms [11]. In all cases, the basic building blocks of these reconstructions are Cu tetramers surrounding sulfur atoms. This is true even on Cu(111), which lacks groups of atoms of the proper coordination before sulfur exposure. The reactivity of Cu on Ru(0001) is also quite high, as shown by the formation of copper–sulfide films [12].

2. Experimental

Our experiments were performed in a UHV STM. The base pressure was 4×10^{-11} Torr. The UHV chamber is equipped with Auger electron

spectroscopy (AES). The Ru(0001) substrate was cleaned by repeated cycles of oxygen adsorption, and flashing to 1500°C . Terraces larger than $0.5 \mu\text{m}$ can be routinely found. Cu was deposited from a resistively heated W basket with a typical deposition rate of 1 ML/min during which the pressure remained below 2×10^{-10} Torr. The films were annealed to 500°C and allowed to cool to room temperature before STM observation and sulfur exposure. Sulfur was generated from a solid-state electrochemical cell (Pt/Ag/AgI/Ag₂S/Pt) [13]. It was permanently heated to 200°C , and a voltage of ~ 0.15 V was applied when a dosage was desired. Under these conditions approximately 85% of the total S flux is S₂.

3. Results and discussion

The initial dosing of sulfur results in decoration of existing Cu threading dislocations. This is demonstrated in Fig. 1, where rows of sulfur atoms are found at each emerging threading dislocation. Closer inspection reveals that the sulfur atoms arrange in rows of four to eight atoms at the core of each dislocation with a spacing of 6 Å between atoms. The high reactivity of the core of the dislocations toward sulfur may be related to the presence of copper atoms in a rectangular arrangement, similar to the tetramer configuration found for Cu(111) and Cu(100) [10,11].

The threading dislocations can be put into two classes according to the stacking sequence of the area where the extra row of atoms is located. In Fig. 1b, added rows in the fcc or hcp are marked with light or dark T symbols, respectively. The number of S atoms decorating the core, i.e. whether there are four or six to eight sulfur atoms, correlates with the type of threading dislocation (see Fig. 1). The reaction with six to eight atoms takes place on threading dislocations where the extra row of atoms is in the fcc stacking, as opposed to the decoration of only four atoms on the other type of threading dislocations.

The increase in the number of sulfur atoms on the surface produces a remarkable effect: new threading dislocations are created. Two mechanisms have been observed for the dislocation proliferation: dissociation of pre-existing dislocations,

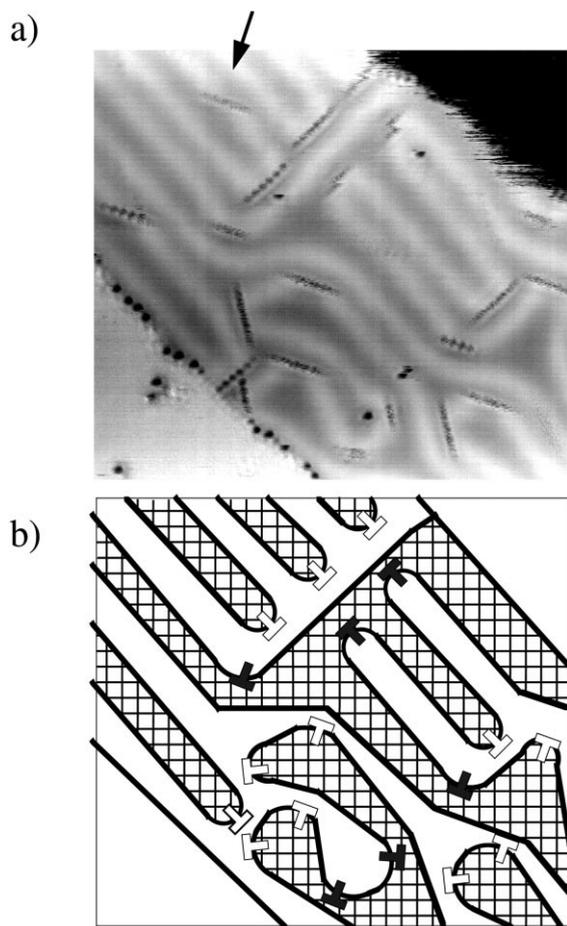


Fig. 1. (a) STM picture of the copper film after exposure to sulfur. The image size is 300 Å by 300 Å. The sulfur adatoms appear as depressions; (b) schematic of the same area, indicating the Shockley partials (thick black lines), the fcc (hatched areas) and hcp stacking (white areas), and the threading edge dislocations (marked T). There are two types of threading dislocation, marked by dark and light T symbols, respectively. They appear differently decorated in the STM image.

and nucleation of new dislocations. We have found no analog of these processes in the bulk.

