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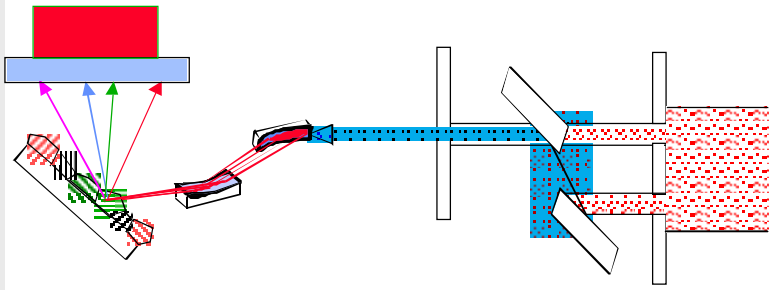
Penetrating, submicron x-ray beams probe the mesoscopic crystalline structure of polycrystalline materials in three dimensions. Crystalline morphology, strain, texture and phase can now be studied nondestructively with a spatial resolution below the grain size of most materials. This new information will lead to a more complete understanding of the mesoscopic structure and dynamics of materials and their relation to materials properties.



3-D X-ray Crystal Microscope**

By Gene E. Ice* and Bennett C. Larson

1. Introduction

Most materials are composed of small single-crystal grains that are packed together in a complicated network of phase and grain boundaries (Fig. 1b). These grains evolve with time due to applied and internal forces that are redistributed and modulated by the anisotropic properties of adjacent grains. Although local three-dimensional grain-by-grain interactions ultimately determine the structural behavior of materials, these interactions have until now been virtually impossible to observe directly; the powerful microscopy tools typically used for determining grain-morphology and structure are either surface limited or require very thin samples. What has been needed is a true 3-D probe of individual grain structure and interactions for nondestructive investigation of polycrystalline structures on mesoscopic length scales of ~0.1-100 μm. Newly developed x-ray microbeam techniques now provide such a 3-D crystal microscope.

X-ray diffraction is one of the few tools that can probe local grain structure, stress and dynamics in three dimensions. Powder diffraction provides a statistical *average* of size, orientation, stress and phase for polycrystalline grains, but individual grain-to-grain interactions are hidden in the powder average.[1] Single-crystal x-ray structural microscopy with 3-D resolution is needed to obtain specific information on individual grains. Initial steps were made in this direction by Kirkpatrick and Baez[2] some 50 years ago using the crossed focusing mirror technique that bears their name, and by Keller and Hirsch[3] in 1952 using small bore capillaries to produce x-ray microbeams. In the mid-1950's, transmission electron microscopy (TEM) revolutionized materials investigations by direct observation of crystal microstructure in thin samples. However, three-dimensional microstructural measurements on mesoscopic length scales (~0.1-100 μm) have taken much longer to develop; true 3-D TEM specimens are not possible and a number of major technical challenges needed to be overcome for x-ray microscopy. For example, focusing sufficient x-ray flux into a submicron beam with adequate collimation for high-resolution diffraction has required the ultra-high brilliance of x-ray synchrotron sources. X-ray brilliance – photons/s/eV/mm^2/mrad^2 – is the figure of merit for x-ray microdiffraction and has increased more than 12 orders of magnitude since the 1950's.[4]

The enormous increase in x-ray brilliance, combined with remarkable advances in x-ray mirrors, Fresnel zone plates,

and refractive lenses as focusing optics, now provides sufficient intensity and angular resolution for x-ray microbeam studies of individual grains in a polycrystalline matrix with submicron resolution. Three-dimensional absorption and fluorescence x-ray tomography has been available with ~0.7 μm resolution for several years. Monochromatic x-ray microbeams with ~0.15 μm resolution have been developed using Fresnel zone plate diffractive optics[5] and even refractive x-ray optics[6] (using multiple lenses) can now produce submicron beams. However, only mirrors are achromatic with the low divergence needed for 3-D crystal structure investigations. White (polychromatic 8-22 keV) x-ray beams as small as ~0.5 x 0.5 μm^2 have been produced using elliptically figured Kirkpatrick-Baez mirror pairs.[7]

