

Imaging Single, Individual Molecules

Investigator: J. Zuo, MRL, University of Illinois

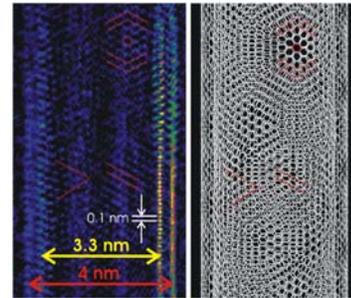
By using a tightly focused, highly coherent beam of electrons – and carefully reconstructing images from the electron scattering, or diffraction, data – the ability to determine the exact atomic positions in an individual carbon nanotube has been demonstrated. Other techniques based on x-ray, neutron, and electron scattering typically average over many repeating units, or many molecules, to obtain average atomic positions. By making the interrogating electron beam less than a nanometer (five to ten atomic spacings) in diameter, it is possible to get diffraction information from individual molecules. If the beam is sufficiently coherent, appropriate treatment of the diffraction data can allow reconstruction of images of high resolution and high contrast. This has been shown by solving the structure of a single, specific double-walled carbon nanotube – a complicated problem, as it consists of one tube nested in another, each having a different helical pitch. The technique has the potential to allow imaging of atomic arrangements in individual non-periodic structures, such as biological macromolecules.

Reference: J. M. Zuo, I. Vartanyants, M. Gao, R. Zhang, and L. A. Nagahara, *Science* 300, 1419 – 1421 (2003).

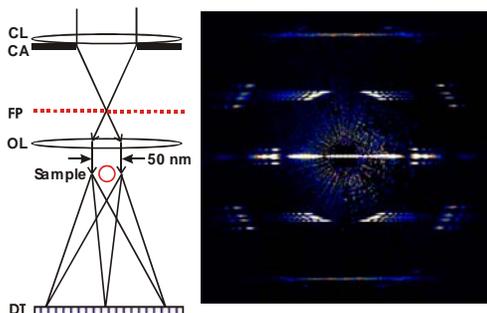
Imaging the Structure of a Single Macromolecule

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The ability to directly image the atomic-scale structures of single molecules would enable significant advances in many areas of technology and engender revolutionary new understandings in the materials and biological sciences.



The reconstructed atomic resolution image of a double wall carbon nanotube and a structure model. *Science* 300, 1419 (2003)



(left) A single double wall nanotube is illuminated with a narrow beam of electrons. (right) The diffraction pattern of the tube

Research at the University of Illinois has led to the development of an advanced new application of electron microscopy that uses data from coherent electron diffraction to construct such structural images. The team has successfully reconstructed the image of a double wall carbon nanotube and determined the atomic-scale structures of both inner and outer tubes.

