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Linking dislocation dynamics and chemical reactivity on strained metal films

J. de la Figuera *, K. Pohl, A.K. Schmid, N.C. Bartelt, R.Q. Hwang

Sandia National Laboratories, Livermore, CA 94550, USA

Abstract

The interaction of a model strained metal film with oxygen is studied by scanning tunneling microscopy. Two monolayers of copper on Ru(0001) present a well-defined dislocation network composed of threading dislocations and Shockley partial dislocations separating areas of fcc and hcp stacking. We find that oxygen first reacts with these threading dislocations. Then, for exposures up to ~ 0.4 L_{O_2}, new threading dislocation arrays appear on the surface. With the addition of more oxygen, the mesoscopic structure of the film changes from a striped array of Shockley partials to a disordered array of triangular fcc regions bounded by dislocations, as oxygen proceeds to etch away the hcp areas of the copper film. © 1998 Published by Elsevier Science B.V. All rights reserved.

The relationship between strain and chemical reactivity in strained metal films is of primary concern in areas such as corrosion and performance reliability in a variety of applications. It is well established that surface stress can enhance corrosion, but little is known about the local processes that mediate this increased chemical reactivity. One reason for this is that the detailed structure and strain-relief mechanisms in ultrathin metal films have only recently been investigated on the nanometer scale. To date, the most studied systems have been fcc(111) oriented films. For these systems, dislocations are introduced into the film to relieve the stress even at film thicknesses of less than one monolayer (ML). These misfit dislo-

cations can form well-ordered networks, as shown recently [1–3]. Furthermore, these dislocation networks are not confined to a particular combination of materials or lattice mismatch values. Rather, they are determined by the geometry of the (111) fcc surface [4] that provides for the possibility of hcp *and* fcc stacking. The goal of our work is to investigate the relationship between these dislocation networks and chemical reactivity.

To this end, we have performed scanning tunneling microscopy (STM) investigations of the initial stages of the modification of dislocation networks present on strained metal films upon controlled exposure to molecular oxygen. In order to understand systematically the relationship between the film strain state and chemical reactivity, we have chosen to study a system where the atomic structure and the dislocation network that accommo-

* Corresponding author. Fax: (+1) 925 294 3231;
e-mail: juan@io.ca.sandia.gov

dates strain are well characterized. Specifically, films of copper on Ru(0001) form a sequence of dislocation structures as a function of thickness in response to the 5.46% lattice mismatch between copper and ruthenium (copper having the smaller lattice constant) [2,5,6]. This system has been investigated carefully by a number of techniques so detailed information about the film structure at various thicknesses is available. In this work, we have focused on 2 ML copper films, because the highly ordered dislocation array present in annealed films provides us with a nearly ideal system to explore the relationship of dislocation structure and reactivity. The key observation driving this investigation is the contrast with the behavior upon oxygen exposure of the bulk-like Cu(111) surface, as characterized by a sticking coefficient on the order of 10^{-3} [7] and the absence of morphological changes at low oxygen doses. On strained Cu(111) film on Ru(0001), the sticking coefficient ranges from values comparable to clean ruthenium (near unity) for the pseudomorphic first layer down to values comparable to bulk-like copper for films thicker than four layers.

The experiments were carried out in an ultrahigh vacuum (UHV) chamber equipped with room-temperature STM and Auger electron spectroscopy (AES). The base pressure of the system is well below 5×10^{-11} Torr.

The Ru(0001) substrate was cleaned by repeated cycles of oxygen adsorption at exposures to 9 L_{O_2} and desorption by flashing to 1500°C. The cleanliness was checked by AES and STM. Terraces wider than 1 μm could be found on the surface. Copper was deposited from a tungsten basket heated resistively with a typical deposition rate of 1 ML/min. The pressure during copper deposition remained below 2×10^{-10} Torr. The films, with a coverage of slightly less than 2 ML copper, were annealed to 500°C and cooled to room temperature before oxygen exposure. The surface morphology is composed of a 2 ML thick film decorating the ruthenium steps, with the remaining surface covered with a 1 ML copper pseudomorphic film.