In addition to beam intensity considerations, the fact that three-dimensional crystal lattices Bragg-scatter x-rays over tiny angular ranges, further complicates the application of single-crystal techniques to polycrystals with micron sized grains. In general, the probability of Bragg-scattering a monochromatic beam from a randomly oriented crystal grain is about one chance in 10^4; grains must be precisely oriented to fulfill Bragg reflection conditions. Of course, for large single crystals, sample rotations pose no problem because the x-ray beam remains on the single crystal regardless of the crystal orientation. However, as shown in Fig. 1b, in a polycrystalline material the grain from which a Bragg reflection arises cannot be unambiguously identified. Furthermore, the diffracting grain can move out of the x-ray beam by so called "sphere-of-confusion" errors in the sample goniometer or by the inherent rotational movement of grains relative to the x-ray beam penetrating into the sample (typically tens to thousands of microns). To avoid these issues, an alternative approach involving white beams has been developed to allow the study the inter- and intra-granular crystallography of polycrystalline materials without sample rotation.

2. Polychromatic X-Ray Diffraction

The approach that we have taken is outlined in Fig. 1a. In this configuration, a polychromatic (i.e. white) x-ray beam passes by the side of an insertable scanning monochromator[8] and is focused to a submicron spot by a nondipersive Kirpatrick-Baez mirror pair. As the white beam probes the sample, a complete diffraction pattern is generated at an x-ray sensitive CCD for each illuminated grain. The solid angle of the CCD and the bandpass of the incident beam (typically ~8 – 22 KeV) are optimized for ~ 10-20 reflections from a simple FCC lattice. Similar so called "Laue diffraction techniques[9] are routinely used in x-ray laboratories to orient single crystals, but are normally inadequate for high-precision measurements of crystalline phase, texture or strain. In our case, micron size beams, calibrated high precision CCD cameras, and computer indexing and analyses of the diffraction patterns, allow high-precision measurements.

In principle, only four reflections are required to determine the deviatoric strain tensor[9], however, ten or more reflections are used in practice to improve the measurement precision. Fortunately, the deviatoric or shear-strain tensor[1] can be determined directly from the white beam diffraction pattern[9]; the deviatoric strain contains information on the shape and symmetry of the unit cell but does not characterize the absolute volume (dilitation). Interactive computer software analysis programs have been developed to identify and index overlapping diffraction patterns from multiple grains; the deviatoric stress/strain is then determined directly from the white beam diffraction patterns by least-squares fitting of the six components of the deviatoric stress tensor.[9,10] To determine the full stress/strain tensor (including the dilatation) for a grain, the energy of one of the reflections in the pattern is determined by inserting the monochromator into the incident beam and performing an energy scan of the reflection.[8]

At present, the location of individual crystal grains along the beam path can be determined with ~2-5 μm resolution through the use of geometrical triangulation as illustrated schematically in Fig. 1c.[8] The 3-D resolution is linked to the spatial resolution along the beam, and although triangulation procedures can be improved, other methods are presently under development that will provide substantially better depth resolution. Two beamlines based on the general principles described here have been commissioned to date; one at the Advanced Light Source (Berkeley, CA USA)[12] and one at the Advanced Photon Source (Beamline 7-ID APS, Argonne, IL USA). A third such beamline facility is nearing completion at the APS (Beamline 34-ID).

