High-Resolution Electron Microscopy of Twist and General Grain Boundaries

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High-resolution imaging of atomic structures of twist and general grain boundaries (GBs) is reported in samples prepared by a thin-film technique in which [011] and [001] oriented Au grains are epitaxially grown side by side, allowing the investigation of a wide range of GB geometries. GBs with tilt as well as twist components typically have structural modulations along the interface and often show a surprising amount of coherence between lattice planes crossing the interface. The [110], 90° symmetric twist GB does not remain planar, but reconstructs into atomic-scale microfacets.

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As is well documented, grain boundaries (GBs) are of great importance for materials performance in many technical applications. Therefore, great effort has been directed towards the determination and control of grain and GB morphology in polycrystalline systems. As a basis for understanding various physical phenomena associated with GBs, knowledge of the structure and composition at the atomic level is crucial. The complexity of this task can be appreciated if we consider that three parameters are needed to describe the misorientation axis and angle between two grains and an additional two parameters are necessary to describe the GB plane. Within this five-dimensional phase space, atomistic computer simulations of GBs have provided considerable information for a wide range of two dimensionally periodic tilt, twist, and general GBs [1,2]. However, real-space observations of atomic-scale GB structure by high-resolution transmission electron microscopy (HREM) have largely been limited to tilt GBs [3] due to the requirement that the crystal lattices on both sides of the interface be parallel to a low-index zone axis. Although tilt GBs, in which the misorientation vector is parallel to the GB plane, are important due to their generally low GB energies [1], the misorientation vector typically is inclined in a random polycrystal. Such interfaces are referred to as general GBs and, when the misorientation vector is perpendicular to the GB plane, as twist GBs.

Structural studies of [001] twist GBs in Au, using x-ray scattering techniques, can give average values of atomic positions in periodic boundaries [4,5], but in contrast to HREM are not sensitive to local structural deviations such as defects, ledges, and structural multiplicities. A general GB suitable for HREM observation was found by Shamsuzzoha *et al.* in a textured foil of aluminum and analyzed directly from atomic-resolution images [6]. However, the geometry of the GB cannot be controlled in this manner, moreover, the probability is extremely low for two neighboring grains in a polycrystal to be aligned sufficiently well (<10 mrad) for axial illumination HREM.

In this Letter we report for the first time observations of the atomic-scale structure of a series of geometrically well-controlled general and twist GBs in Au using the HREM technique. In order to apply the axial illumination HREM technique to general and twist GBs, the grains joined at the GB must have two different low-index directions parallel to each other and to the GB plane. To accomplish this an epitaxy technique [7] is employed to form GBs between (001) and (011) oriented grains. This technique can be applied to any material that allows epitaxy on at least two different low-index planes.

A schematic plan view of the film geometry is shown in Fig. 1. An (011) Au film *B* is physically transferred onto a (001) NaCl substrate *A* at an in-plane rotation θ between the [100] directions in *A* and *B*. Low energy ion-beam sputtering and physical masking are used to remove most of film *B*, except in certain areas, such as in *B* of Fig. 1. This template is used to epitaxially grow by *e*-beam evaporation a film of (001) and (011) grains side by side. After transfer to a Au specimen grid and an anneal near 573 K, samples suitable for HREM are obtained by standard ion-milling techniques. Since most GBs grow normal to the film surface, an HREM edge-on observation of general GBs is possible. The orientation of grain *B* in Fig. 1 is related to grain *A* by a rotation of