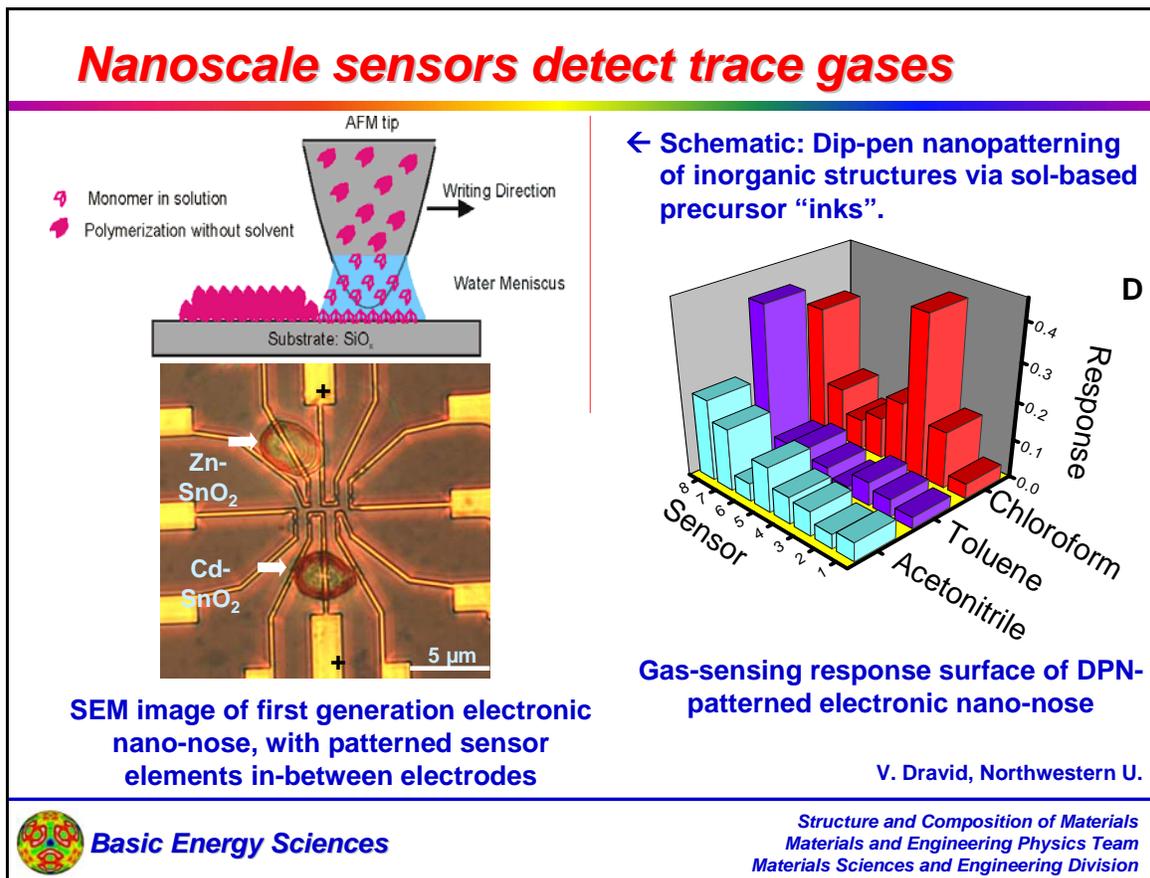


An Electronic "Nose" for Sniffing Out Gases

Investigator: V. Dravid, Northwestern University

Nanoscale disks of tin oxide with various additives are sensitive to specific gases, and combining them in arrays provides a reliable and discriminating detector. The disks are deposited by a dip-pen lithography technique using an atomic force microscope. The process uses standard silicon substrates and semiconductor patterning techniques for forming the connecting electrodes. The nanodisk sensors undergo measurable, reproducible, and proportionate changes in resistance when exposed to trace quantities of gases. An initial array with eight disks has shown that individual gases elicit particular patterns of response of the chemically distinct sensor units. Acetonitrile, toluene, and chloroform were readily discriminated. The gas recognition ability, instant response and rapid recovery, compact size, and integration with the established microelectronics platform are critical advantages of this technology.

Reference: M. Shu, S. Li, and V. P. Dravid, invention disclosure, Northwestern University (2003).



Structural Rules Developed for Atomic Arrangements at Oxide Surfaces

Investigators: L. Marks and N. Erdman, Northwestern University

The oxides known as perovskites have useful ferroelectric, magnetoresistive, and charge transport properties and applications in catalysis and thin film growth. While their bulk structure is well known, structural rearrangements of atoms on their surfaces are more difficult to understand. Recent work has employed transmission electron microscopy methods to specify the atomic positions, coordinations, and bonding configurations at surfaces of one representative material, strontium titanate. Using a combination of diffraction and high resolution imaging techniques with sophisticated filtering, several observed surface structures were shown to contain edge-sharing units of titanium-oxygen polyhedra. The assemblies of these structures are analogous to the creation of "block structures" in other oxides such as niobia. The derived bonding and structural motifs are consistent with bulk chemical concepts, and so these may be applied in combination with other standard principles (such as minimization of surface dipoles, and maximization of atomic coordination) to the prediction and understanding of oxide surface structures.

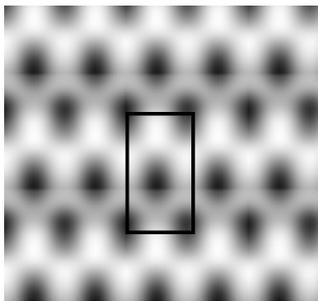
Reference: N. Erdman, et al., *Nature* 419, 55 (2002).