To expose the film to oxygen, the chamber was backfilled with O_2. The exposures are given in Langmuir, estimated from the pressure reading of the UHV pressure gauge. A range of oxygen backpressures between 2×10^{-10} and 10^{-8} Torr was used. Most of the exposures were done while the sample was under scanning conditions. In order to check the absence of tip effects we also did experiments with separate exposure and imaging steps.

The structure of the 2 ML copper film on Ru(0001) is reminiscent of the well-known herringbone reconstruction of the Au(111) surface [1,8]. To partially relieve the lattice misfit strain between copper and ruthenium, the atomic density in the copper film is higher than that of the ruthenium substrate, resulting in large ordered domains of dislocations as shown in Fig. 1a. The higher density of copper atoms is accommodated by the formation of symmetrically equivalent domains of Shockley partial dislocations with Burgers vector $a_0/6[112]$ in the film plane [2,9]. These dislocations, imaged as bright stripes in Fig. 1a, separate "ribbons" of copper with either fcc or hcp stacking relative to the substrate. The brighter appearance is due to the atoms at the partial dislocations that reside near bridge sites which are slightly buckled outwards relative to the more highly coordinated fcc and hcp sites. This stripe arrangement partially relaxes the lattice misfit with the ruthenium only in the direction perpendicular to the partial dislocations, leaving the surface highly stressed in the direction parallel to the Shockley partials [10]. On large areas of the surface, symmetrically equivalent domains of Shockley partials rotated by 120° are observed. At the boundaries between these domains, Shockley partials with different Burgers vectors meet and form dislocations that "thread" from the Cu–Ru interface to the surface. These threading dislocations have their Burgers vectors in the plane along the compact [110] directions [4]. The atomic arrangement at the core of the threading dislocations is highly distorted [11].

Exposing the 2 ML copper film to oxygen leads to substantial structural changes to the film even at small doses. Fig. 1 shows an overview sequence of STM images taken upon different oxygen exposures. With increasing oxygen exposure, one-layer-deep holes are formed in the film (Fig. 1d) by the
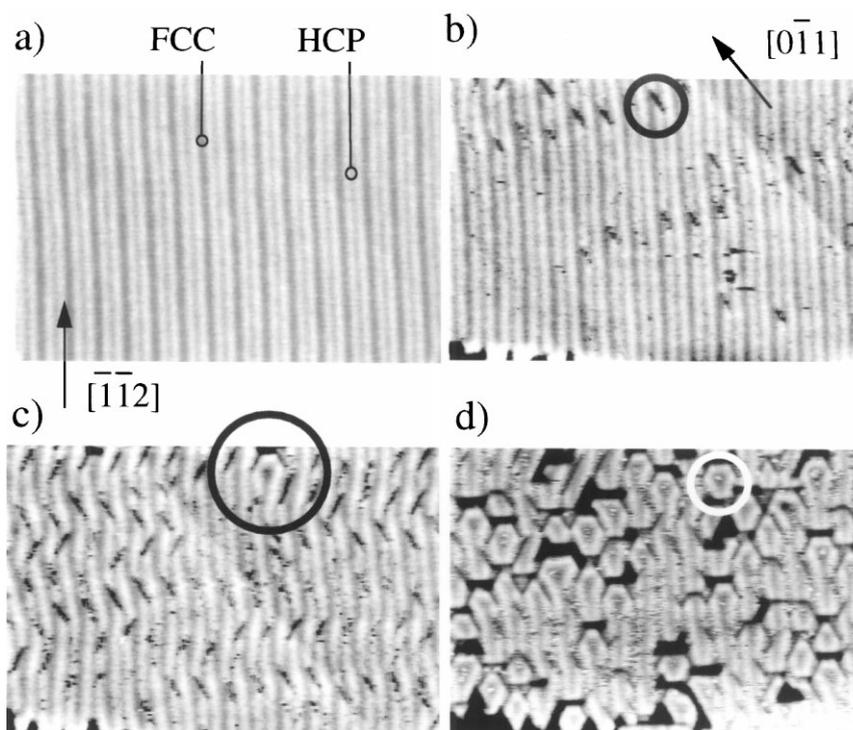
Fig. 1. Sequence of images of the same area of a 2 ML copper film on Ru(0001) for increasing exposures to oxygen. The image size is 750 Å by 500 Å. (a) Domain of alternating fcc and hcp areas (dark ribbons, wide ones being fcc and narrow ones corresponding to hcp) separated by Shockley partial dislocations (white lines). (b) Image taken after $\sim 0.6\,L_{O_2}$. Defects (referred to as "cuts") appear along the Shockley partials, like the one marked by a black circle. The orientation of the defects is along compact [110] directions. (c) Exposure to $\sim 0.9\,L_{O_2}$. More cuts appear on the surface. Some of them have collapsed, breaking up the ribbon of fcc stacking, as at the point marked with a black circle. (d) Exposure to $\sim 2.4\,L_{O_2}$. The surface is covered by a disordered array of triangular areas, and oxygen is etching the hcp areas between them. A single trigon (an fcc region bounded by a dislocation loop composed of threading dislocations and Shockley partials) is marked by a white circle.