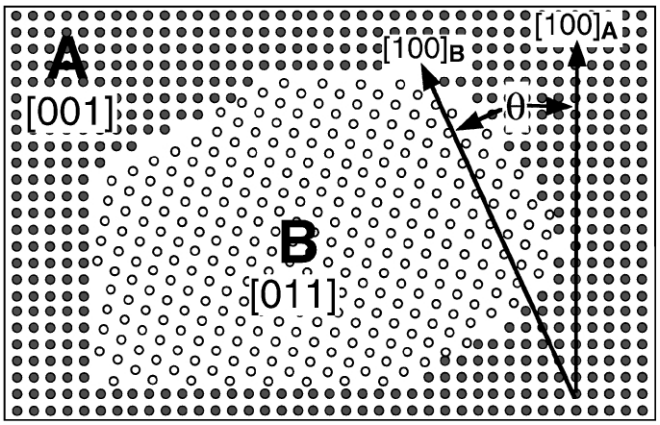

FIG. 1. Schematic plan view of epitaxial film growth geometry using (011) seed crystals on (001) NaCl. Crystal *B* is formed by a 45° rotation about $[100]_A$ plus a rotation of θ about $[001]_A$.

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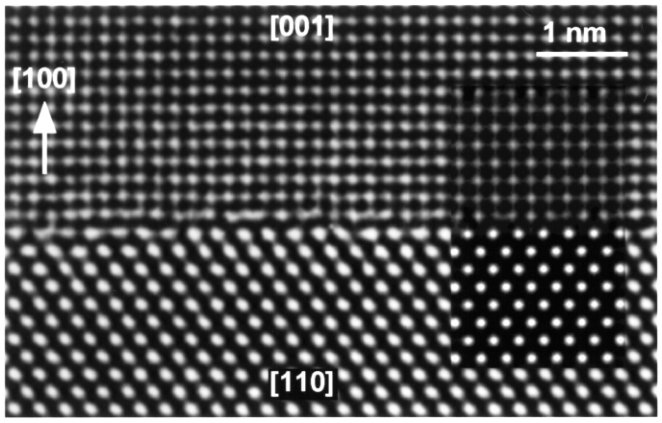

FIG. 2. HREM image of a twist GB with a misorientation angle of $\psi = 45°$ about [100] (see arrow). The viewing directions in both grains are indicated in this and the following HREM images. The inset is a simulated HREM image, based on a rigid atomic model. Note structural disorder in atomic planes next to the GB.

A about $[100]_A$ by 45° followed by a rotation θ about $[001]_A$. For $\theta > 0$ the compound misorientation vector, given by the rotation axis and misorientation angle ψ, will typically not lie in the plane of the film. Thus, practically all of the boundaries manufactured by this technique are general GBs, characterized by finite twist and tilt components. However, for $\theta = 0°$ (see Fig. 2) and $\theta = 45°$ (see Fig. 3), the pure twist GBs with misorientations [100], $\psi = 45°$ and [110], $\psi = 90°$, respectively, are generated at the appropriate GB inclinations (i.e., the proper rotation of the GB plane about the film normal). In this Letter we report results from three bicrystals ($\theta = 0°$, 45°, and 27°).

We note that, in contrast to periodic GBs, which are normally considered in theoretical as well as experimental investigations, all of the GBs prepared by the above technique are aperiodic at least in one direction. In the direction of the film normal the stacking of (002) and (022) planes on opposite sides of the GB directly leads to an incommensurate structure. However, if a sufficient number of planes is considered, approximation by a rational stacking sequence is always possible. This also applies to the structures along the GB. In this context, the main issues to be investigated are the identification of typical GB structural units and the general structural features that arise in forming connections between lattices across general GBs.

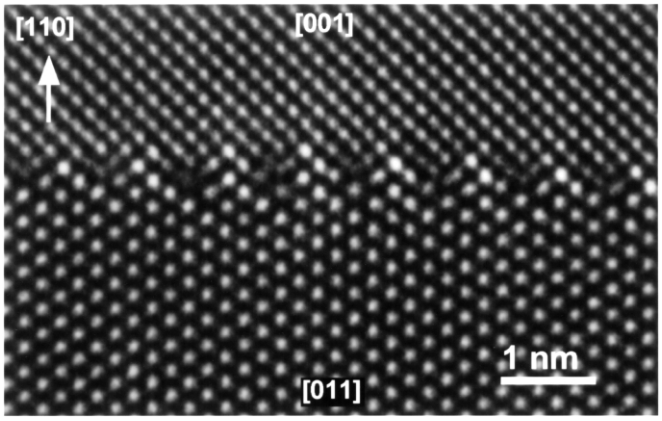

FIG. 3. HREM image of $\psi = 90°$, [110] twist GB. The GB does not remain planar, but reconstructs into atomic-scale microfacets bounded by (111) and (200) planes in grains B and A, respectively.

