Collective Effects in Grain Boundary Migration

K. L. Merkle* and L. J. Thompson
Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439

Fritz Phillipp
Max-Planck-Institut für Metallforschung, Heisenbergstrasse 1, D-70569 Stuttgart, Germany
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In situ high-resolution transmission electron microscopy is used to study grain boundary structure and kinetics in bicrystalline Au films at elevated temperature. We report the first direct evidence for the existence of cooperative atomic motion in grain boundary migration. Certain nanoregions at grain boundaries, typically involving up to several hundred atoms, are found to switch back and forth between neighboring grains. Reversible structural fluctuations at temperatures near $0.5T_m$ and above have been discovered in [110] and [001] tilt, as well as in general grain boundaries.

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Grain boundaries (GBs) determine many important properties (e.g., mechanical, electrical, corrosion resistance) of crystalline materials. Techniques to control and improve material properties frequently involve thermally activated GB migration. Although considerable progress has been made in characterizing and understanding GB migration, the underlying atomic-scale mechanisms remain largely unknown [1,2]. In metals thermally activated GB mobilities are sensitive to small amounts of impurities and can differ by several orders of magnitude as a function of GB geometry. Understanding this dependence on structural variables has been a long-standing problem. It was first proposed by Mott that cooperative motions by groups of atoms at the GB could lead to greatly enhanced GB mobilities [3]. Molecular dynamics simulations of GB migration in twist GBs have indicated the existence of cooperative motions in GB migration [4,5]. Experimental investigations of the pressure dependence of GB migration have also strongly implied a cooperative mechanism, at least for certain [110] tilt GBs [6]. The results of microstructural investigations of [001] tilt GB migration in Au thin films have been interpreted in terms of a cooperative atomic reshuffling mechanism [7], but have not provided direct experimental evidence at the atomic scale. Atomic-level observations by high-resolution electron microscopy (HREM) observations showed fast motion of a ledge at a general GB, suggestive of cooperative atomic motion [8]. Although strong indications for collective effects come from such observations, unambiguous information regarding the existence of collective mechanisms and a detailed knowledge of the atomic-scale processes and their dependence on GB crystallography has been missing.

In this Letter we show the existence of cooperative atomic motion in GBs observed in real time at the atomic scale by HREM at high temperature. Collective effects are indicated by positional fluctuations of the GB as a function of time. The crystal regions that switch their orientation back and forth reversibly between neighboring grains contain up to several hundred atoms.

To be able to study the kinetics of atomic GB migration processes we used thin film samples of Au that contained well-defined high-angle GBs. The GBs typically could be studied at island grains that conveniently allowed observation of all possible GB inclinations for a given misorientation. High-purity films (99.9999% Au) were epitaxially grown by UHV electron-beam evaporation. The specially prepared (110) and (001) NaCl substrates had been partly covered by (110) and (001) seed crystals, respectively, at an in-plane rotation of the desired magnitude to obtain high-angle [110] and [001] tilt GBs [9]. We note that by choosing the same film orientation on either side of the GB, the surface energy should not play a role as the driving force for GB migration. Thus, within a strictly planar GB migration would manifest itself by statistical excursions of GB position.

Electron-transparent sections were prepared by low-energy Ar-ion milling. Since it was desirable to observe the various GB facets at temperatures near $0.5T_m$ (and above), over extended periods of time, the effects of Au surface diffusion and the formation of GB grooves at high temperature needed to be minimized. Therefore both Au surfaces were protected by thin layers (1–2 nm) of SiO_2. The atomic resolution high-voltage electron microscope (ARM) at the Max-Planck-Institut in Stuttgart [10] was utilized for observations at an electron beam voltage of 1250 kV. Video sequences at magnifications of 600 000× or 800 000× utilized a GATAN image intensified camera and were recorded on BETACAM magnetic tape. Subsequently, the tapes were transcribed to the digital DV-NTSC video format (640 × 480 pixels) for analysis. In order to precisely compare HREM recording as a function of time, video processing included digital stabilization to within a small fraction of the interatomic distance in the images.

