Nanocrystalline copper films are never flat

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We used scanning tunneling microscopy to study low-angle grain boundaries at the surface of nearly planar copper nanocrystalline (111) films. The presence of grain boundaries and their emergence at the film surface create valleys composed of dissociated edge dislocations and ridges where partial dislocations have recombined. Geometric analysis and simulations indicated that valleys and ridges were created by an out-of-plane grain rotation driven by reduction of grain boundary energy. These results suggest that in general, it is impossible to form flat two-dimensional nanocrystalline films of copper and other metals exhibiting small stacking fault energies and/or large elastic anisotropy, which induce a large anisotropy in the dislocation-line energy.

Nanocrystalline (NC) metals are widely used as electrical contacts and interconnects in ultralarge-scale integrated circuits (1). Technologically important properties of these materials, such as their electrical and thermal conductivity (2, 3), and detrimental processes such as electromigration (4) are strongly influenced by the presence and density of surfaces, grain boundaries (GBs), and dislocations within them. Also, surface roughness of films can affect materials grown on existing NC films, such as dielectrics, and will affect the performance of tunneling devices based on these metals by modulating the tunnel barrier width (5). Many NC films contain grains with a preferred orientation; for example, face-centered-cubic (fcc) metals such as gold and copper (Cu) often grow with (111) surface orientation (6), so it might be expected that individual grains and GBs would coalesce to form films with smooth surfaces. However, GBs in metals such as Cu are composed of stacking faults (SFs) whose energies have a directional dependence that could induce grain rotation and concomitant surface roughening.

We investigated NC Cu films from the multi-grain scale ~1 μm down to the atomic scale using scanning tunneling microscopy (STM). We can use STM to map the local three-dimensional topography of GB intersections at surfaces with picometer precision. Also, STM operation is unaffected by the degree of tilt axis misalignment from high-symmetry directions that typically hampers transmission electron microscopy analysis of GB structure (7, 8). We identified shifts in the GB tilt axis away from that of the original low-angle GB (LAGB) in NC Cu films. We show that this phenomenon is accompanied by GB energy minimization associated with a change in the dislocation-line direction, which results in the unavoidable introduction of ridges and valleys into the film.

We prepared high-quality NC Cu films (thicknesses of 20 or 50 nm) by means of physical vapor deposition on top of a 7-nm-thick tantalum layer that had been coated on a silicon wafer (all deposition processes were performed at 300 °C in a glovebox). The resulting NC Cu thin films (Fig. 1A) show that in addition to the (111) plane, there was a 2.4° misalignment between the close-packed (111) direction and the [111] normal of the two adjoining grains; the (111) surfaces of these grains were atomically flat.

Fig. 1. GBs at ridges and valleys in (111) films of Cu. (A) Perspective view of the STM topography of NC Cu film. Tunneling parameters are I = 20 pA and U = 0.2 V. GBs at ridge and valley locations are highlighted by arrows. (B) Close-up view of one GB at valley location. (C) Close-up view of one GB at ridge location. (D) Profile of valley and ridge line cross sections marked by the dashed lines in (B) and (C), respectively. The color of each curve is consistent with that of lines in (B) and (C).
Shockley partials. The first Shockley partial produced a step up on the (111) surface of height \( a/6 \) [211] \( \cdot [111]/\sqrt{3} = a/3\sqrt{3} = 70 \) pm, which is one-third of the (111) interplanar spacing. This result is consistent with the measured step profile in Fig. 2B and earlier measurements (7). The second Shockley partial produced an equal and opposite step down (Fig. 2B, inset), where two partials are explicitly shown. The two partials had finite core widths; hence, the \( \pm 70\) pm step profiles were spread out rather than abrupt.

We found that GBs at valley and ridge locations had different corrugation amplitudes (Fig. 1, B and C). The corrugation along the valley GB was between 60 and 80 pm, which is consistent with a series of Shockley partial pairs, whereas along the ridge it was smaller, \( \pm 30 \) pm (Fig. 1D). A GB with atomic resolution at a ridge is shown in Fig. 2C. Burgers circuits revealed undissociated edge dislocations, and the location of each dislocation core was precisely determined. This result differed from the dissociated lattice dislocations in the GBs observed in valleys and was consistent with the breakdown of inversion symmetry of Cu (111) film due to the presence of LAGB (10).