3. Applications

Characterization of buried thin films represent an important class of 3-D measurements that can exploit the penetrating power of an x-ray microprobe without direct depth resolution. For example, metal interconnects in electronic microdevices have been studied with x-ray microbeams to probe the processes associated with stress and electromigration induced voiding in metal interconnect wires.[10] The orientation, stress, and microstructure of these glass passivated metal wires are of particular interest, and Fig. 2, shows a map of inter-and intra-grain orientations in bamboo-like Al wires on a fabricated microchip[10]. Plastic deformation in the form of ~ 0.5 degree intra-grain angular bending can be seen and tensile elastic strains in the range of 0.02 – 0.1% are observed along these 2 micron wide wires. Larger stress/strain levels have been reported in narrower interconnect wires and during electromigration tests.[13,14] Vicinal epitaxy and stress in CeO_2 buffer layers and YBCO high-temperature superconductor

films on cube-textured Ni substrates are further examples of buried layer systems under investigation using this technique.

The greatest potential to be realized from x-ray crystal microscopy is in its capacity to nondestructively probe true three-dimensional structures and to correlate strain and crystal rotations in three dimensions. Fig. 3 shows an example of a 3-D crystal microscope image generated by a white x-ray microbeam that strikes the sample at a 45 degree angle and traverses the planar grain-boundary between grains labeled A and C. The sample is an Al(0.2%)Mg tri-crystal that had been deformed 20% in plane-strain at 200^{o}C [11,15]; the beam enters the sample ~40 μm to the left of the triple-junction and about 30 μm below the grain boundary, as depicted in the figure.

Diffraction spots are present from both grains (A-long arcs and C-short vertical streaks) and strong depth dependent crystal disorientation streaking is evident in the Laue difffaction spots on the CCD image. The rich substructure of the (026) reflection in Fig. 4 indicates the presence of dislocation cell walls that are known to be formed under these deformation conditions. With the aid of custom interactive Laue diffraction analysis software, the individual diffraction features of the deformed Laue spots can be indexed crystallographically using the corresponding diffraction features in various reflections. This makes it possible to determine the local crystal orientation matrices, from which precise (~0.01^{o}) rotation angles and rotation axes between the individual deformation structures can be determined. The expanded views of the (026) reflection (measured at two different detector distances) illustrate schematically the triangulation procedure to determine the depth along the beam of microstructure generating individual diffraction peaks. As mentioned above, this method has already demonstrated ~2-5 μm depth resolution, with a more direct method under development that promises substantially better resolution. When better depth precision is achieved, this procedure will then provide 3-D stress/strain tensor information.

4. Future

Continuing advances in x-ray sources and x-ray optics suggest that microbeams with spatial resolution approaching the diffraction limit will be possible in the not too distant future. Volume elements with 100 nm edges can be envisioned that will allow detailed studies of strain distributions within single grains, near grain boundaries, near cracks and other inhomogeneities. Improved high-speed CCD cameras will accelerate the data collection to the point that quasi-realtime images of evolving polycrysalline dynamics can be anticipated. The massive data collection and analysis requirements (~100-1000 Megapixels/sec) will push technological limits, but such developments will make the 3-D x-ray crystal microscope an indispensable tool providing fundamentally new information for the study of materials microstructure and evolution.