Figure 1 shows single frames of a video sequence at 30 frames/s of a [110] tilt GB (misorientation $\theta = 14°$) at 893 K. The HREM images can be interpreted in a qualitative way as projections of the atomic structure;

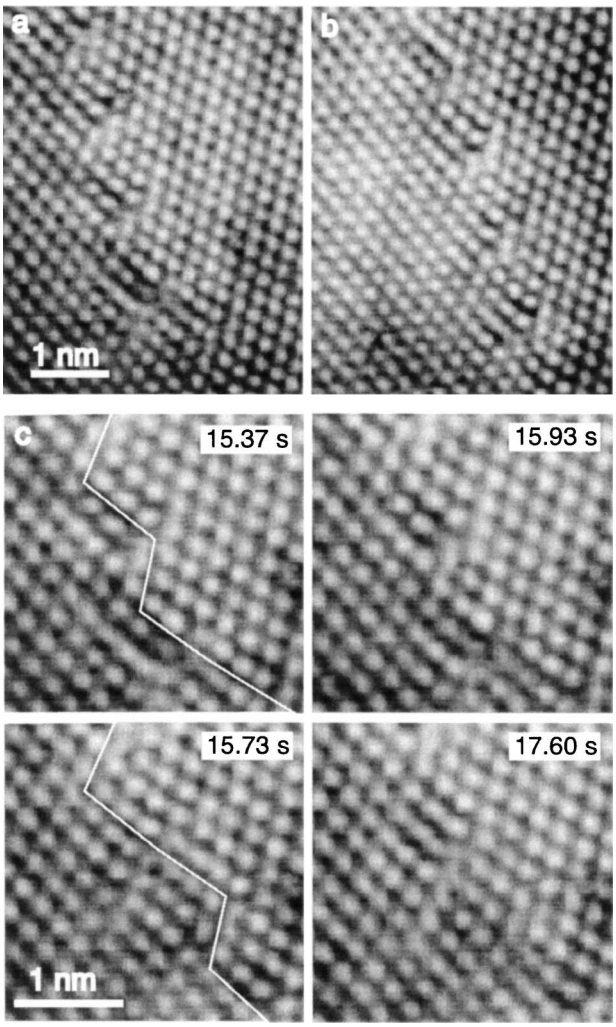

FIG. 1. HREM images of [110], $\theta = 14^\circ$ tilt grain boundary in Au at 893 K. Individual frames from a video sequence recorded near optimum defocus. (a) GB at $t = 15.37$ s. (b) GB has moved to the right at $t = 44.93$ s. GB is near $(6, -6, 1)$ symmetric orientation. (c) Detail of (a) depicted at various times in the four panels. A small region composed of eight atomic columns switches orientation between the two grains. Note stacking disorder and misfit localization at dislocation cores. For a real-time movie see Ref. [17].

white motifs represent atomic columns [11]. Between Figs. 1a and 1b the GB has moved a short distance ($\sim$1 nm). While the GB appeared more or less stationary during most of this sequence, a number of small, rapid GB movements were observed. An example is shown in the panels of Fig. 1c which depict identical regions of Fig. 1a as a function of time. At $t = 15.73$ s a small region at the GB has switched from the right to the left grain as indicated by the white line which has been superposed on the HREM image to guide the eye. In the 3rd and 4th panels of Fig. 1c at $t = 15.93$ and 17.6 s the grains switched back to the GB structures in the earlier panels. We estimate that these reversible fluctuations involved 150 to 300 atoms that switched back and forth between the orientation of the two grains. Since at this temperature such fluctuations were not observed at other facets of this bicrystal we conclude that the orientation of the GB plane plays an important role in activating the mechanism.

A [110], $\theta = 20^\circ$ tilt GB is shown in Fig. 2 near the symmetric $(1, -1, 7)$ orientation. At 823 K substantial fluctuations took place at the GB core. Again, as above, fluctuation effects depended on GB geometry. In Fig. 2 two sets of (111) type planes can be coherently connected across the GB, interrupted only by localized regions of misfit. The competition arising from a multiplicity of possible structures, differing only by the position of the misfit localization, may contribute to the structural instability at high temperature in this case. In contrast, other GBs at this misorientation often are quite stable when the GB plane orientation is such that just one set of (111) planes is coherently connected between grains. The (557) (113) asymmetric tilt GB is an example of such an interface. The latter is characterized by a dissociated GB core formed by a sequence of stacking faults [12]. Although this boundary can move by slip, no reversible fluctuations were observed. We note that [110] tilt GBs often are dissociated [12,13] and may also, such as in Figs. 1 and 2, be associated with bending of lattice planes, indicating a finite width over which the crystal orientation changes.