An example of the dissociation of threading dislocations is shown in Fig. 2. A threading dislocation at an elbow of the Shockley partials advances by cutting Shockley partials (see arrows marked in Fig. 2a and b). The end result is a trail of new threading dislocations. A schematic of the processes (Fig. 2c and d) observed with STM reveals that the threading dislocation is repeatedly

dissociated into two new threading dislocations, which follow the Burgers vector relation $\frac{1}{2} a_0[0\bar{1}1] = \frac{1}{2} a_0[1\bar{1}0] + \frac{1}{2} a_0[\bar{1}01]$. All new threading dislocations appear decorated with sulfur. Note that this reaction conserves the total Burgers vector. In the final configuration the sum of the squares of the Burgers vectors is, however, greater than in the starting configuration. In bulk dislocations, the energy density per unit length is proportional to the square of the Burgers vector (Ref. [1], p. 80), and the increase in the energy density disallows the previous reaction. It may be crucial in the present case that the length of the threading dislocations is extremely short (two atomic layers): the net cost of creating a single dislocation can be negative if the contribution of the adsorbed species at the core overcompensates for the cost of the elastic distortion produced by the dislocation.

The nucleation of new edge dislocations has also been observed. This occurs at the Shockley partials, and the process breaks them (see arrow at top of Fig. 1). The mechanism involves extracting atoms from a Shockley partial, and has been described in detail [14] in the related system of O/Cu/Ru(0001). Again, the contribution of the adsorbed species to reducing the energy cost of creating a new dislocation is probably the driving force for this process.

The newly generated threading dislocations change the mesoscopic ordering of the misfit network. To accommodate the new dislocations (up to 10^{13} cm^{-2}), an arrangement of parallel Shockley partials with only occasional threading dislocations gives rise, upon sulfur exposure, to an array of dislocation loops composed of alternating partial and threading dislocations, as shown in Fig. 3d. The dislocation loops, with triangular shape, surround areas of fcc stacking with the threading dislocations decorated with sulfur at the corners, and Shockley partials at the sides of the triangles. This structure is found in clean Cu/Ru(0001) only in films three layers thick. The array of dislocation loops is remarkably well ordered.

The proposed sequence of events is shown schematically in Fig. 3. The lines of sulfur atoms, as for the lower exposure images (cf. Fig. 1), point to the location of the threading dislocations on