To explain how grain tilting gives rise to the ridge and valley features seen in STM, we begin by considering the in-plane misorientation and assume that the dislocation lines are parallel to the surface normal [111]. The GB in Fig. 2A displayed a periodic sequence of edge dislocations. The solid lines and dotted lines ran along the [112] and [110] directions in the adjoining grains, respectively. The repeat vectors \( \mathbf{p} \) in the boundary plane of the two adjoining crystals are \( +4 + 3 \) \( a/4 \) [112] \( \pm 3a/4 \) [110] \( = a/2 \) [4711] and \( a/2 \) [7411], each of length \( p = \sqrt{11}/2 \) (Fig. 2A). The Burgers vector content \( B = 3a/\sqrt{2} \) in each period \( \mathbf{p} \) is related to the boundary misorientation \( \theta \) by Frank’s formula, \( \sin(\theta/2) = B/(2p) \). The estimated value \( \theta = 17.9^\circ \) was near the measured angle 16.2° in Fig. 2A. Thus, the GB in Fig. 2A was a symmetric tilt GB whose boundary lies along the mean of the (110) planes of the adjoining grains.

However, it is unlikely that the dislocation lines are parallel to the surface normal [111] because, if so, the SF ribbon plane between the partials would be \( [112] \) (on average), with small separation and high elastic repulsive energy between the partials [11]. The low-energy SFs in Cu are on [111] planes, not [112] planes. If the dislocation lines were parallel to [112], which is 19.47° from the [111] surface normal, the SFs could be on the low-energy [111] planes. To minimize the SF energy and the overall dislocation-line energy, it is likely that the direction of the dislocation lines—and hence that of the composite rotation axis to form the GB—lies somewhere between [111] and [112], which is consistent with the atomistic simulation below.

To effect this change, we introduced a second rotation so that the GB rotation comprises an in-plane rotation \( \mathbf{p}_1 = 1/\sqrt{3} [111] \tan(\theta/2) \) followed by a rotation \( \mathbf{p}_2 = \mathbf{g} \tan(\varphi/2) \), so that the composite rotation (22)

\[
\mathbf{p} = \mathbf{p}_2 + \mathbf{p}_1 = \begin{pmatrix} p_2 + p_1 \times p_2 \end{pmatrix} - l_1 \mathbf{p}_1 - l_2 \mathbf{p}_2
\]

was perpendicular to [110]. It follows then from Eq. 1 that \( \mathbf{g} = \cos(\theta/2)/(1/\sqrt{3})[112] + \sin(\theta/2)/(1/\sqrt{2})[110] \), and the Rodrigues vector of the composite rotation is

\[
\mathbf{r} = \tan(\theta/2)/(\tan(\varphi/2)/\sin(\theta/2)/\sqrt{3} [112] + 1/\sqrt{3} [111])
\]

which ensured that each dislocation has no net step height at the surface. The angle \( \varphi \) between [111] and the composite rotation axis, which is also the inclination angle between [111] and the dislocation lines, follows directly from Eq. 2: \( \tan \varphi = \tan(\varphi/2)/\sin(\theta/2) \). For small \( \theta \), this reduces to \( \varphi = \theta \tan \varphi \).

\( \mathbf{p}_2 \) is a rotation about an axis lying in the boundary plane that tilts the (111) surfaces on either side of the GB through the angle \( \varphi \), creating a valley or ridge. During the \( \mathbf{p}_2 \) rotation, the GB boundary plane remains along the mean of the (110) planes and bisects the (111) planes of the adjoining grains (Fig. 3A). The rotation \( \mathbf{p}_2 \) inclines the direction of the dislocation lines toward [112]. In the limit where \( \varphi = 1/2 \sqrt{2} \) (that is, \( \varphi = 19.47^\circ \)), the dislocation lines are entirely parallel to [112].

The distribution of experimentally measured values of \( \theta \) and \( \varphi \) is shown in Fig. 3B. Each open circle corresponds to a GB at a valley, and each solid circle corresponds to a GB at a ridge; there is no obvious difference between the data at ridge and valley locations. The purple line in Fig. 3B is a plot of \( \tan \varphi = \tan(\varphi/2)/\sin(\theta/2) \), which is 19.47°, which sets the upper limit of the out-of-plane rotation angle \( \varphi \) for a given in-plane rotation angle \( \theta \). The black line with slope 0.25 is a linear fit to the data for valley GBs. These results mean that on average, the dislocation line was inclined 14.04° from the [111] direction instead of 19.47°. As discussed in (10), we attribute this 5° difference to the Cu-Ta interface, which inhibits tilting of the Cu (111) planes.