removal of copper atoms from the second layer. Eventually, after exposures of $\sim 3\,L_{O_2}$, the surface shows a disordered collection of triangular dislocation features (a "trigon" phase, as described below), while the hcp regions between trigons are etched away creating holes. We propose that this occurs by a dislocation climb mechanism, i.e., copper atoms are removed from the core of the threading disloactions in the *second* layer. The film re-structures to facilitate this process. The detailed nature of this re-structuring is the focus of the rest of this paper.

Exposure of the copper film to small amounts of oxygen ($<0.05\,L_{O_2}$) produces a reaction with the *pre-existing* threading dislocations present at boundaries between domains of different orientation of Shockley partials[1]. The oxygen is imaged as depressions (0.2 ± 0.1 Å deep with bias voltages of ~ -1 V), but it is not atomically resolved. At oxygen exposures higher than $0.05\,L_{O_2}$ all of the pre-existing threading dislocations at the surface appear decorated. After the initial supply of threading dislocations is exhausted, no changes on the film, as observed by STM, are detected until $\sim 0.4\,L_{O_2}$.

Oxygen exposures higher than $0.4\,L_{O_2}$ induce the nucleation of new threading dislocations in the film. The nucleation is observed within the large

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[1] As in the herringbone structure of Au(111), not every elbow in the Shockley partials corresponds to a threading dislocation and so not every elbow presents oxygen decoration.

domains of parallel Shockley dislocations where threading dislocations were previously not present (such as the one in Fig. 1a). Upon increasing oxygen exposure, defects appear that "cut" across the Shockley partials (see the one marked by a black circle in Fig. 1b). The positions of these defects appear correlated: they are often found on neighboring partials at the same positions along the partials. The cuts disappear slowly in tens of minutes if the oxygen exposure is stopped. The orientation of these cuts is always along a compact direction, but only one of the three possible directions is selected depending on the local geometric arrangement of Shockley partials. It is defined as follows: if the angle between the Shockley partial direction l and its Burgers vector b is less (more) than $90°$, the direction of the cut is given by rotating from the Shockley Burgers vector direction by $30°$ clockwise (counterclockwise). In other words, when crossing from hcp to fcc domains the cuts have one orientation, and when crossing from fcc to hcp they have their orientation rotated by $60°$. The presence of the dislocation network constrains severely the allowed mechanism for this rupture, breaking the threefold symmetry of the (111) layer. As the oxygen exposure increases, the density of cuts increases and they start to interact until the ribbons of fcc regions are severed at multiple points, and the hcp areas in between are etched away creating holes exposing the first copper layer (marked by a black circle in Fig. 1c). We image this holes in the film as 1 Å deep depressions, clearly deeper than the depressions we see due to oxygen reacting with the threading dislocations of the film.

