Spotting the Atoms in Grain Boundaries

To know how the boundaries between crystals affect polycrystalline structural and electronic materials, it is necessary to know quantitatively where the atoms are

THE mechanical and electronic properties of polycrystalline materials can depend dramatically on the boundaries between neighboring regions of different crystallographic orientation, that is, on the grain boundaries. Until recently, however, materials scientists have been unable to see where the atoms in grain boundaries actually reside, which is the essential information needed for deciphering exactly how these interfaces exert their sometimes dominating influence.

Now, thanks to the availability of improved instruments and powerful computer image simulation and processing techniques, high-resolution transmission electron microscopy (HRTEM) is beginning to provide atomic-level peeks at the structure of grain boundaries in semiconductors, metals, and ceramics. Not only do the images strikingly illustrate structural features of grain boundaries, but, with the aid of the computer simulations, they can also yield quantitative information on atomic positions with an accuracy of 0.2 angstrom or so, says William Krakow of the IBM Yorktown Heights Laboratory, who has been imaging grain boundaries in gold.

The complementary technique of x-ray diffraction potentially can give atomic positions in grain boundaries to even better accuracy, but it requires an intense source of x-rays if the weak two-dimensional diffraction pattern is to be seen. X-ray diffraction also requires that the grain boundary structure be periodic over a considerable distance, whereas HRTEM can deal with grain boundaries that are not so homogeneous. Stephen Sass of Cornell University, where there is both a new high-resolution electron microscope and a synchrotron radiation x-ray source, expects the merits of the two techniques to be clarified over the next couple of years.

Advanced ceramics provide one reason why materials scientists would like to know the structure of grain boundaries. Structural ceramics that are made of inexpensive, readily available materials and that can maintain their strength at temperatures well above the melting point of exotic and expensive metal alloys are of obvious interest. However, the mechanical properties of candidate materials sometimes degrade at temperatures lower than expected because of a glassy phase that forms at the grain boundaries when powders are compacted at high temperature to form a dense body.

In metal alloys, such as steels, grain boundaries can manifest a similarly negative influence by attracting minority alloying elements. Segregation of alloying elements in this way reduces the strength of the grain boundary and makes the alloy susceptible to brittle fracture. And, because of the relatively large atomic spacings that occur there, grain boundaries are ready conduits for the enhanced diffusion at comparatively low temperatures of foreign or alloying elements in polycrystalline materials. It is believed, for example, that grain boundary diffusion is a cause of the failure of electrical contacts and conductors in integrated circuits.

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The study of grain boundaries goes back decades. Materials scientists recognize two basic types, twist and tilt boundaries, although generalized combinations of these also occur. The lattice on one side of a grain boundary is rotated with respect to that on the other. The rotation for a twist boundary is around an axis perpendicular to the interface, whereas the rotation for a tilt boundary is around an axis parallel to the interface. One can visualize these boundaries easily with a simple cubic lattice.

In any case, HRTEM works well only for tilt boundaries because of the way images are formed. HRTEM depends for image contrast on the interference between electron beams diffracted from different crystallographic planes and the undiffracted or direct beam. When the specimen is oriented so that its atoms are arrayed in columns parallel to the direct beam, the microscope generates a so-called lattice image that looks like a two-dimensional projection of the crystal structure along the direction of the direct beam.

Usually a tilt boundary to be imaged is chosen or specifically prepared so that the tilt axis is an important crystallographic direction, such as a cube edge, diagonal, and so on. In this case, the atoms on both sides of the boundary remain in well-defined columns when the boundary is viewed edge on and the tilt axis is parallel to the direct electron beam. It is, in general, not possible to maintain this condition with twist boundaries.

All other factors being equal, the resolution in HRTEM varies as $E^{-3/8}$, where E is the electron beam energy. The resolution obtainable with the previous generation of transmission electron microscopes with a beam energy of 200 kiloelectron volts (keV) is 2.3 angstroms or worse, depending on the quality of the objective lens. The newest 300- and 400-keV instruments do much better with guaranteed resolutions of better than 2 angstroms.

According to Alain Bourret of the Grenoble Center for Nuclear Research in France, who pioneered HRTEM investigations of grain boundaries in semiconductors, the new generation of microscopes will dramatically broaden the variety of materials that can be examined. The critical factor is the minimum spacing between the columns of atoms in the projected crystal structure. For interpretable images, these spacings cannot be smaller than the resolution of the microscope. The new microscopes therefore permit imaging materials, metals in particular, whose lattice spacings are less than the resolution of the older instruments. They also permit use of projections prohibited in the past because of small spacings between atom columns.