An HREM image of a (100) twist GB with misorientation angle $\psi = 45°$ is shown in Fig. 2. The image was recorded utilizing a 4000EX JEOL microscope at a beam voltage of 400 kV and a defocus value near -65 nm. Similar imaging conditions were used throughout, resulting in white contrast features at the positions of atomic columns on both sides of the GB. The inset to Fig. 2 is obtained from an HREM multislice image simulation using a rigid atomic model and the experimental imaging conditions. Compared to the rigid model, the experimental image shows some structural disorder in the planes directly bordering the GB. This is best seen in the (200) plane of the upper grain and when observing the image under a shallow angle along the length of the GB. We note that this GB geometry is highly symmetric, with identical projections upon 90° rotations around the GB normal and inverted GB structures at 45° from the former. The TEM images give no indication for misfit localization or coherency at the GB. Atomic-height ledges are common, indicating a possible migration mechanism for this GB.

The $\psi = 90°$, (110)-type twist GB is expected to be formed at facets that are bounded by the (220) and $(0, 2, -2)$ planes in grains A and B, respectively. Figure 3 shows that this boundary, in contrast to the (100) twist GB does not remain planar, but reconstructs into microfacets that are bounded by (100)- and (111)-type planes. Approximately every second (111) plane appears coherently connected to every third (100) plane across the GB. The quite large misfit of this configuration causes considerable bending of lattice planes near the GB. This is best seen when viewing Fig. 3 at a shallow angle from the bottom of the figure, along the (200) planes, which connect in semicoherent fashion with the (220) planes in the top grain. The planes are coherent near the apex of the triangular features, whereas regions of misfit localization and strong disorder are present near the bottom of the sawtooth features. The repeat period is approximately seven (220) or five (200) interplanar spacings ($\sim$1 nm). Coherency for this boundary indicates that the GB energy was lowered by the reconstructed structure. That this GB reconstructs is not particularly surprising, since atomistic computer simulations have indicated that periodic (110) high-angle twist GBs have very high GB energy and are strongly disordered within a few lattice planes of the GB [1,8,9]. Therefore, it is likely that in the presence of a highly disordered lattice at the interface, the GB

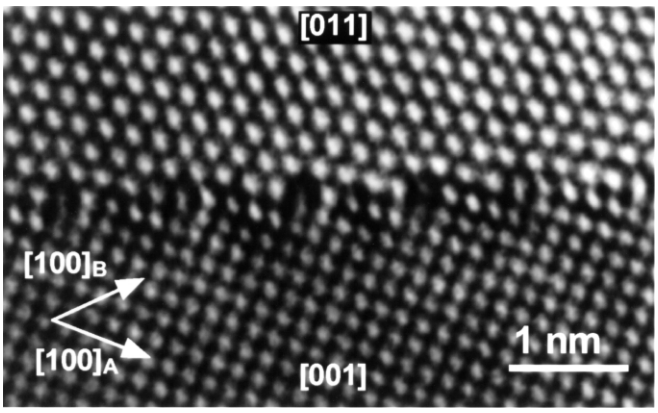

FIG. 4. Asymmetric (233)(250) GB with tilt and twist components. Note almost identical repeat structures characterized by misfit localizations.

energy can be lowered by reconstruction into microfacets and thereby maintaining a well-connected, albeit distorted lattice, right up to the GB.