In Fig. 2 the typical appearance of such a cut is presented along with our model of its structure. Based on the STM images, we propose that the partial dislocations are severed by the creation of vacancies. This process is illustrated in Fig. 2b, where the atomic rows of the top copper layer are shown schematically as lines. As an atom is extracted from the partial dislocation (Fig. 2c), the vacancy left on the surface can be represented as a pair of oppositely oriented threading dislocations (Fig. 2b). The pair of new threading dislocations (Fig. 2d) can glide apart along the compact direction in which the cuts appear experimentally

(Fig. 2a), a process which does not require additional vacancies (but which may be promoted by the extraction of more vacancies). The new threading dislocations are joined by a new Shockley partial. Any other orientation of the threading dislocations fails to enclose the fcc area with a dislocation line in the film plane and is thus incompatible with the geometric constraints. As the threading dislocations separate and the cuts grow, the pre-existing Shockley partials bend. This bending can be seen in Fig. 1c. In this model, the gliding process is crucial to the eventual formation of the triangular dislocation loops and holes shown in Fig. 1d. This is shown in Fig. 3. As the threading dislocation glides across the fcc region (Fig. 3b) it interacts with the Shockley partial bounding the other side of the fcc stripe. This structure then dissociates into two new threading dislocations (Fig. 3c). Although this dissociation does not need the extraction of additional copper atoms, it may be enhanced in that way. After relaxing the position of the new threading dislocation we end up with a triangular dislocation loop which is known as a trigon: an fcc region bounded by a dislocation loop with copper in hcp stacking outside the loop [4] (Fig. 3d). Continued exposure produces a surface covered with a disordered array of trigons (see Fig. 1d).

The final structure (Fig. 1d) permits the removal of the second copper layer by dislocation climb from the threading dislocations. The hcp regions between trigons are etched away, creating holes which extend only through one layer. To separate the trigons, the threading dislocations bounding them on three sides in turn have to be retracted. That movement is perpendicular to the gliding plane of those dislocations, so copper atoms have to be extracted from the core of the dislocations in addition to the etching of the hcp areas.

The surface modifications induced by oxygen on the copper film can be interpreted in the following general picture. There are two likely driving forces for the removal of copper from the second layer to form adatoms. First, the oxygen bond to ruthenium is much stronger than that to copper. Thus the removal of copper from the second layer allows better access to the ruthenium substrate by the oxygen. Our experiments on the first copper layer show that oxygen does in fact form holes in that
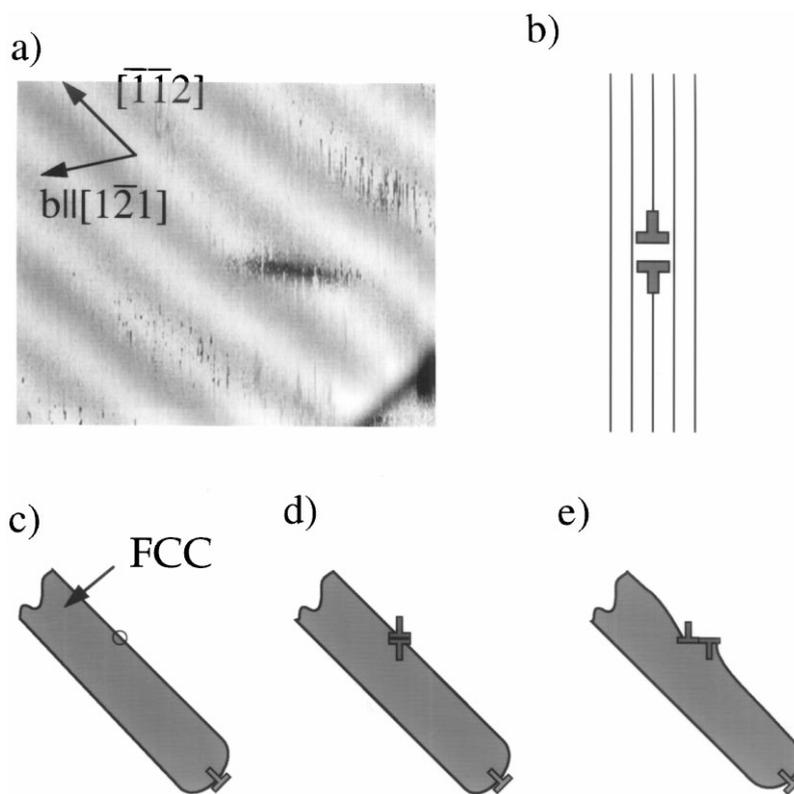
Fig. 2. Schematic and STM images of the nucleation of threading dislocations. (a) STM image of a "cut" along a Shockley partial. The directions of the Shockley partial dislocation and its Burgers vector are indicated. (b) Schematic of a vacancy as a pair of threading dislocations. On the surface, the extraction of an atom can be viewed as the generation of a pair of edge dislocations. (c)–(e) Schematics of the nucleation of a pair of threading dislocations on top of a Shockley partial (see text for details).