Figure 3 contains individual consecutive frames of a rapid, reversible fluctuation in a [110], $\theta = 50.5^\circ$ tilt GB at 983 K. A short segment of the (113) symmetric tilt GB is connected to an asymmetrical facet bounded by a (111) plane in the lower crystal. Across the asymmetric facet, (111) planes in the top crystal connect to (002) type planes in the lower crystal. The misfit is accommodated by an extra (002) plane in the lower crystal (see arrow in

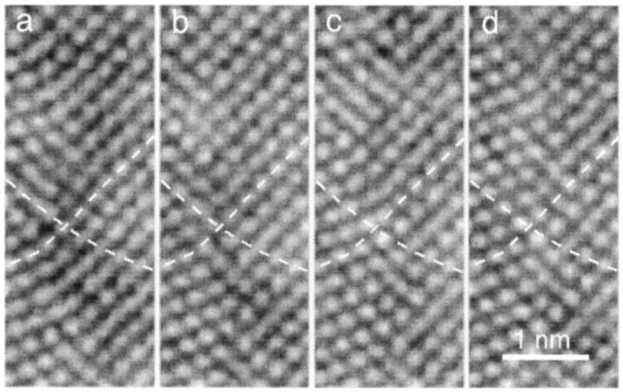

FIG. 2. Structural fluctuations at gain boundary core of Au [110], $\theta = 20^\circ$ at 823 K. (a) $t = 0$ s, (b) $t = 0.87$ s, (c) $t = 7.5$ s, (d) $t = 9.7$ s. Note the coherent connection between two sets of (111) planes across the interface. Two such planes are indicated by dashed lines in (a) and copied into (b), (c), and (d) for comparison. Regions of misfit localization (characterized by disruption of interplanar coherence) are in dynamic motion and alternate between panels. Atomic agitation within (111) planes is indicated by blurred atomic column contrast. For a real-time movie see Ref. [17].