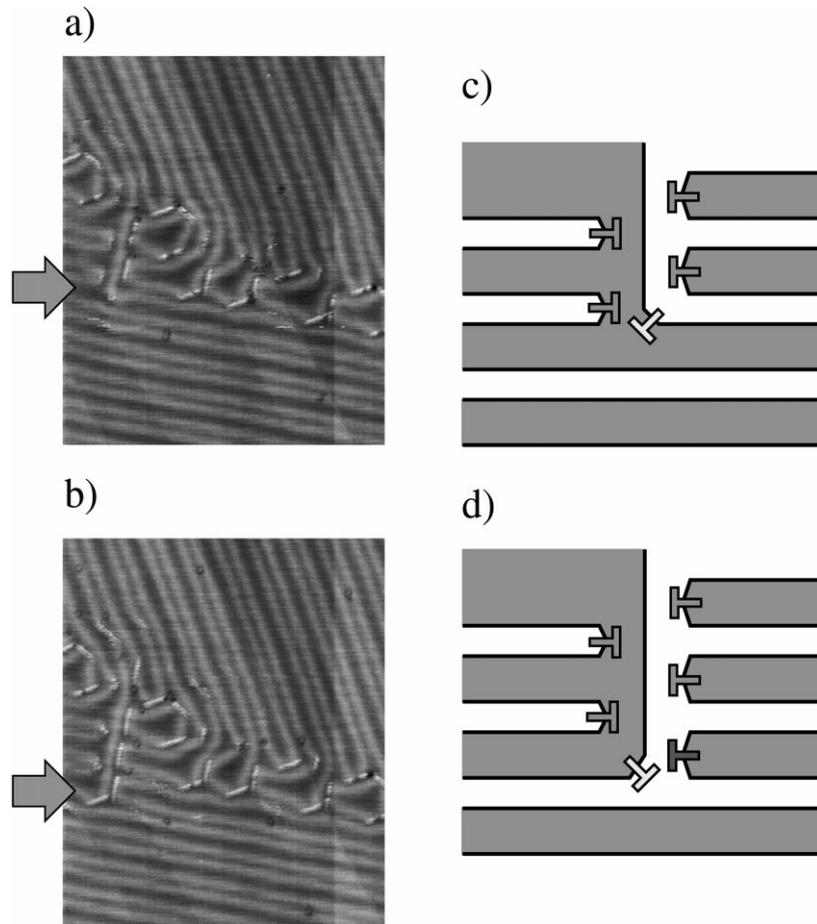


Fig. 2. Dissociation of threading dislocations upon exposure to sulfur. (a, b) Frames from a STM movie (the images are 500 Å wide) taken while the sample was being dosed with sulfur. The arrows point to the position of the advancing threading edge dislocation. (c, d) Diagrams of the steps observed in the STM images.

the film. The number of sulfur atoms per line is six to eight, indicating that the threading dislocations have the extra plane in the fcc area. A diagram showing both the hcp/fcc areas and the dislocations is shown in Fig. 3b. The resulting configuration is a triangular arrangement of dislocation loops that can be obtained from the starting parallel Shockley partials (Fig. 3a) by introducing new threading dislocations.

4. Conclusions

This multiplication of threading dislocations in the film is a fundamentally new process, triggered

by the interaction of the adsorbed species with the surface, and favored by the short length of the dislocations. The new dislocations are accommodated by changing the mesoscopic dislocation network already present in the film, thus creating dislocation loops. The dislocation loops are quite stable [their size fluctuates in time, probably through a climb mechanism involving Cu adatoms, similar to that found on 1 ML Cu/Ru(0001) [15]]. The creation of the threading dislocations can be explained assuming that the presence of sulfur weakens the Cu–Cu bond between the Cu atom neighbors to the adsorbed sulfur, until the energy of creating a dislocation is small or negative. [A weakening of the metallic bond due to adsorbates