We calculated the energies of GBs in free-standing (111) films using molecular statics with periodic boundary conditions and an embedded-atom–method interatomic potential (fig. S1 and table S1) (10). Each repeat cell contained a pair of parallel GBs with equal and opposite misorientations. The GB structures were relaxed at the prescribed in-plane and out-of-plane rotation angles, \( \theta \) and \( \varphi \), respectively. When a GB created a valley at the top surface of the film, it produced a ridge at the bottom surface, and vice versa (Fig. 3A). The GB energy as a function of the inclination angle \( \varphi \) is shown in Fig. 3C. Regardless of the in-plane angle \( \theta \), the GB energy was minimized at \( \varphi = 19.47^\circ \). This result shows that the out-of-plane angle \( \varphi \) corresponds to a reduction in the GB energy by aligning the dislocation lines along [112], which enabled the SFs between the partials to lie on low-energy [111] planes, yielding larger partial dislocation separation and lower elastic energy. The reduction of LAGB energy is therefore attributed to the anisotropy of the dislocation energy. In the case of Cu, this anisotropy is predominantly due to the anisotropy of SF energy.

The simulation results agreed with our film-tilting analysis at the atomic scale. The atomic structures of GBs with an in-plane angle \( \theta = 3.89^\circ \) and three out-of-plane angles \( \varphi \) are shown in Fig. 4 from different viewing directions. When \( \varphi = 0 \) (Fig. 4A), the SF ribbon is in the [112] plane on average and is composed of narrow facets of high-energy (001) faults between [111] facets. As \( \varphi \) increases, we find an increased inclination angle and wider SF ribbons, with fewer jogs along their lengths and wider dislocation terminals at the surface (Fig. 4B). When \( \varphi = 1.37^\circ \) (Fig. 4C), corresponding to \( \varphi = 19.47^\circ \), there are no jogs along the SF ribbon, and the partial dislocation separation is maximized. Also, the SF ribbon is wider at the surface where the GB forms a valley (top surface) than where it forms a ridge (bottom surface) (Fig. 4, B and C) (10). This trend is consistent with our experimental observation (Fig. 2C), although in the experiment, the partial dislocation separation appeared to reduce further than in the simulations (to near zero).

Fig. 2. Atomic structure of emergent LAGBs. (A) Atomic-resolution STM image of a valley GB segment with \( \sim 3^\circ \) out-of-plane angle. The green path shows a Burgers circuit. The white dotted lines are along [110] and solid lines along [112]. The repeat sequence 3, 4, 4 is shown along [112]. The components of \( \mathbf{p} \) are shown in units of \( a \). The measured boundary misorientation angle \( \theta \) between the grains is 16.2°. (B) Atomic-resolution STM image of a second valley GB area with a smaller out-of-plane angle. The image contains two dissociated edge dislocations across the GB. (Inset) Plot of the step profile (data points) of the dissociated edge dislocation, which shows the equal and opposite Shockley partials (arrows). (C) Atomic-resolution image of a ridge GB segment.
The occurrence of ridges and valleys at emerging low-angle tilt boundaries reported here can be generalized to Cu films with different surface orientations. Elimination of jogs and high-energy fault planes between partials requires both the dislocation-line direction and Burgers vector to be in the same (111) plane. Therefore, only (112) films are expected to be immune to tilting because in this case, the dislocation lines already lie in the (111) plane without any out-of-plane rotation. However, (112) fcc films are thermodynamically unstable (6, 13); hence, flatness cannot be achieved. The principles set forth here can also be extended to films of other fcc materials, such as silver and gold. More generally, however, they can also be applied to any material that has highly anisotropic dislocation-line energy, which has contributions from the structure of the dislocation core and the elastic response of the surrounding medium.

Out-of-plane grain rotation and surface tilting are expected to influence technically important properties of NC metal films and wires that are size-dependent and sensitive to GB structure (2, 3). For example, the resistivity of Cu wires increases precipitously with decreasing the diameter because of increased contributions from interfacial scattering and surface roughness as the grain size falls below the mean free path (~40 nm in Cu) (2, 14). This work suggests that grain rotation and tilting can be modulated by engineering SF energy through GB doping and/or controlling the film-substrate interaction so as to provide a potential means to manipulate the properties of NC metals.

REFERENCES AND NOTES
10. Materials and methods are available as supplementary materials.

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SUPPLEMENTARY MATERIALS
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Supplementary Text
Figs. S1 and S2
Table S1
References (15–17)
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Flat-out failure of copper films
As integrated circuits shrink in size, so does their nanocrystalline metal wiring. Defects at the interfaces between crystallites (grain boundaries) can degrade wires' electrical and thermal conductivity, as well as their longevity. Using scanning tunneling microscopy, Zhang et al. showed that the surfaces of nanocrystalline copper films are not flat but rather have ridges and valleys created by the grains rotating out of plane, which then introduces grain boundary defects. Such defects might be avoided if films of different orientations could be grown.

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