The Importance of Threading Dislocations on the Motion of Domain Boundaries in Thin Films

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Thin films often present domain structures whose detailed evolution is a subject of debate. We analyze the evolution of copper films, which contain both rotational and stacking domains, on ruthenium. Real-time observation by low-energy electron microscopy shows that the stacking domains evolve in a seemingly complex way. Not only do the stacking boundaries move in preferred directions, but their motion is extremely uneven and they become stuck when they reach rotational boundaries. We show that this behavior occurs because the stacking-boundary motion is impeded by threading dislocations. This study underscores how the coarse-scale evolution of thin films can be controlled by defects.

Because of its technological importance, the growth of a crystalline material on top of a dissimilar crystalline material, heteroepitaxy (*1*), has been intensively investigated (*2*). To accommodate its physical differences with the substrate, films commonly develop spatial domains that differ somewhat from each other (*3*). Examples include rotational domains, which differ only in how a crystallographic direction within the plane of the film is oriented with respect to the substrate directions. For films of simple metals (*4*), additional domain types can be distinguished by the stacking sequence of the close-packed layers that lie parallel to the substrate. These stacking domains are separated by planar boundaries (stacking faults) lying within the film. Stacking- and rotational-domain boundaries can substantially degrade the properties of the film by, for example, scattering charge carriers, quenching excitations, or serving as pathways for enhanced mass transport (*5*–*7*). Although these defects can sometimes be healed (*8*, *9*), this process is only partially understood.

Here we investigate how rotational- and stacking-domain boundaries in strained copper films move and interact with each other. We use the unique capabilities (*10*) of low-energy electron microscopy (LEEM) to follow the evolution in real time. Based on the known structure of the different boundaries, the experimental observations can be explained by the interactions of the dislocations present at the domain boundaries. The large-scale evolution of the thin film can be understood by considering the individual interactions of the dislocations that form the different boundaries.

Thin films of Cu on Ru(0001) present both rotational and stacking domains (*11*–*15*). Typical grain sizes are on the order of hundreds of nanometers. The stacking domains can be observed with LEEM under bright-field conditions (*16*) as two different gray levels on a continuous two-monolayer (ML) film (Fig. 1A). In addition to the stacking domains, copper films two layers thick on Ru(0001) show an in-plane uniaxial relaxation. Given that the Ru(0001) substrate has threefold symmetry, domains occur where the relaxation direction lies in each of the three equivalent directions, giving rise to three rotational domains. Each rotational domain diffracts low-energy electrons in specific directions (fig. S1A). In a real-space LEEM image formed using the electrons diffracted from a given domain type, only film regions of that domain type appear bright (fig. S1B). By taking successive images with diffracted beams corresponding to the three different domains, the full rotational-domain microstructure of the film can be determined. To show the film's entire rotational-domain structure in one image, we color each rotational domain either red, green, or blue (Fig. 1B).

Because each of the three rotational domains can have two stacking domains, the complete microstructure has six types of domains. In Fig. 1C, the six different regions are coded by three colors (rotational domains) and two gray levels (stacking domains). The two types of domain boundaries, namely stacking and rotational boundaries, are distinct.

At temperatures below 350°C, the rotational domains do not evolve with time (*17*). We focus on the evolution of the stacking boundaries and their relationship with the rotational domains. The evolution of the stacking domains, as followed in real time in Fig. 2, A to C, is quite discontinuous; several minutes may elapse without changes. But sometimes the boundaries between stacking domains move very quickly, as shown by the blurred edges in Fig. 2B. When fast motion occurs, the stacking boundary moves along the unique in-plane direction of the rotational domain (Fig. 2D). Superimposing the rotational and stacking domains also shows that the fast motion of stacking-domain boundaries takes place within rotational domains. The slowing down of their motion, on the other hand, frequently occurs at the boundaries between rotational domains.

To further highlight the observed effect of the rotational-domain boundaries on stacking-boundary motion, we exposed the film to sulfur. Sulfur removes the rotational domains in the copper film (*18*, *19*), changing its structure so that only a single rotational (orientational) domain occurs (figs. S3 and S4). The stacking domains are preserved (Fig. 3A and fig. S3). Without rotational domains, the stacking boundaries advance smoothly with time, in marked contrast to the clean Cu films.