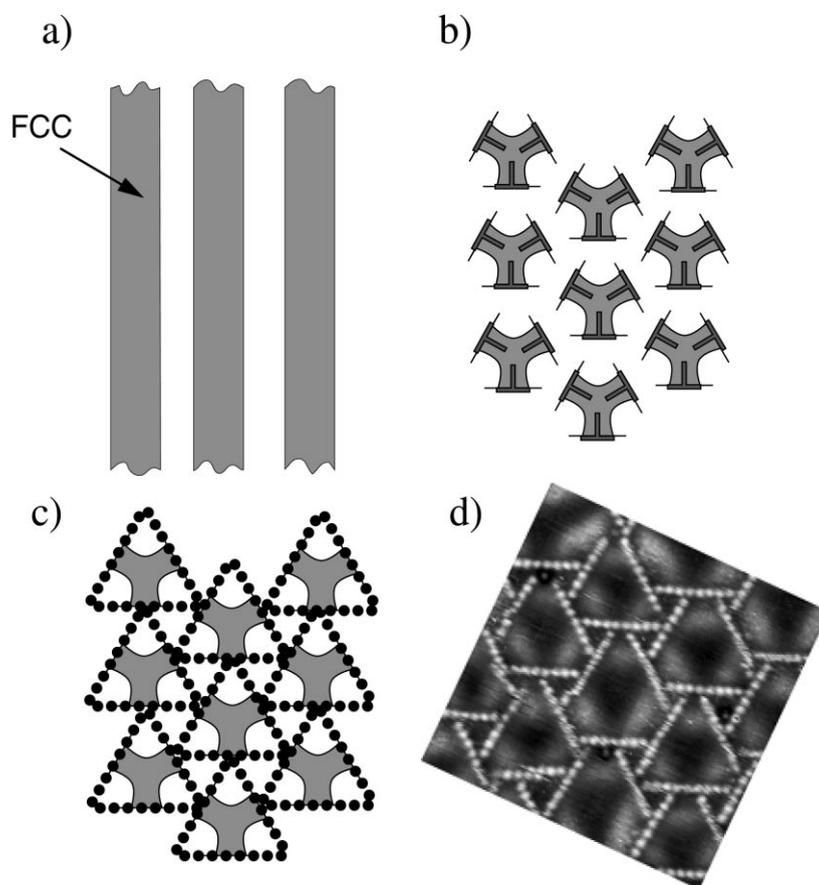


Fig. 3. Formation of a network of dislocation loops at a higher sulfur dose: (a) diagram of the clean 2 ML Cu/Ru(0001). The gray areas indicate fcc stacking, and they are arranged in parallel ribbons; (b) after dislocation multiplication, the ribbons have transformed into dislocation loops as shown schematically. The ‘T’ symbols indicate the threading edge dislocations; (c) diagram showing the decoration of the threading dislocations by sulfur adatoms (dots); (d) STM image of the triangular network (the size of the image is 170 Å by 170 Å).

has been confirmed by *ab initio* calculations for O and H on P(111), see Ref. [16].]

In summary, the exposure to sulfur of a two-monolayer copper film on Ru(0001) generates new threading dislocations. The new dislocations are accommodated by a change in the dislocation network that relieves the misfit between film and substrate. At higher sulfur doses a triangular network of dislocation loops composed of threading dislocations and partial Shockley dislocations is formed. The role of the surface allowing or facilitating dislocation processes forbidden in the bulk is

important when trying to envision how strain is relieved in thin films.

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References

- [1] J.P. Hirth, J. Lothe, *Theory of Dislocations*, 2nd edn. Krieger, 1982.
- [2] A. Samsavar, E.S. Hirschorn, T. Miller, F.M. Leibsle, J.A. Eades, T.-C. Chiang, *Phys. Rev. Lett.* 65 (1990) 1607.
- [3] J.F. Wolf, H. Ibach, *Appl. Phys.* A52 (1991) 218.
- [4] J.H. van der Merwe, *J. Appl. Phys.* 34 (1963) 123.
- [5] C.B. Carter, R.Q. Hwang, *Phys. Rev. B* 51 (1995) 4730.
- [6] C. Günther, J. Vrijmoeth, R.Q. Hwang, R.J. Behm, *Phys. Rev. Lett.* 74 (1995) 754.
- [7] J.C. Hamilton, S.M. Foiles, *Phys. Rev. Lett.* 75 (1995) 882.
- [8] D.D. Chambliss, R.J. Wilson, S. Chiang, *Phys. Rev. Lett.* 66 (1991) 1721.
- [9] Q.T. Jiang, P. Fenter, T. Gustafsson, *Phys. Rev. B* 42 (1990) 9291.
- [10] M.L. Colaizzi, I. Chorkendorff, *Phys. Rev. B* 50 (1994) 8798.
- [11] M. Foss, R. Feidenhans'l, M. Nielsen, E. Findeisen, T. Buslaps, R.L. Johnson, F. Besenbacher, *Surf. Sci.* 388 (1997) 5.
- [12] M. Kuhn, J.A. Rodriguez, *J. Phys. Chem.* 98 (1994) 12059.
- [13] C. Wagner, *J. Chem. Phys.* 21 (1953) 1819.
- [14] J. de la Figuera, K. Pohl, A.K. Schmid, N.C. Bartelt, R.Q. Hwang, *Surf. Sci.* 415 (1998) L993.
- [15] A.K. Schmid, N.C. Bartelt, J.C. Hamilton, C.B. Carter, R.Q. Hwang, *Phys. Rev. Lett.* 78 (1997) 3507.
- [16] P.J. Feibelman, *Phys. Rev. B* 56 (1997) 2175.