It is because of the limited resolution of the 100- and 200-keV microscopes available to them that Bourret and his collaborators have concentrated on the semiconductor germanium, which has larger spacings than metals in the following special sense. Germanium has the diamond cubic structure. When projected along the diagonal of a cube face (<110> projections), the atom col-

umns lie in pairs. The two columns in a pair cannot be resolved, but the neighboring pairs are readily distinguished as they are more than 3 angstroms apart. The column spacings in most other projections are too small to resolve, although <100> projections along a cube edge are just feasible.

So far, electron microscopists have not solved any materials science problems with their HRTEM images of grain boundaries, but they are verifying some of the concepts introduced by theorists to explain grain boundary structures. They have also been surprised on several occasions.

In analyzing the structure of tilt grain boundaries, the basic variable is the rotation angle between comparable lattice planes on each side of the boundary. In models of small-angle tilt boundaries, most of the atoms are common to the lattices on both sides of the boundary. As the angle increases, the grain boundary structure becomes more complicated, and fewer of these coincidence sites remain. However, at certain tilt angles, the fraction of coincidence sites jumps, giving rise to a symmetric and periodic boundary structure. Almost 30 years ago, J. Hornstra of the Philips Research Laboratories in Eindhoven, The Netherlands, devised geometric models for some of these special tilt boundaries.

Theoreticians, including Walter Bollmann of the Battelle Institute in Geneva, Switzerland, expect that the configurations at these high-coincidence angles have lower energy than others and therefore tend to be the ones that occur in nature. According to the structural unit theory of Adrian Sutton of the University of Oxford and Vaclav Vitek of the University of Pennsylvania, for example, the structure of a high-coincidence-angle tilt boundary comprises a repeating sequence of polyhedra (the structural units) whose vertices are the atoms in the boundary region. A tilt boundary at an angle intermediate between two high-coincidence angles contains a mixture of polyhedra associated with these angles. These structures may also incorporate deviations from periodicity (secondary relaxations) due to the presence of defects, and shifts (rigid body translations) of the lattice on one side of the boundary with respect to that on the other.

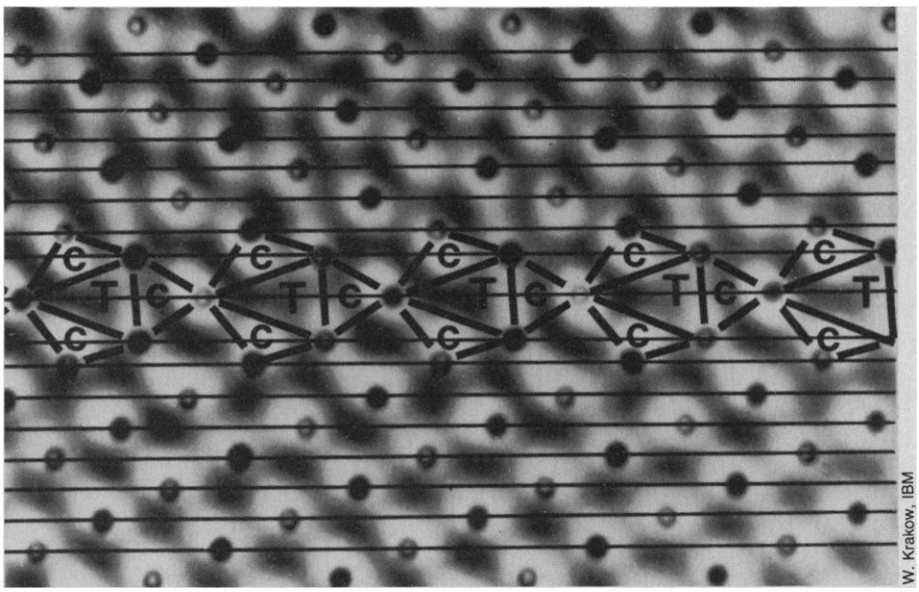
At Grenoble, Cecille d'Anterroches and Bourret have shown that these ideas are qualitatively correct for some tilt boundaries in germanium. They prepared a series of four germanium bicrystals, each containing a single tilt boundary with a specified rotation angle and tilt axis. Computer image simulation is an important part of their HRTEM technique. Although an image looks like a projection of the crystal structure, it is by no means certain that spots in the image actually correspond to the positions of atom columns.