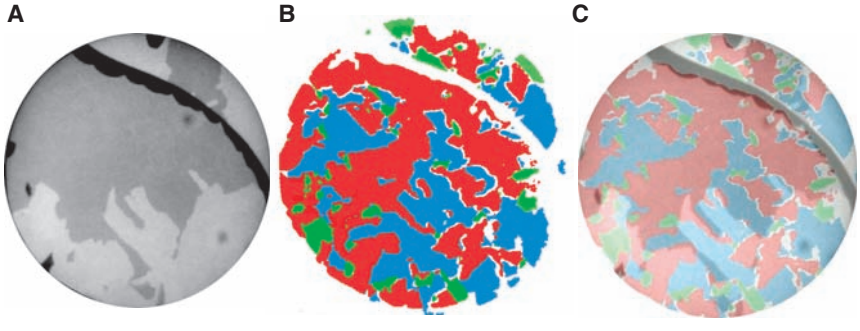

Fig. 1. Domains in two Cu layers on Ru(0001). The field of view of the LEEM images is 5 μm. (**A**) Bright-field LEEM showing the two different stacking domains, which correspond to the two gray levels in the image. The black areas are regions of the copper film that are three layers high. The incoming electron energy (38 eV) is selected to give good contrast between the stacking domains. (**B**) Composite color image obtained from the superposition of the three dark-field images of fig. S1, where the colors indicate the orientation of each rotational domain. The areas that are not shown in any color correspond to 3-ML Cu. (**C**) Full domain microstructure of two copper layers on Ru, obtained by superposition of the previous images.

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In addition, the stacking boundaries do not move in any preferred direction.

Hence, the rotational domains have a great influence on the evolution of the stacking domains—within a rotational domain, the stacking boundaries move rapidly. But at the rotational boundaries, the stacking boundaries become impeded. This complicated behavior can be understood by considering the defects at the domain boundaries—the rotational boundaries contain threading dislocations that act as obstacles to the stacking-domain boundaries.

To understand why the observed evolution occurs, we need to describe the stacking and the rotational domains in more detail. The rotational domains in clean 2-ML copper films are caused by the uniaxial relaxation of Cu atoms in a nearest-neighbor direction through the introduction of parallel arrays of misfit dislocations at the Cu/Ru interface (*15*, *20*). At the boundaries of the rotational domains, there are arrays of edge dislocations (*20*) that thread out from the substrate/film interface to the film/vacuum interface. Within the rotational domains, no such "threading" dislocations occur. The threading dislocations, which are only two atoms long, are marked in Fig. 4, A to C, and fig. S2C by yellow "T" symbols.

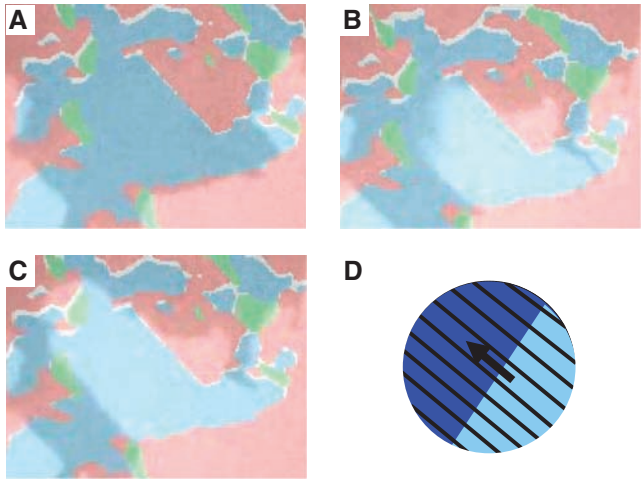

Fig. 2. (**A** to **C**) Evolution of the stacking-domain structure at 250°C. The size of the images is 1.8 μm by 1.3 μm. From image (A) to image (B), 30 s have elapsed. Image (B) appears blurred at the end of the advancing stacking boundary because of the temporal averaging used (1 s). The fast motion direction is aligned with the underlying rotational domain, as indicated schematically in (**D**). The time difference between images (B) and (C) is 5 s.