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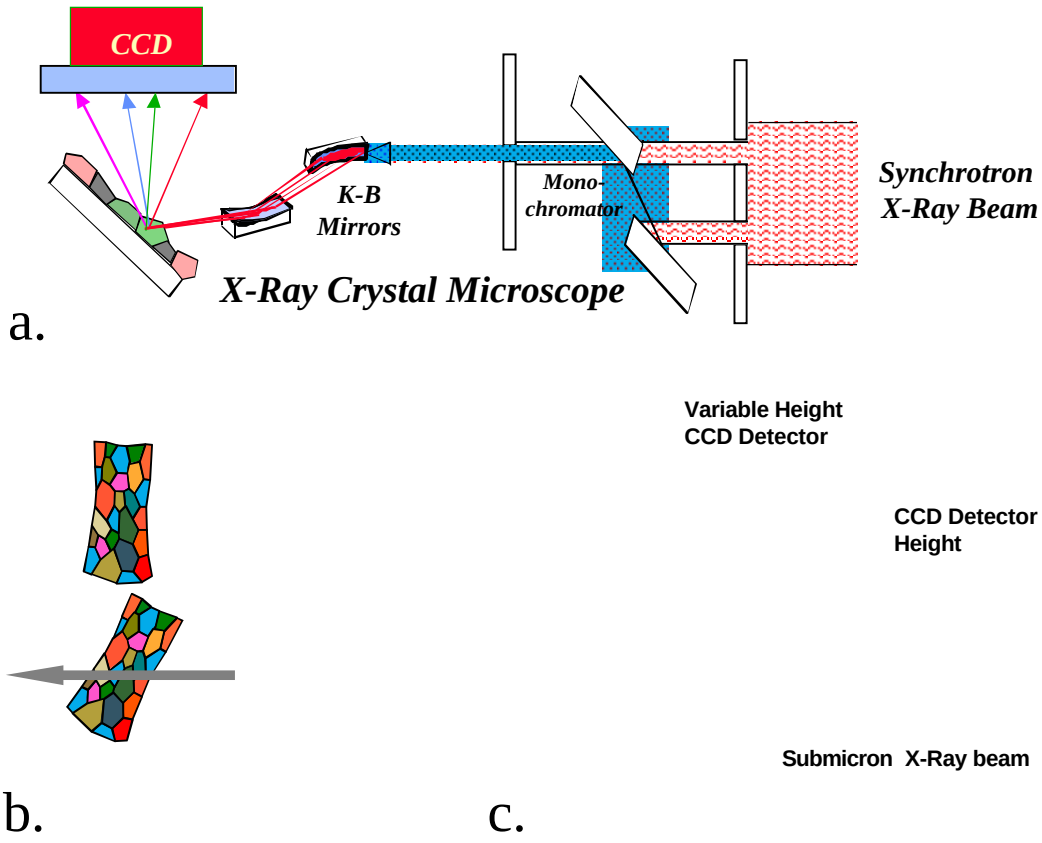

Fig. 1 (a). Components of a 3-D x-ray crystal microscope utilizing white x-ray microbeams: broad bandpass synchrotron x-rays (or x-rays monochromated by an (insertable) double crystal monochromator) are focused by nondispersive Kirkpatrick-Baez mirrors to submicron sizes at the sample position. The diffraction pattern is collected by a high-precision CCD x-ray detector for computer analysis and storage. (b) Penetrating x-ray beams intercept many grains as they traverse a polycrystalline sample. White beam diffraction or scanning monochromatic beam diffraction do not require sample rotation for diffraction measurements and therefore avoid changes in the grains positioned in the measurement volume that are inherent with goniometer rotations and sphere of confusion errors associated with diffractometer rotations. (c) Spatial resolution along the beam is achieved by triangulation using measurements at several detector positions.