Interpretation of images becomes increasingly problematic as the spacing between atom columns drops toward the resolution of the microscope and as the thickness of the specimen increases to much beyond 100 angstroms or so. Moreover, that grain boundaries are defects that interrupt the periodicity of the crystal lattice further complicates affairs. The solution is to compute the image expected for a model structure, compare it with the actual image, modify the model if necessary, and so on until a good match between simulated and actual images is obtained. The model giving the best match is presumed to be the actual structure. In their study of a symmetric tilt boundary with an angle of 38.9°, for example, d'Anterroches and Bourret found that the image agreed with the geometric model of Hornstra provided that a 0.3-angstrom expansion perpendicular to the grain boundary was added.

Last year, Bourret and Jean-Jacques Bacmann published a review of several investigations of tilt-boundary structure in germanium that were carried out at Grenoble. In general, they reported, the boundaries prefer the periodic configurations associated with the special high-coincidence angles and will go to great lengths to adopt them. Boundaries nominally at orientations requiring other configurations will, for example, decompose into periodic sections separated by defects, such as atomic steps. Or they will develop facets in such a way that the preferred configurations can be adopted on the facets. More recently, the French researchers reported a still more extreme example of the preference for periodic structures with low energy in which an initially high-energy tilt boundary split apart to form three boundaries surrounding small triangular crystalline areas (microcrystals).

Because the lattice spacings in metals are smaller than in semiconductors, most electron microscopists interested in HRTEM of grain boundaries have avoided them. Nonetheless, Krakow and David A. Smith of IBM have succeeded in obtaining quantitative positions of atoms in tilt boundaries in gold. Gold is just on the borderline for study with a 200-keV microscope, however. With this instrument, a <110> projection of gold, which has a face-centered cubic structure, looks the same as a projection of germanium, except that the spots represent single atom columns, not pairs, that are 2.4 angstroms apart. Because this spacing is so close to the resolution of the microscope, the IBM researchers had to make maximum use of computer simulations. They also used image-processing techniques to sharpen up the actual images.

One additional electron microscopy wrinkle Krakow and Smith resorted to was the use of the second pass band of the contrast transfer function that describes the performance of the objective lens. Working in the second pass band corresponds to using electron beams diffracted from more closely spaced lattice planes than in the first pass band and therefore enhances the resolution of the 200-keV microscope sufficiently to obtain lattice images of gold, but it also



Gold tilt boundary: *The white spots represent atom columns in this superposition of the computer-processed image of a 26.5° symmetric tilt boundary with a model structure indicated by the black dots. The capped trigonal prism structural units are also indicated.*

makes the instrument much more sensitive to such things as the alignment of the electron beam relative to the specimen. The increased sensitivity complicates the operation of the microscope and requires that simulations be made on a large main-frame computer, says Krakow.

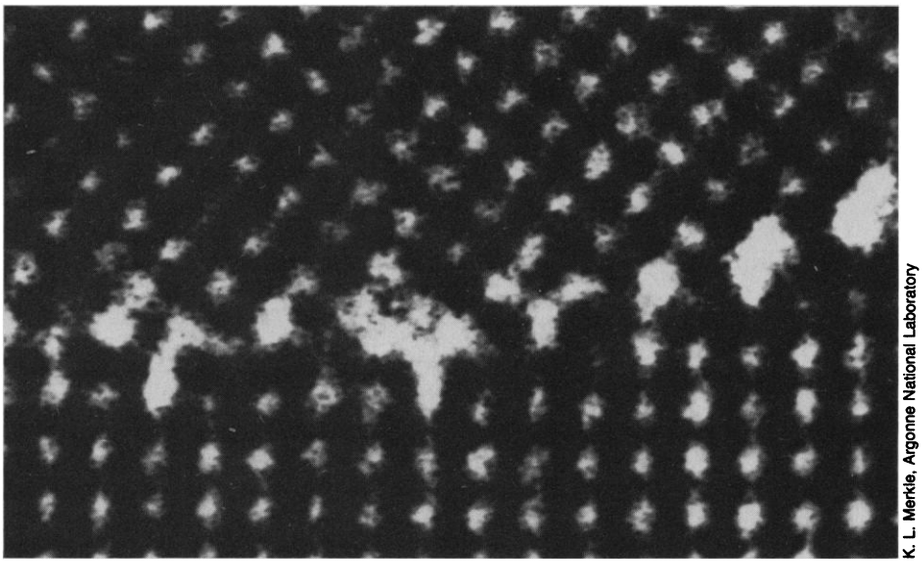
The IBM researchers did not prepare bicrystals with a single tilt boundary, but instead made thin foils containing islands of one crystallographic orientation embedded in a sea of another orientation. The boundary of an island has the same tilt angle all the way around. One of the most thoroughly studied boundaries was symmetric and had a tilt angle of 26.5°. At angles lower than this, tilt boundaries consist of regions of atoms common to both lattices (that is, perfect crystals) separated by stringlike defects called dislocations. In other words, the boundary is an array of parallel dislocations. As the angle increases, the spacing between dislocations decreases until, at about 26°, the dislocations just touch and begin to lose their separate identities.

