The Three-Dimensional X-ray Crystal Microscope: A New Tool for Materials Characterization

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The three-dimensional (3-D) X-ray crystal microscope is a new nondestructive tool for the 3-D characterization of the mesoscopic and nanoscopic materials structure. A prototype microscope is installed on beamline 34-ID at the advanced photon source and has begun initial operation. The prototype microscope has a routine spatial resolution of approximately $0.5 \times 0.5 \times 1\ \mu m^3$ and can probe tens to hundreds of microns below a sample surface, depending on the composition of the sample. For each volume element measured, the microscope can determine between 10 and 16 parameters. The measured parameters are the local crystallographic phase (1 deg of freedom), the Eulerian angles of crystal orientation (3 deg of freedom), and the plastic and/or elastic strain-tensor elements (6 to 12 deg of freedom). The time required to collect each volume element varies between 1 and 14 seconds, depending on the precision of the parameters and the sample complexity. Much faster data acquisition and much better spatial resolution are certain in the near future. Some initial results are presented to illustrate how the 3-D X-ray crystal microscope can provide unprecedented information about the 3-D structure of materials.

I. INTRODUCTION

THE properties of polycrystalline materials depend on three-dimensional (3-D) scalar and tensor distributions including anisotropic/inhomogeneous elasticity, local stress, grain-boundary behavior, and a host of other mesoscopic parameters. For example, macroscopic applied forces are redistributed locally by second phases, fibers, defects, grain boundaries, heterogeneous grain orientations, and plastic deformation. Unfortunately, despite remarkable recent progress in microscopy, most high-resolution microprobes are inherently surface sensitive and can only measure a 3-D structure by serial sectioning methods. Serial sectioning methods are inherently destructive, relieve local and macroscopic stress, and virtually preclude time-evolution studies. A truly nondestructive 3-D probe of crystal structure is needed to resolve long-standing fundamental issues of materials physics and to connect directly to advanced modeling efforts.

To address this need, we have recently commissioned a novel 3-D X-ray crystal microscope at the advanced photon source.[1,2,3] This microscope is possible due to major technical advances in X-ray sources, detectors, and optics.[4,5] Ironically, the 3-D X-ray crystal microscope uses the oldest X-ray diffraction method: Laue diffraction. Laue diffraction is used to solve an intrinsic problem associated with conventional microdiffraction: sample rotations complicate the spatial mapping of crystalline properties below 5 μm. Indeed, as described in Reference 1, diffraction with monochromatic X-rays requires substantial rotations of the sample to achieve a Bragg condition. Such rotations bring different parts of the sample into and out of the X-ray probe beam due both to sphere-of-confusion limitations of existing goniometers and due to the penetration depth of the beam (Figure 1(a)). Laue diffraction avoids the complications of sample rotation, since a Laue pattern is generated at each grain sampled by the X-ray beam (Figure 1(b)).

A schematic of the 3-D X-ray crystal microscope is shown in Figure 2. In a typical experiment, a polychromatic X-ray beam impinges on a nondispersive Kirkpatrick–Baez (K–B) mirror pair. The total-external-reflection elliptical mirrors focus the X-ray beam to a submicron-sized spot on the sample.[5] The sample is rastered in the X-ray beam by a precision three-axis stage to select a line through the sample for analysis. The Laue patterns generated by each voxel within the sample are collected by an X-ray-sensitive charge-coupled device (CCD). The overlapping Laue patterns from each voxel along the X-ray beam are decoded by a differential aperture that scans across the surface of the sample.[2] From the decoded Laue patterns, it is possible to determine the phase and orientation of the crystalline structure within each voxel. In addition, it is often possible to determine the deviatoric strain tensor and/or the deformation tensor.

In order to determine dilatation (hydrostatic) strain, an *additional* step is required: the energy of at least one reflection must be determined. Currently, the energy of a reflection is measured by inserting a nondispersive monochromator into the X-ray beam and tuning to the energy of one Bragg reflection. The monochromator can be tuned over an ~10 keV range without displacing the X-ray probe focal position.[4] Alternatively, the energy of a Bragg reflection can be removed from the incident polychromatic X-ray beam with a precision-tunable filter. For example, we will soon test a 127-μm-thick Si Laue crystal that can tunably scatter an ~1 eV bandpass out of the X-ray beam from 10 to 20 keV at near-normal incidence to the beam. This approach has certain advantages in terms of equipment complexity and compactness, but has not yet been

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demonstrated. It also lacks the signal-to-noise advantage of monochromatic beam measurements. Similarly, all the spatial-resolution advantages of polychromatic microdiffraction can be retained, with the signal-to-noise advantages of monochromatic measurements, by taking many CCD images while a narrow-bandpass incident X-ray energy is scanned. Unfortunately, this approach is also very time consuming.