Electron Microscopy Clarifies Structural Motifs and Bonding at Surfaces of Oxides

L. Marks and N. Erdman, Northwestern University

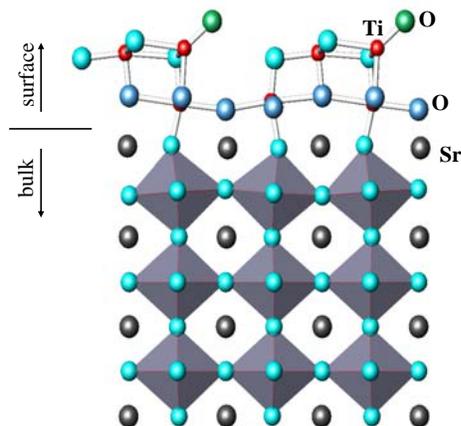
An important frontier in solid-state inorganic chemistry is the prediction of surface structure of an oxide. A solution of the 2×1 SrTiO₃ (001) surface structure was obtained through a combination of high-resolution electron microscopy and theoretical direct methods. Results indicate that surface rearrangement of TiO_{6-x} units into edge-sharing blocks determines the SrO-deficient surface structure of SrTiO₃.

High resolution electron microscopy



Surface image of SrTiO₃ - dark features correlate with Ti atoms on surface (unit cell marked). Image width is 1.6 nm.

DFT-constructed surface



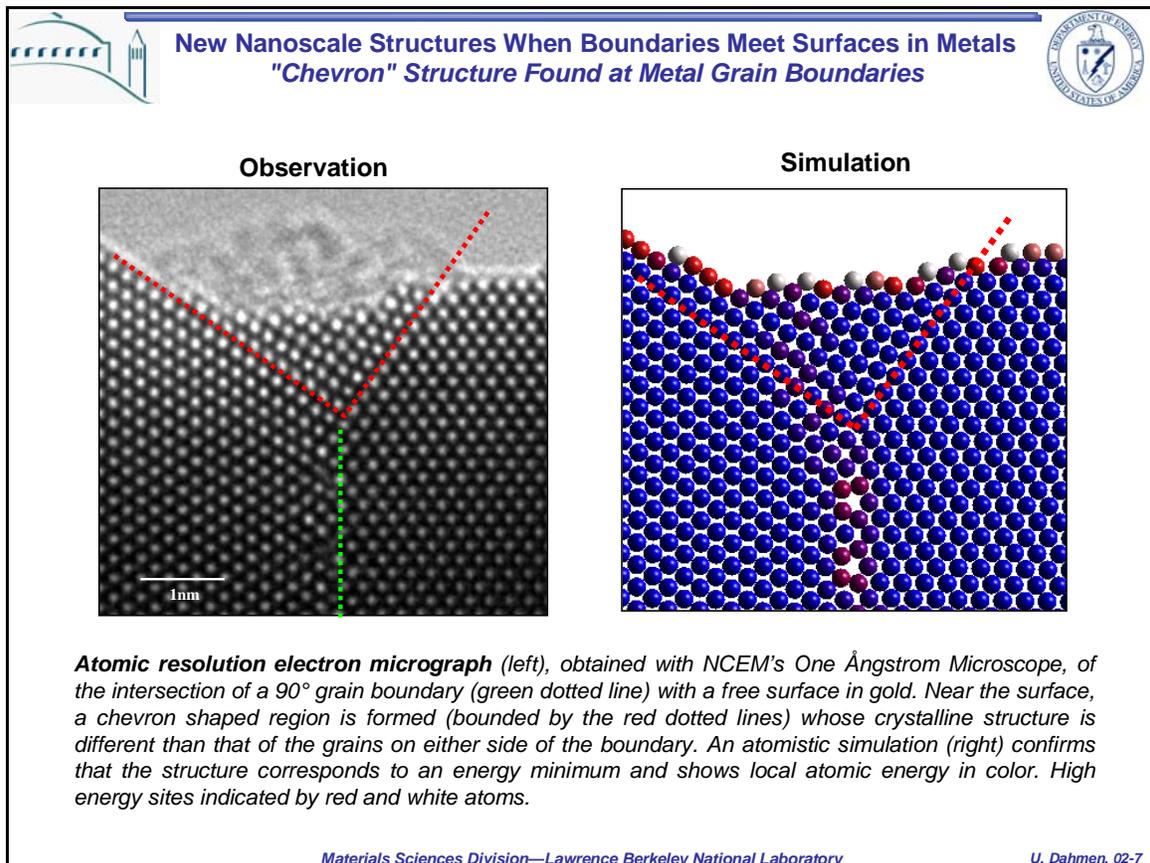
N. Erdman, et al. *Nature* 419, 55 (2002)