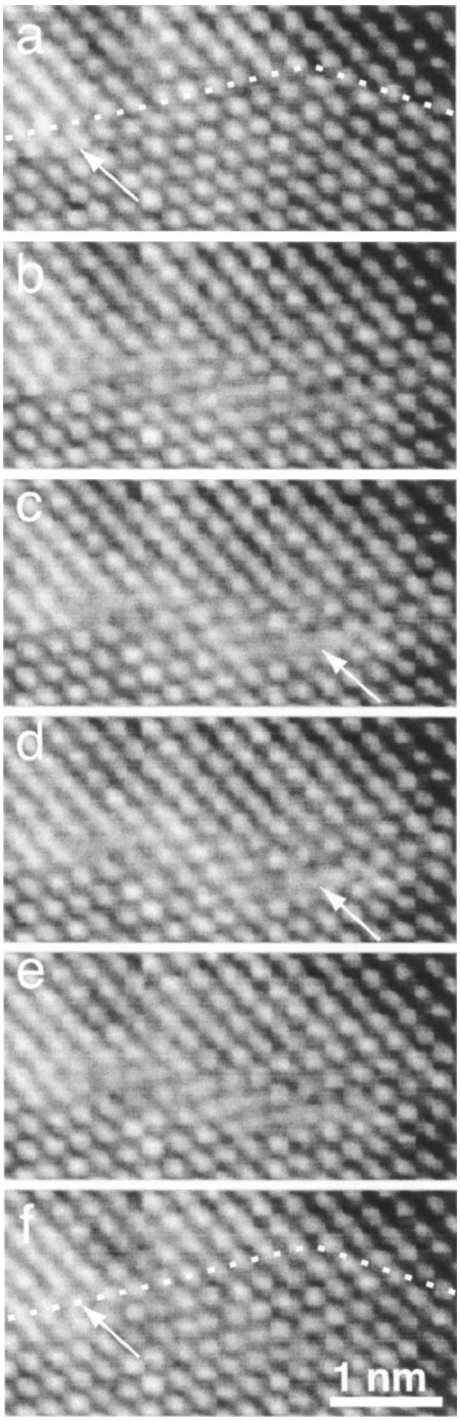

FIG. 3. Time sequence of rapid reversible GB movement in Au [110], $\theta = 50°$ at 983 K. (a) $t = 0$ s, (b) $t = 0.03$ s, (c) $t = 0.07$ s, (d) $t = 0.10$ s, (e) $t = 0.13$ s, (f) $t = 0.17$ s. The initial GB position is indicated by a dashed line in (a) and in (f), when the GB returns to its original location. At intermediate times the GB is surrounded by a region of reduced atomic column contrast, probably due to the high activation of atomic movement near the GB. Arrows point to misfit localizations during GB motion. The degree of coherence between the (002) and (111) planes on the bottom and top, respectively, is best seen when the figure is viewed at a shallow angle in the direction of the arrows. For a real-time movie see Ref. [17].

Fig. 3a). Within 0.03 s the (113) GB has moved close to 1 nm in distance, sweeping a volume of 300 to 700 atoms (Fig. 3b). In the vicinity of the moving GB the atomic column contrast is somewhat blurred (Figs. 3b–3e), suggesting a high level of local atomic agitation. Nevertheless, atomic columns are still clearly defined. Hence, the crystalline lattice seems to be maintained throughout. The coherence between lattice planes crossing the GB is disturbed in Fig. 3b; however, in Figs. 3c and 3d the lattice misfit has moved but is again well localized (see arrows). In Fig. 3e the misfit is delocalized again, just before the GB moves back to its original position in Fig. 3f.

An asymmetrical [001] tilt GB at 573 K is depicted in Fig. 4 indicating in Fig. 4b an excursion on the order of one interatomic distance to the right near the center of the image, returning after a few seconds in Fig. 4c to its original position. This movement would have involved on order of 100 atoms.

The reversible GB fluctuations observed here in various tilt GBs must have affected up to several hundred atoms and are a clear indication for the cooperative motion of groups of atoms. Martensitic transformations similarly involve small, cooperative motion of many atoms [14]. Such transformations are driven by the lower free energy of the product phase. In contrast, collective effects in GB migration involve no intrinsic change in free energy. Therefore, in the absence of a driving force for GB migration truly reversible spatial fluctuations can occur.

The island model of GB migration involves the action of small groups of atoms that would be attached as proposed by Mott [3], possibly by melting and solidification, to the growing crystal. However, the present observations indicate that crystallinity is maintained, at least within the temporal resolution of the experiment. It appears likely that similar to martensitic transformation, small cooperative atomic motions accomplish the necessary lattice rotation. Such collective mechanisms (atomic reshuffling)

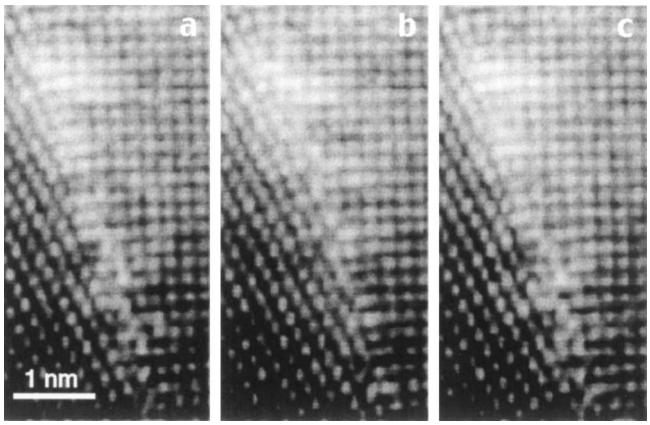

FIG. 4. HREM images of a Au [001], $\theta = 26°$ tilt GB at 573 K. (a), (b), and (c) Time averaged images at an exposure of 0.33 s at $t = 0$, 1, and 4 s, respectively. For a 10× time-lapsed movie see Ref. [17].