To determine atom positions in the 26.5° tilt boundary, Krakow and Smith joined with Jeffrey Wetzel of IBM, who calculated the expected positions of atoms by an energy minimization technique. Then they calculated images of this model structure at various values of a microscope parameter called the defocus in order to find the operating conditions under which the calculated image looked like the model. Finally, they compared the computer-processed version of the actual image taken under these conditions directly with the model and found that they also agreed. One of the distinctive features of the boundary is the repeated sequence of polyhedra (capped trigonal prisms) similar to that expected according to the structural unit model (see figure on page 843).

For the numerous other boundaries investigated so far that have lower and higher rotation angles, the IBM researchers took the tack of generating the model structure from the centroids of the spots in the computer-processed version of the actual image of the boundary. If the image simulated from this model matched the actual image, it was assumed that the microscope was faithfully reproducing the actual structure. One particularly interesting boundary investigated in this way had a nominal tilt angle of 27.5°, which is near that of the 26.5° boundary. However, this boundary had a completely different structure, comprising atoms from two crystallographic planes, one on each side of the boundary, that coalesced.

The observation of two structures for almost the same tilt angle and orientation raises the possibility of phase transitions at grain boundaries, which not only would be of interest in their own right, but might also have technological implications if some phases had beneficial properties and materials scientists could control their occurrence.

In the last year or so, several of the new 400-keV microscopes have been delivered to eager electron microscopists. Grenoble now has one, and IBM has one on order. Arizona State University was the first U.S. recipient, and Karl Merkle, John Reddy, and Charles Wiley of Argonne National Laboratory, who started their study of the ceramic nickel oxide with a 200-keV instrument, are now collaborating with David J. Smith and Graeme Wood of Arizona State. Nickel oxide has the cubic rock salt structure in which each positive ion is surrounded by eight equally spaced negative ions and vice versa. In a <100> projection, the atom columns are 2.1 angstroms apart with each column being a 50–50 mixture of nickel and oxygen.



K. L. Merkle, Argonne National Laboratory

Faceted NiO boundary: *The white areas represent the areas between atom columns and show the relatively wide spaces at the grain boundary. The segment of the 38° boundary on the left is asymmetric with the grain boundary parallel to a (100) plane in the lower half of the bicrystal. The segment on the right is approximately symmetric.*

Already in the still young project, the investigators have made several observations of interest. For example, previous conventional transmission electron microscopy experiments had suggested that the region near grain boundaries in pure nickel oxide bicrystals was not crystalline. The HRTEM images demonstrate clearly that crystallinity is maintained up to the grain boundary. The images also show the faceting behavior noted by the Grenoble group for germanium that is motivated by the net energy reduction, even though the grain-boundary length is increased, due to configurations that have lower energy per unit length.

One feature that also stands out in the images is the widespread occurrence of asymmetric structures at the special tilt angles, whereas most theoretical work has concentrated on symmetric structures. Symmetric means that comparable crystallographic planes on each side of the bicrystal make the same angle with the plane of the grain boundary. Asymmetric means that the angles are different. In nickel oxide, there apparently is a preference for the grain boundary plane to be parallel to a cube face [(100) plane] in the rock salt structure. Since this is generally only possible for one side of the boundary, the boundary is asymmetric (see figure on page 844).

Although other groups are also using high-resolution instruments to look at grain boundaries, the number will likely never be large because of the major investments in equipment and people needed to do it productively. The most important factor, IBM's Krakow told *Science*, is assembling a team of two, three, or more researchers who specialize in different aspects of the problem under investigation. ■ ARTHUR L. ROBINSON

ADDITIONAL READING

A. Bourret and J. J. Bacmann, "Atomic structure of grain boundaries in semiconductors studied by electron microscopy (analogy and difference with surfaces)," *Surf. Sci.* **162**, 495 (1985).

W. Krakow, J. T. Wetzel, D. A. Smith, "Observation and interpretation of the atomic structure of a $\Sigma = 19/[110](\bar{3}31)$ tilt boundary in Au thin films," *Philos. Mag.* **A53**, 739 (1986).

K. L. Merkle, J. F. Reddy, C. L. Wiley, D. J. Smith, G. J. Wood, "Atomic resolution studies of tilt grain boundaries in NiO," *Mater. Res. Soc. Symp. Proc.*, in press.