New Nanoscale Structures When Boundaries Meet Surfaces in Metals

Investigator: U. Dahmen, Lawrence Berkeley National Laboratory

A newly discovered type of nanoscale “defect” may be connected to unusual behavior of metal catalysts and thin films, which are critical to the chemical and electronic industries. Where two grains (individual crystallites) touch each other is known as a grain boundary. A distinct linear region, or channel, with a V-shaped cross section has been discovered along the intersection of a grain boundary with an external surface. Atomic-resolution observations of gold surfaces using a state-of-the-art electron microscope, and related atomic-scale simulations, show that this channel has a different crystal structure than the remainder of the material. One implication is that when the grains become sufficiently small, these channel regions may dominate the surface and result in very different reactivity and catalytic activity than expected based on the bulk structure. These channel defects may also pin grain boundaries, slowing or preventing their motion and affecting the processing of thin films for microelectronics. Furthermore, the channels can be thought of as naturally occurring solid nanoscale wires along the surface of a material, whose arrangement could be controlled by appropriate processing.

Reference: T. Radetic, F. Lançon, and U. Dahmen, *Phys. Rev. Lett.* 89, 085502 (2002).

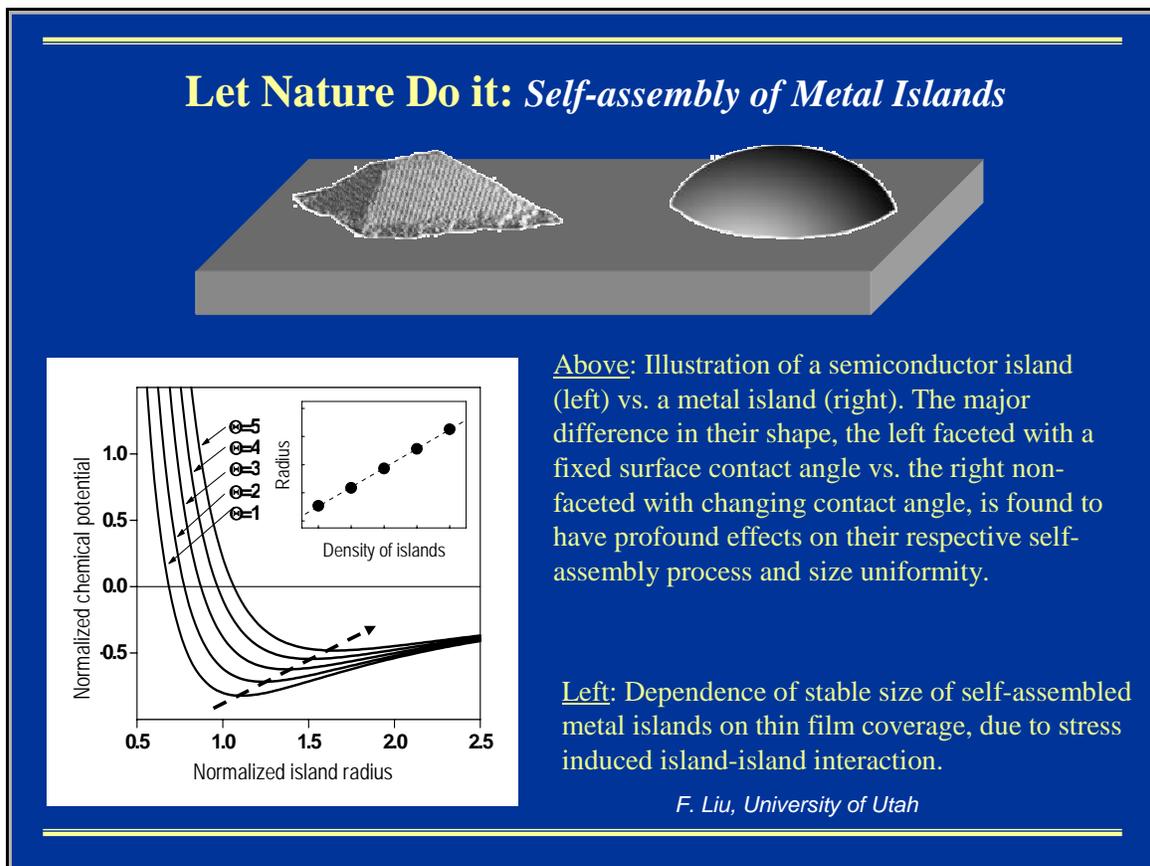


Let Nature Do It: Self-Assembly of Uniform Metal Islands

Investigator: F. Liu, University of Utah

Nanotechnologies of the future will demand the creation of large arrays of nanostructures, such as quantum wires and quantum dots, with uniform size and spacing. One approach to the creation of such arrays is to let nature do it, by self-assembly of three-dimensional (3D) islands in heteroepitaxial growth. Remarkable size uniformity has been achieved for the growth of both 3D elemental and compound semiconductor islands. However, the size uniformity of 3D metal islands is less common and generally harder to achieve. A mechanism of growing uniform 3D metal islands has now been demonstrated. A new model was proposed for the growth of 3D metal islands on insulator substrates with an additional term of island edge energy. The existence of such an island edge effect makes the island shape dependent on island size and induces self-assembly of islands with uniform size. It provides a general scheme of nanofabrication for creating uniform sized 3D metal islands.