A general GB at $\theta = 45°$ is imaged in Fig. 4. Both lattices bordering this GB maintain their basic structure right up to the GB core where a (233) plane is opposed by a (250)-type plane in the lower crystal. The misorientation axis is inclined to the GB plane, thus including twist and tilt components. Several distinct misfit localizations at regular intervals are apparent. By viewing the image at a shallow angle from the lower right it can be seen that the regions of misfit correspond to the positions where two (200) planes meet one (111) plane of the upper crystal. Again, noticeable bending of lattice planes near the interface is indicated. Periodic modulations associated with local strain are observed in the general GB of Fig. 5. The structural repeat distance of $\sim$1.6 nm seems to be governed by the mismatch between (111) and (200) planes impinging on the interface at an approximate ratio of 7:8, respectively. This asymmetric (755)(100) GB is faceted along the (100) plane. Thus, faceting along low-index planes, which is a common feature of periodic tilt GBs [1,10,11], may also play an important role in lowering GB energy in general GBs.

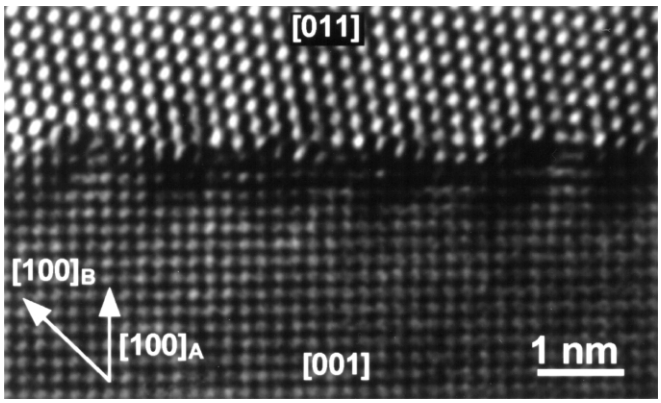

FIG. 5. HREM image of (755)(100) GB with tilt and twist components. Strain fields are causing image contrast effects at structural modulations.

HREM images of a bicrystal at $\theta = 27°$ are displayed in Fig. 6 for three different inclinations of the GB plane.