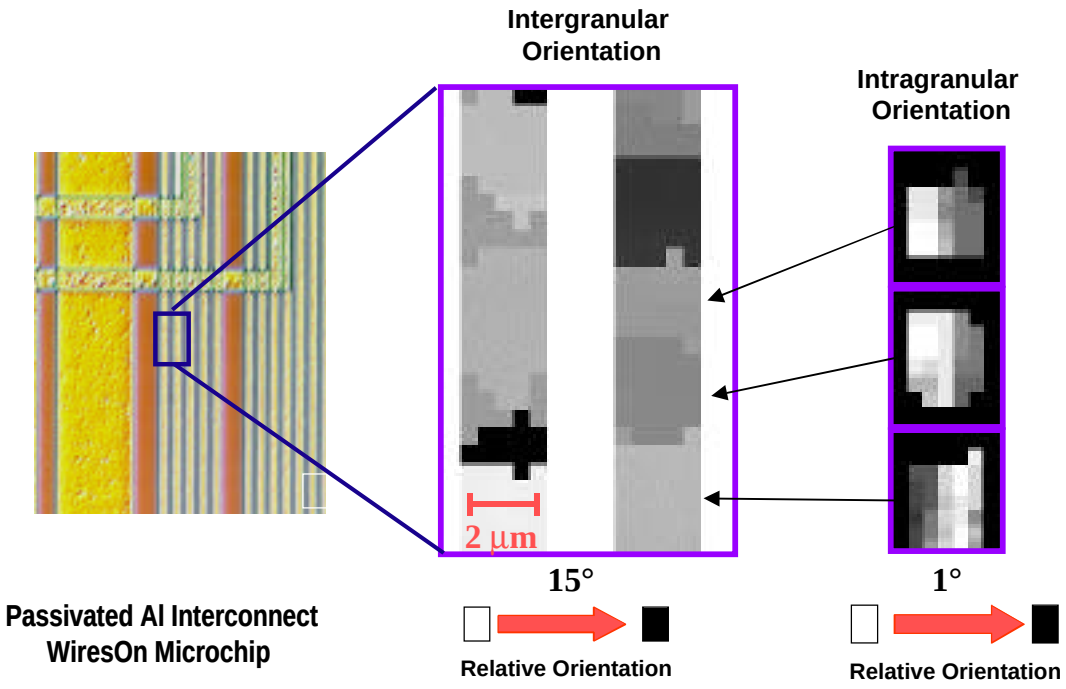

Figure 2. X-Ray microbeam measurements of inter- and intragrain orientations in Al interconnect wires. The orientations of aluminum 111 plane normals relative to the chip surface normal are indicated by shading. An overall bamboo like structure is observed along the wire and tilt disorientations of ~0.5 degrees are observed within individual grains.