layer as well, allowing Ru–O bonds to form. Secondly, it is known that oxygen can pull atoms out of copper layers, as when forming the Cu(100) $(2\sqrt{2} \times \sqrt{2})R45°O$ missing row reconstruction [12]. This extraction effect can be rationalized taking into account the general tendency of oxygen to form lower coordinated structures with copper, as in the oxygen-induced added row reconstructions on Cu(110) or in the Cu–O structures reported on oxidized copper surfaces on ruthenium [13]. This tendency has been ascribed to the stronger $O(2p)$–metal(d) interaction when the metal atoms have a low coordination number [12].

The lowest barrier pathway for the removal of copper atoms from the top layer is through climb of threading dislocations. Threading dislocations are likely to be the most reactive sites of the surface since the coordination of the copper atoms

is lowest at those points. The observed restructuring of the copper film can be thought of as simply the process that provides the threading dislocations for reaction. Vacancy cuts at the partial dislocations are presumably energetically favorable paths to the formation of new threading dislocations. Once the new dislocations are created, as in the cut structure, the elastic response of the film will rearrange the dislocation configuration towards forming trigons. The relaxation of the film after removal of atoms can be observed in related systems such as the modification of the gold reconstructed surface [14] by pulling out atoms with the tip: the formation of a trigon takes place, although the gold trigons so made are metastable [15]. The stability of trigons in our system is probably related to the presence of oxygen at the threading dislocations.
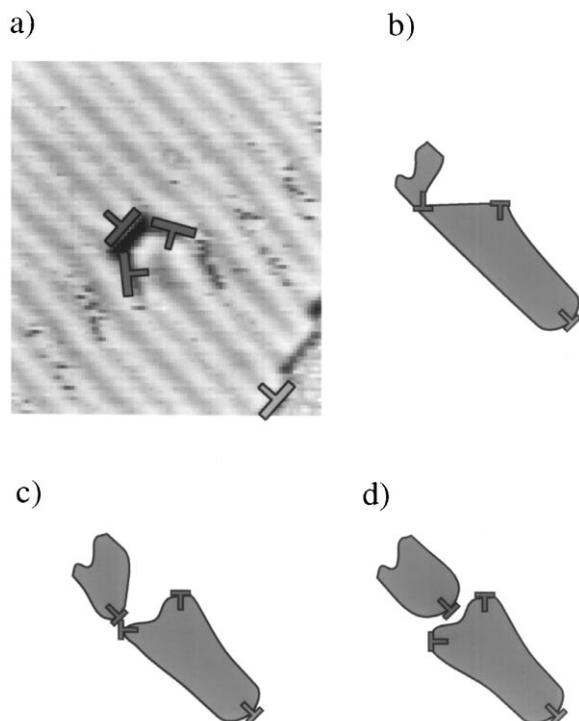
a)

b)

c)

d)

Fig. 3. Evolution of the nucleation of two threading dislocations. (a) STM image of the same area as Fig. 2, after completing the breaking up of the fcc ribbon. The location of the threading dislocations is marked by T symbols. All the dark grey marks indicate threading dislocations generated by exposure to oxygen. The remaining light grey mark indicates a pre-existing threading dislocation. (b)–(d) Schematic evolution of the pair of threading dislocations which eventually give rise to a trigon.