Reference: *Phys. Rev. Lett.* 89, 246105 (2002).



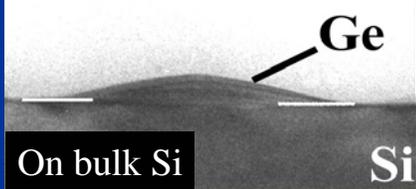
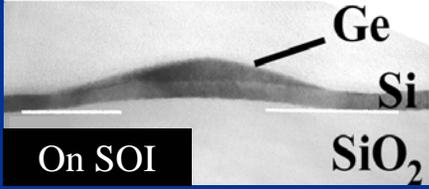
Nanostressor: Reshape Materials at Nanoscale

Investigator: F. Liu, University of Utah

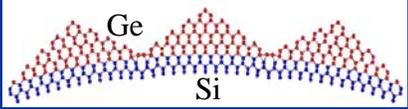
At the nanometer scale, structures made from ostensibly hard materials like silicon (Si) could start to look surprisingly 'soft' when exposed to nanostressors. Si is the ubiquitous material used for electronic devices. As the size of devices continues to shrink toward the nanometer scale, properties of the nanometer Si thin film depart from the bulk form. This work demonstrates a novel idea of using nanostressors to tune the properties of Si thin films at the nanometer scale. When germanium (Ge) islands grow on Si that rests on an insulator substrate, the stressful Ge islands, acting as nanostressors, reshape the ultra-thin Si film in a dramatic fashion, inducing an anomalously large and localized bending of Si film underneath the Ge islands, which in turn modify the large and local electronic and optical properties of Si. Such effects are expected to occur generally in any solid thin film and become more prominent as semiconductor devices shrink to ever smaller scales.

Reference: *Phys. Rev. Lett* **89**, 136101 (2002); *Phys. Rev. Lett* **89**, 136101 (2002); *Nature Materials* Research Highlights, Sept. 2002 September 2002 Nanotechnology News (www.nanotechnow.com/2002-september-news.htm).

Nanostressor: Reshape Materials at Nanoscale


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Cross-sectional TEM image illustrating the function of a nanostressor (Ge dot): reshaping the underlying Si lattice at the nanometer scale with anomalous large local bending and hence modifying the local electronic properties of Si on SOI substrate (right), in contrast to normal conditions on bulk Si substrate (left).