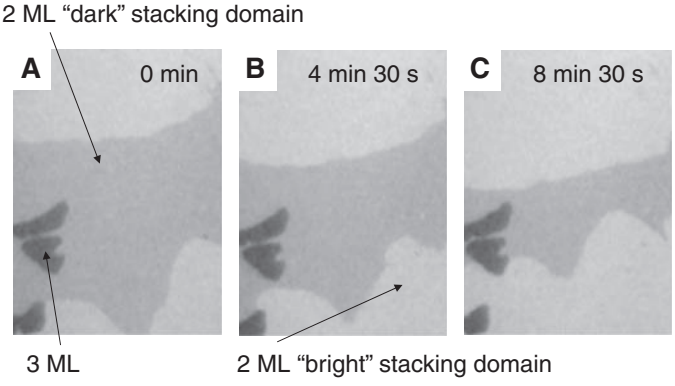

Fig. 3. Evolution of stacking domains in a 2-ML Cu film modified by sulfur. The bright-field LEEM images were taken at 38 eV and are 1.4 μm by 1.9 μm in size. Image (**A**) was taken at 135°C after the sulfur exposure. Images (**B**) and (**C**) were taken at 152°C. The stacking-domain boundaries do not move in preferred directions, unlike sulfur-free films, which contain rotational domains.

The second Cu layer of a 2-ML film can be located in two different positions that avoid unfavorable on-top positions. These two different stacking sequences give rise to the two stacking domains (*15*). Although the two domains should have different energies, the energy difference is too small to be reliably determined by ab initio methods (<4 meV per atom, as estimated by density functional theory calculations) (*15*). Because this energy difference is small, however, islands of both stacking types can nucleate. Indeed, when 2-ML Cu islands grow on top of a complete 1-ML film at our growth temperature, both stacking types occur with about equal probability. Following the growth in real time with LEEM shows that individual islands retain their stacking character until a continuous 2-ML film is formed by island coalescence. The boundaries separating coalesced islands of unlike stacking then move because even a small difference in energy per atom represents a strong driving force to convert the higher-energy stacking domain into the lower-energy one by moving the boundary between them. The boundary separating domains of different stacking sequence is a Shockley partial dislocation located between the two Cu layers (shown as a gray line in Fig. 4, A to C). This directed motion is in contrast to the dislocation motion on 1-ML Cu on Ru(0001) (*21*). In this case, the Shockley partial dislocations undergo thermal fluctuations because no driving force to push the dislocations exists.

The domain evolution can be interpreted in terms of the dislocation structures of the stacking and the rotational domains described above. The stacking-boundary dislocation can glide within rotational boundaries without encountering intersecting (threading) dislocations (Fig. 4, A and B). Because the energy (Peierls) barrier needed to move such a dislocation is small [<0.25 meV/Å, as estimated by embedded atom method calculations (*22*, *23*)], such glide motion is expected to be very fast. We observe that the stacking boundaries can move as fast as ~10^3 nm/s.

When moving across rotational domains, however, the stacking-boundary dislocation must cross the threading dislocations present at the rotational boundaries (fig. S2). Given the

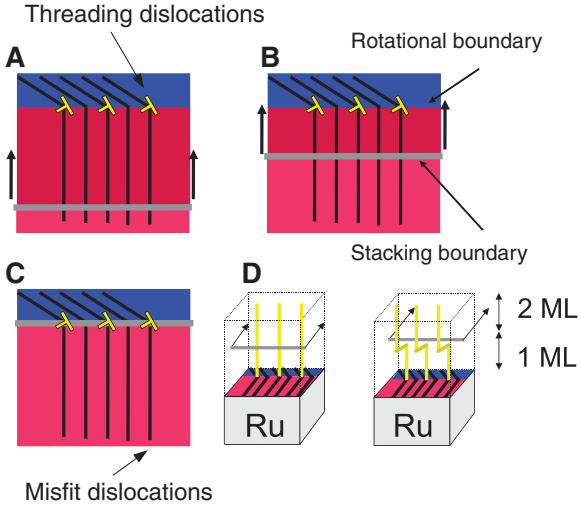

Fig. 4. Explanation of stacking-boundary motion. (**A** and **B**) Fast motion of the stacking boundary is observed within rotational domains because the dislocation (boundary), marked by the gray line, can move by glide because no threading dislocations are encountered. (**C**) Schematic of a stacking boundary crossing between rotational domains. (**D**) Three-dimensional schematic of the crossing of the rotational boundaries by a stacking boundary. The Cu film (outlined cubes) lies on the Ru substrate (light gray). The misfit dislocations, located at the Ru-Cu interface, are shown as black lines. The stacking boundary, a dislocation within the Cu film between the two copper layers, is shown before and after crossing the threading dislocations present at the rotational boundary. After the crossing (right drawing), jogs are left on each threading dislocation (marked by dark yellow). The corresponding kinks on the stacking boundary are not drawn.