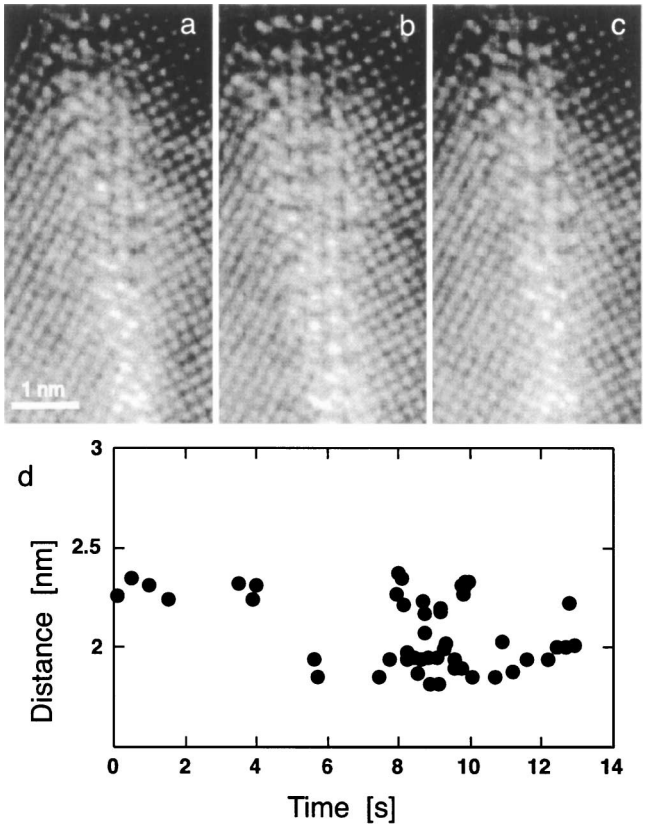

FIG. 5. Structural fluctuations in a general GB in Au [001], $\theta = 36°$ at 663 K. (a), (b), and (c) depict an identical area from a video sequence at 8.03, 8.47, and 9.8 s, respectively. Viewed along [001], the inclined GB gives rise to Moiré fringes due to overlapping crystalline lattices in the direction of the electron beam. The bands of approximately sinusoidal contrast modulations that run vertically across the center of the image indicate the projected area of overlap of the two crystals. The changes of width and position of the fringe patterns reflect temporal changes of the inclined GB plane. (c) A plot of the position of the fringe pattern (distance of left edge from the border of the original video frames) as a function of time. For a real-time movie see Ref. [17].

have been proposed, based on experimental observations [6–8] and atomistic simulations [4,5].

GB fluctuations can also occur in general GBs, i.e., GBs with finite twist and tilt components, as in Fig. 5, which shows the temporal behavior of an inclined GB at 663 K. The band of Moiré fringes changes its position and width as a function of time, indicating a change in GB plane with time. The position of the left-hand edge near the center of the image is displayed in Fig. 5d, showing movements on the order of 0.5 nm.

Collective atomic motion has been a long-standing issue in mechanisms of GB migration. In the temperature regime where GB migration takes place we have shown the existence of reversible GB fluctuations that involve up to several hundred atoms. The fluctuations depend on GB structure and may be influenced by the presence of defects, such as stacking faults, steps, and misfit dislocations. During the transformation that produces the appropriate lattice rotation of small groups of atoms, crystallinity appeared to be maintained. Collective effects involving groups of atoms may also play a role in the dynamics of other solid state processes [15,16]. Elucidating the role of GB geometry in activating collective effects in GB migration will require development of atomistic models of possible pathways taken by cooperative atomic motions.

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*Corresponding author.
Email address: merkle@anl.gov

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[17] See AIP Document No. EPAPS: E-PRLTAO-88-019223 for Quick Time movies Q1 to Q5 corresponding to Figs. 1 through 5, respectively. This document may be retrieved via the EPAPS homepage (http://www.aip.org/pubservs/epaps.html) or from ftp.aip.org in the directory /epaps/. See the EPAPS homepage for more information. Note that the movies are highly compressed compared to the original video recordings. Except for Q4 at 3 frames per second (fps), the movies are real-time at 30 fps. The movies allow viewing of somewhat larger areas than what is printed in the figures.