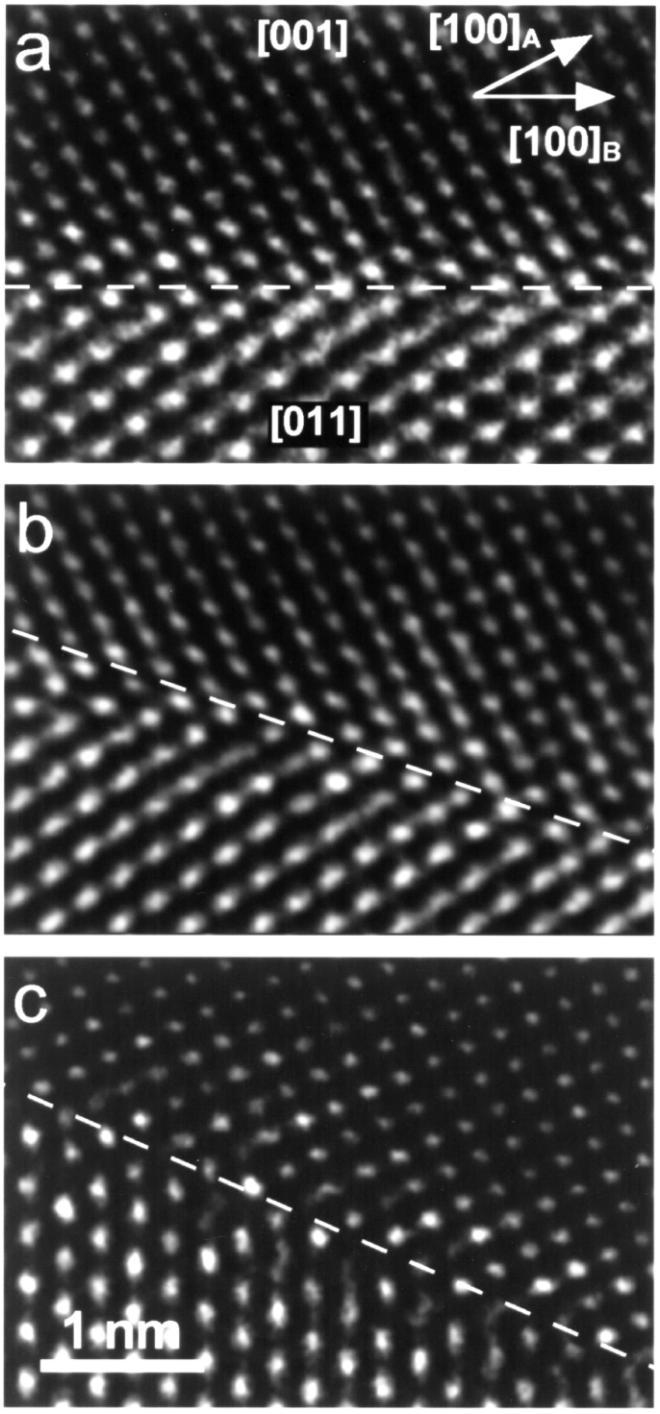

FIG. 6. HREM images of the same bicrystal ($\theta = 27°$) for three general GB inclinations. GBs are indicated by dashed lines with inclinations relative to horizontal: (a) 0°, (b) 17°, and (c) 24°. Note that the (111) planes in the lower crystal form an angle of $\sim$8° with the (200) planes in the top grain. Coherency is maintained in (a) and (b). Bending of lattice planes is also observed in (a) and (b).

Figures 6(a) and 6(b) show coherent connections between (111) planes in the lower crystal and (200) planes in the upper crystal which are misaligned relative to each other by an angle of about 8°. For a given geometry of an unrelaxed bicrystal coherent connections between given sets of planes are possible only for one specific inclination of the GB plane. In Fig. 6(b) the GB plane inclination (at 17° to the horizontal) closely corresponds to this geometrical coherency condition. However, in Fig. 6(a), the GB inclined at 0° to the horizontal surprisingly is still coherent. In this case one extra (111) plane should impinge over the width of the horizontal facet in Fig. 6(a), based on a rigid model. Avoiding the misfit localization due to such a defect is possible only by severe elastic distortions of the lattice. This is apparent in Fig. 6(a) since the coherently connected (111) and (200) planes are bent over a quite large region near the GB. Thus, the GB apparently can distribute the misfit in a continuous fashion over a finite width. However, when the GB is inclined at steeper angles than in Fig. 6(c), coherency is lost and considerable structural disorder is evident at the location of the GB.

In summary, several distinct GB structures and relaxation modes have been identified in HREM investigations of twist and general GBs in Au. Most commonly, there is, in analogy to periodic tilt GBs, a tendency to establish coherence between low-index planes across the GB. This typically results in semicoherence, misfit localization, and almost periodic structural modulations along the GB. The coherent connection between lattice planes was in one instance found to extend over a quite large range of GB inclinations. This exemplifies the strength of the interatomic interactions within the planes and the ability of the lattice to accommodate large elastic strains. We have demonstrated that general GBs are well structured at the atomic scale, i.e., the lattices retain their identity right up to the GB core which often displays features that are related to tilt GB structures, such as the tendency for misfit localization and the formation of low-index facets. As in the case of tilt GBs, these features appear to be associated with a lowering of GB energy through maximizing the overall structural order in the GB [12]. We have for the first time demonstrated the atomic-scale reconstruction of a high angle (110) twist GB. The techniques developed in this work open up a new dimension for systematic investigations of the atomic structure of GBs by HREM.

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