Burgers vectors of the involved dislocations (*24*), a jog is produced on each threading dislocation when the stacking boundary crosses the "forest" of threading dislocations (Fig. 4D). In turn, the stacking-boundary dislocation acquires a kink for each crossing. The production of a jog on each threading dislocation costs energy, and the total energy barrier of all the needed crossings is much larger than the Peierls glide barrier encountered for pure glide within a rotational domain. Thus, the threading dislocations impede the stacking-boundary motion. Because the threading dislocations only occur at the rotational-domain boundaries, we explain the experimental observation that the stacking boundaries become stuck at the rotational boundaries. The crossing of the threading dislocations is temperature activated: The lower the temperature, the longer the stacking boundaries are pinned at the rotational boundaries. In contrast, the glide motion within rotational boundaries is independent of temperature in the observation range.

We can also understand why stacking boundaries preferentially advance (Fig. 2) along the unique direction of the misfit dislocations within each rotational domain. The array of misfit dislocations within each rotational domain constitutes a periodic array of obstacles for stacking-boundary motion unless, as observed, the stacking-boundary dislocation moves along the misfit dislocations themselves.

The experiments under sulfur exposure can also be explained by the atomistic details of the dislocation structures. When sulfur is deposited on a 2-ML Cu/Ru(0001) film, the striped pattern of misfit dislocations responsible for the rotational domains breaks down (fig. S3), and a well-ordered triangular pattern appears (*18*, *19*) that lacks rotational domains (fig. S4B). The unit cell of this pattern (fig. S4) is a small triangular unit with sides composed of misfit dislocations and threading dislocations at the three corners (*18*). Nevertheless, the stacking domains still persist and are observed as before in bright-field conditions (Fig. 3). As in 2-ML Cu/Ru(0001) without sulfur (Fig. 1A), there are still two different possibilities for stacking the second Cu layer on top of the first. However, the threading dislocations are now uniformly distributed within the film. The stacking boundary dislocations now encounter a closely spaced (<7 nm apart) distribution of threading dislocations, so the stacking domains evolve smoothly at our observation scale, which is larger than the film's threading dislocation spacing (the LEEM resolution is ~10 nm). Therefore, the stacking boundaries move smoothly with no preferred directions (Fig. 3).

In summary, we have shown how observing thin-film microstructure evolution in real time and in real space can determine what process controls the healing of crystallographic defects. In the Cu on Ru system, all the microstructure interactions can be observed and understood; it serves as a model of thin-film evolution in which the detailed interactions can be fully modeled (*25*). Given the ubiquity of dislocations in heteroepitaxial films, we anticipate that our key finding, that dislocations interactions control the rate at which extended defects heal themselves, will hold in many other metal and nonmetal systems.

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Supporting Online Material

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Materials and Methods
Figs. S1 to S4
Movies S1 and S2

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A Microbial Arsenic Cycle in a Salt-Saturated, Extreme Environment

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Searles Lake is a salt-saturated, alkaline brine unusually rich in the toxic element arsenic. Arsenic speciation changed from arsenate [As(V)] to arsenite [As(III)] with sediment depth. Incubated anoxic sediment slurries displayed dissimilatory As(V)-reductase activity that was markedly stimulated by H_2 or sulfide, whereas aerobic slurries had rapid As(III)-oxidase activity. An anaerobic, extremely haloalkaliphilic bacterium was isolated from the sediment that grew via As(V) respiration, using either lactate or sulfide as its electron donor. Hence, a full biogeochemical cycle of arsenic occurs in Searles Lake, driven in part by inorganic electron donors.

The microbial life that exists in brines of exceptionally high salinity has been a topic of fascination to microbiologists (*1*, *2*). Primary productivity in hypersaline ecosystems is driven by oxygenic photosynthesis, as typified by salt-adapted microbes like *Dunaliella parva* that provide the organic carbon needed to sustain a microbial food chain. Typical heterotrophs obtained from such locales are either obligate aerobes or fermentative anaerobes (*3*). Some also have the ability to respire nitrate, but the importance of this scarce anion as a respiratory electron acceptor in high-density brines has not been studied. In extremely hypersaline environments that have

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