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Molecular dynamics simulation demonstrating a transition from the extended bending mode (left) to the localized bending mode (right) of nanometer thin Si layer induced by Ge quantum dots with decreasing Ge dot density.

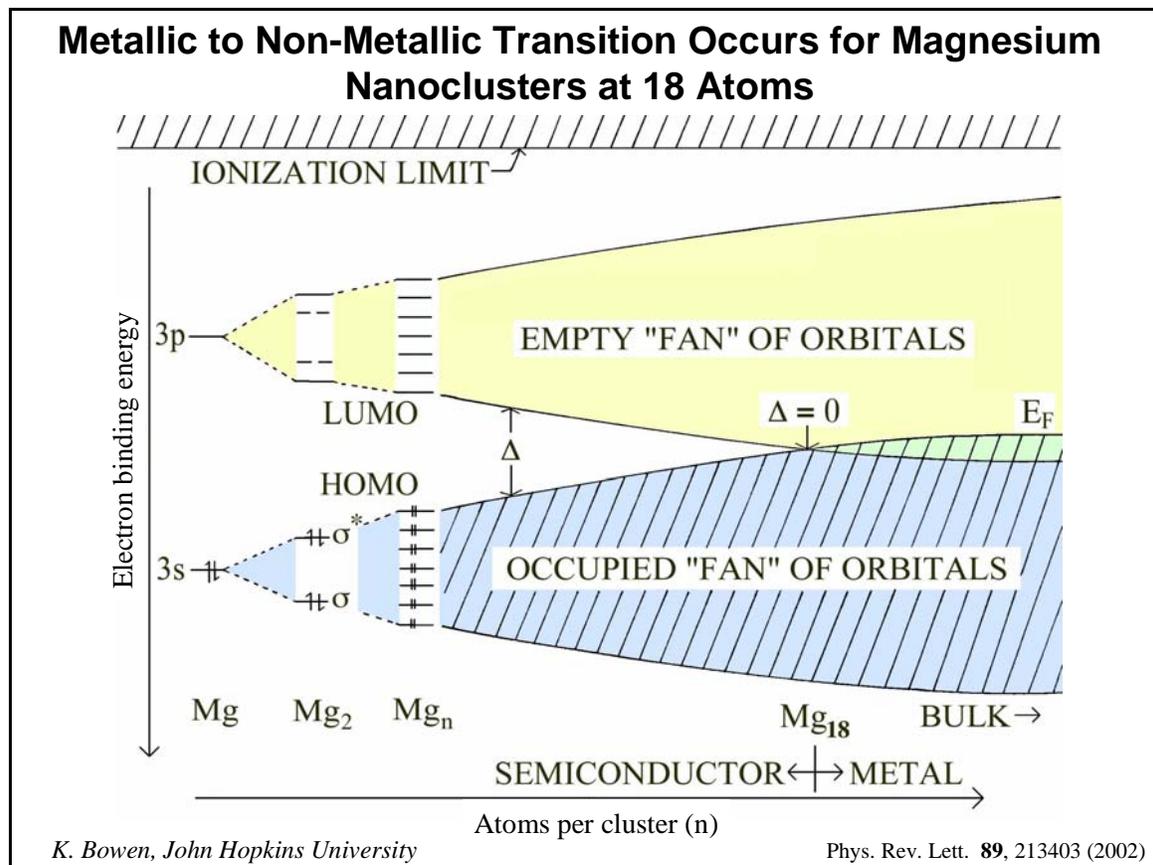
F. Liu, University of Utah

Nano-clusters: At What Point Does Metallic Magnesium Become Non-Metallic?

Investigator: K. Bowen, Johns Hopkins University

A collection of metal atoms does not necessarily exhibit metallic behavior. In the case of magnesium clusters, complimentary experimental and theoretical work reinforce one another that the transition to a non-metallic state occurs when the cluster size reaches 18 atoms. The experimental portion of this work measured the anion photoelectron spectra of these species. The s-p band gap was observed to open at 18 atoms, signaling the onset of non-metallic behavior. Electronic shell structure was also implicated by gap "reopenings" and mass spectral "magic numbers". The theoretical component of this work computed the s-p band gaps measured in the experiment, including the observed shell effects. The agreement between these experiments and theoretical calculations was excellent, with each providing valuable insight to the other.