There has been a similar report of (111) misfit dislocation network transitions in Au(111) upon exposure to sodium [16]. Starting with the Au(111) reconstructed surface, the end result is a triangular network of partial dislocations, without threading dislocations, observed previously in Pt/Pt(111) [17]. Such a network differs from the one presented here in the trigon packing: the trigons are arranged so that their corners touch and annihilate the threading dislocations at the cost of putting atoms in on-top positions. It was suggested that the reason for the structural transformation was a weakening of the bond between the topmost and the second layer due to sodium adsorption. But the effect reflected the response of the entire gold layer, and not the local response of the atoms near the sodium adsorbate. In contrast, in our case the modifications produced by oxygen can be understood by the local effect of the oxygen adatoms extracting copper neighbor atoms.

In order to comprehend the behavior and reactivity of strained copper films on Ru(0001) to oxygen, it is crucial to understand the topology of the defects on the surface: in particular that of the most reactive sites on these surfaces which are the threading dislocations. Their behavior can be very different from bulk dislocations, as proved by the threading dislocation multiplication observed during oxygen reaction with the surface. Our STM study shows that oxygen reacts with a 2 ML copper strained film, at first only at the threading dislocations, and then through modification of the film mesoscopic structure and removal of atoms from the film. The process responsible for these changes, which is consistent with our STM observations, is local extraction of the copper atoms from the film due to oxygen atoms.

Acknowledgements

References

[1] J.V. Barth, H. Brune, G. Ertl, R.J. Behm, Phys. Rev. B 42 (1990) 9307.
[2] C. Günther, J. Vrijmoeth, R. Hwang, R.J. Behm, Phys. Rev. Lett. 74 (1995) 754.
[3] H. Brune, H. Röder, C. Boragno, K. Kern, Phys. Rev. B 49 (1994) 2997.
[4] C.B. Carter, R.Q. Hwang, Phys. Rev. B 51 (1995) 4730.
[5] J.C. Hamilton, S.M. Foiles, Phys. Rev. Lett. 75 (1995) 882.
[6] K. Meinel, H. Wolter, Ch. Ammer, H. Neddermeyer, Surf. Sci. 401 (1998) 434.
[7] F.H.P.M. Habraken, E.P. Kieffer, G.A. Bootsma, Surf. Sci. 83 (1979) 45.

[8] U. Harten, A.M. Lahee, J.P. Toennies, C. Wöll, Phys. Rev. Lett. 54 (1985) 2619.

[9] J.P. Hirth, J. Lothe, Theory of Dislocations, 2nd ed., Krieger Publishing Company, Malabar, FL, 1982.

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

[11] A.K. Schmid et al., Phys. Rev. Lett. 78 (1997) 3507.

[12] F. Besenbacher, J.K. Nørskov, Prog. Surf. Sci. 44 (1993) 5.

[13] C. Ammer, K. Meinel, H. Wolter, H. Neddermeyer, Surf. Sci. 401 (1998) 138.

[14] Y. Hasegawa, P. Avouris, Science 258 (1992) 1763.

[15] Y. Hasegawa, P. Avouris, J. Vac. Sci. Technol. B12 (1994) 1797.

[16] J.V. Barth, R.J. Behm, G. Ertl, Surf. Sci. 302 (1994) L319.

[17] M. Hohage, T. Michely, G. Comsa, Surf. Sci. 337 (1995) 249.