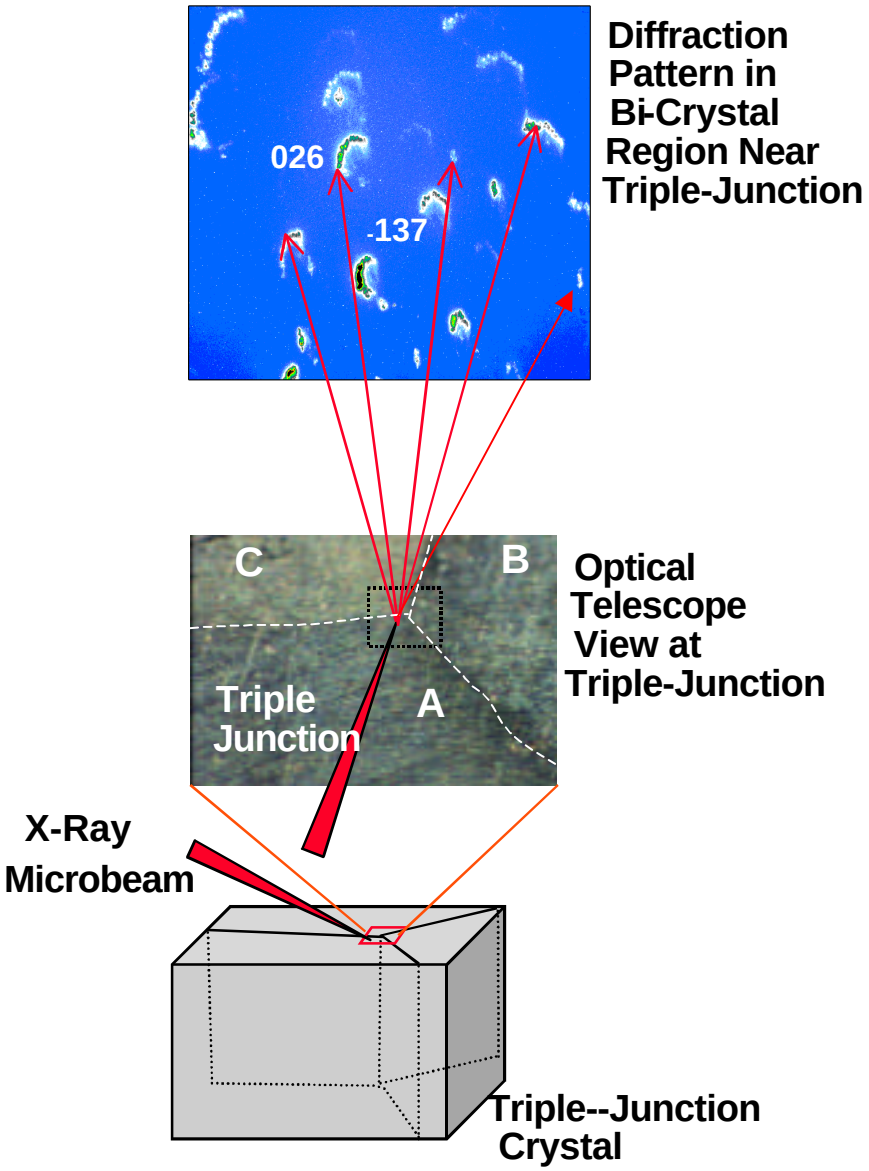

Fig 3. X-ray diffraction pattern (top) from a plane-strain deformed Al tri-crystal showing characteristic deformation streaking associated with lattice rotations as a function of depth along the beam. As indicated in the optical telescope view (middle) and the tri-crystal schematic drawing (bottom), the beam enters and travels ~ 50 μm in crystal A, before crossing the planar boundary into grain C where it penetrates >250 μm and is attenuated. The short vertical Laue spots are from grain A and the larger arc-shaped Laue spots originate in grain C.

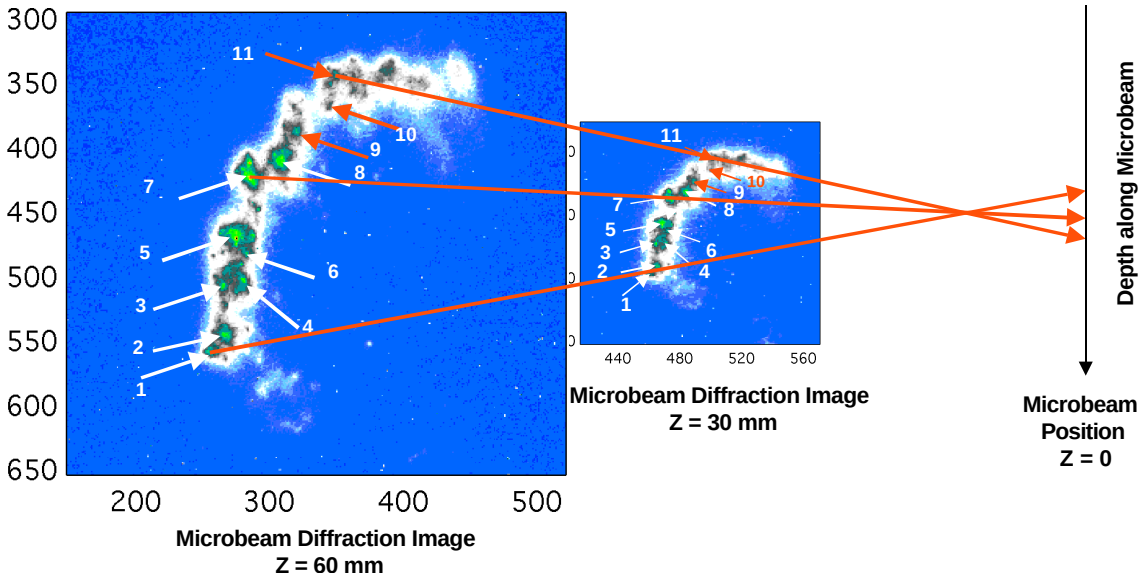

Fig. 4. A schematic view of the triangulation procedure for determining the source position along the x-ray beam for particular features in the diffraction pattern. The CCD images were taken at distances of 30 and 60 millimeters above the microbeam; the microstructure corresponding to points 1 and 10 is rotated by a relative angle of 4.38° around the [-233] direction and triangulation indicates a separation of 194 microns.