Reference: (1) K. H. Bowen et al, *Phys. Rev. Lett.* 89, 213403-1 (2002); supported by Materials Sciences and Engineering Division (2) J. Jellinek et al, *Phys. Rev. Lett.* 89, 213402-1 (2002) supported by Chemical Sciences, Geo-sciences, and Bio-sciences Division.



Atoms Do the Shuffle

Investigator: K. Merkle, Argonne National Laboratory

Although grain boundaries in complex polycrystalline materials play a pivotal role in controlling their mechanical and physical behavior, the mechanism of grain boundary motion in response to external stimuli has been an unsolved mystery. For the first time, direct observations of grain boundaries at high temperatures confirm the crucial role played by the collective motion of small groups of atoms. In an elevated temperature high-resolution transmission electron microscopy investigation of bicrystal gold films, it was found that certain nanoscale regions at grain boundaries, typically involving up to several hundred atoms, switch back and forth between neighboring grains. Such cooperative grain boundary motion was first suggested by Sir Neville Mott in 1940, but has not been confirmed until now. This observation suggested that, rather than being due to alternate melting and solidification of small groups of atoms, grain boundary motion is caused by fully reversible atomic reshuffling. This new fundamental understanding will have significant implications on developing reliable grain boundary models for predicting grain boundary mobility and microstructural stability, and could ultimately enable the design of grain boundaries so as to optimize the mechanical and physical behavior of materials for use in advanced energy-related applications.

Reference: *Phys. Rev. Lett.* 88, 225501 (2002); *Nature Materials* Research Highlights, May, 2002.

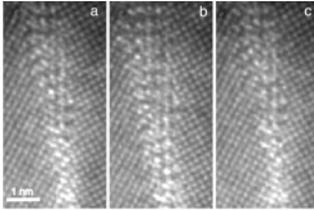
Atoms do the shuffle

Grain Boundary Migration at elevated Temperatures:

- ◆ Necessitates a change in crystal orientation.
- ◆ Depends on relative orientation of grains.
- ◆ Has long been speculated to involve **collective atomic motions**.

High-Resolution Transmission Electron Microscopy reveals Migration Kinetics at the Atomic Scale:

Fully reversible spatial fluctuations show the existence of collective effects in grain boundary migration.

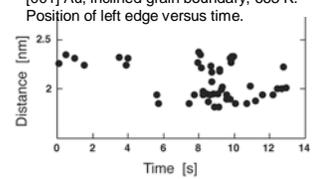


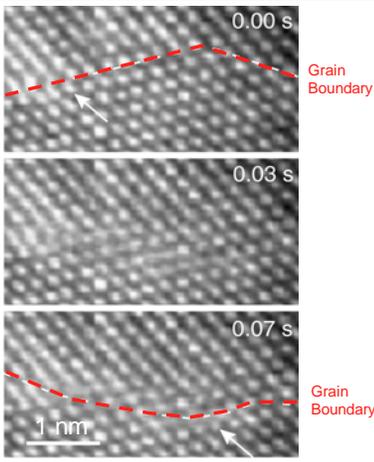
Summary

Cooperative atomic shuffles whose individual movements are small, but involve hundreds of atoms, can rapidly advance a grain towards its neighbor.

These results are of key importance for understanding grain boundary mobility and designing improved materials properties.

[001] Au, inclined grain boundary, 663 K.
Position of left edge versus time.





Grain Boundary

Three consecutive video frames of a gold [110] tilt grain boundary (GB), misorientation 50°, at 983 K. The rapid back-and-forth movements of the GB occurred numerous times and involved collective shuffles of about 700 atoms. The arrows indicate a misfit localization at which the connection between the atomic planes crossing the GB is disrupted.

K. L. Merkle, L. J. Thompson, ANL, F. Phillipp (MPI Stuttgart)



Basic Energy Sciences

*Structure and Composition of Materials
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