Other methods have recently been developed to study crystallographic structure down to submicron features using intense synchrotron X-ray beams as described in this TMS symposium on 3-D characterization. Monochromatic microdiffraction has been employed with both small (probe) beams[6] and with large beams for imaging.[7] These experimental methods work best for single-crystal or highly textured samples, where sample rotations are minimal. Scientists from Risø have recently demonstrated monochromatic "3-D X-ray Diffraction" at the European Synchrotron Radiation Facility (ESRF). Here, high-energy monochromatic X-ray beams focused to a line are used to study polycrystalline samples.[8] Their microscope rotates the sample around one axis and localizes the grain position by triangulation. As described by the article by Juul–Jensen *et al.* (also within this issue), this approach can have advantages with regard to data collection speed and/or with regard to penetration depth, but does not provide the submicron spatial resolution of the 3-D X-ray crystal microscope. More closely related to our current 3-D X-ray crystal microscope are two-dimensional (2-D) and quasi–3-D methods that have been used on polychromatic microscopes at the Advanced Light Source (ALS),[9,10] at Pohang,[11] on an earlier prototype of our microscope at the Advanced Probe Source (APS),[3,12] and on our current instrument. These approaches are very fast for mapping near-surface grain structures, but are less amendable to automation and typically make assumptions about the grain structure as a function of depth into the sample. Attempts to develop fully automated triangulation methods are still in their infancy, but offer the potential for faster data measurements for some simple experiments.

II. PRELIMINARY EXPERIMENTS

Although the 3-D X-ray crystal microscope is still undergoing rapid improvement, it already provides unprecedented information about the structure of materials. The first quasi–3-D measurements studied layered grains, to understand the heteroepitaxial grain growth in thin high-temperature superconducting films. The measurements were aimed at understanding growth conditions that lead to the highly oriented films needed for good performance. Budai and co-workers showed that growth temperature could drastically effect the growth behavior of buffer and superconducting films grown on oriented polycrystalline substrates.[13] This pioneering work was performed with 2-D imaging of the grains in layered materials, where the restricted film thickness, unique crystalline phases, and distinct defect structure of the layers provide the information necessary to localize the sequential structures along the incident beam. The hard (10 to 22 keV) X-rays easily penetrated through the thin high-T_c film and through the intermediate buffer layers. For example, as shown in Figure 3, the large size of the substrate grains and the thin buffer and high-T_c layers meant that away from the substrate grain boundaries, the substrate grain orientation could not be confused for a given buffer and high-T_c grain orientation. Other preliminary studies include triangulation measurements of 3-D local grain orientation in deformed single and polycrystals,[12] 2-D strain in integrated-circuit interconnects, strain in various high-temperature barrier films, and local structure and deformation or solid-solution-driven d-spacing inhomogeneities in various welded materials.[14] Similar measurements are underway at the polychromatic microdiffraction facilities at Pohang and the ALS.

Recent measurements have begun to concentrate on materials problems that require complete 3-D structural microscopy. Measurements are currently underway to investigate the local strain distribution for ion-implanted polycrystalline diamond films. Measurements are also underway to study the mesoscopic structure and strain at the interface of ultrasonic welds. Larson *et al.*[2] have reported measurements of local strain in a bent single-crystal silicon beam. Measured strain-tensor elements are illustrated in Figure 4. The results show the ability to depth-resolve strain even in a large single crystal and to study elastic deformation with exquisite detail. This new level of 3-D characterization can guide and test theories of elasticity. Similarly, Pang has initiated measurements of inhomogeneous plastic deformation in single grains of polycrystalline Al and Ni.[15] Here, rotations of subgrain regions are studied before and after deformation, so the observed deformation behavior can be directly compared with theoretical predictions. As shown in Figure 5, local streaking of Laue peaks results from plastic deformation, and modeling efforts can be used to estimate the unpaired dislocation density within the volume probed by the X-ray beam.[16,17]

Measurements are now underway to characterize the grain-boundary type and distribution for polycrystalline samples and to study how the grain-boundary distributions change depending on processing.[18] This work is of importance for grain-boundary engineering. The experiments are very simple, as indicated in Figure 6. A polycrystalline sample is surveyed to find the approximate location of grain boundaries near the surface. Studies have been initiated with large-grained samples (20 to 30 μm), where there are only a few grains observed within the penetration of the X-ray beam. Three differential-aperture scans are made near the grain boundary to determine the location of the grain boundary at three linearly independent positions. Approximating the local grain boundary by a plane, three grain-boundary positions define the plane orientation and position. Since the orientation of the neighbor grains on each side of the plane are known, their relative rotation defines an axis that can be compared to the grain-boundary normal. In addition to possible coincidence-site lattices (CSLs), the grain-to-grain rotation can be classified as having a twist, tilt, or as a linear combination of tilt and twist character. This information has simply not been available previously. Measurements are now underway on rolled and recrystallized nickel samples.

In addition to CSL and twist/tilt information, detailed measurements of the volume around a grain boundary can be used to study the morphology of various grain boundaries without serial sectioning. Of particular interest will be measurements of grain-boundary motions during processing. Although the present measurements are fairly time consuming, there is adequate intensity to accelerate the detection rate by orders of magnitude, given faster X-ray–sensitive area detectors.

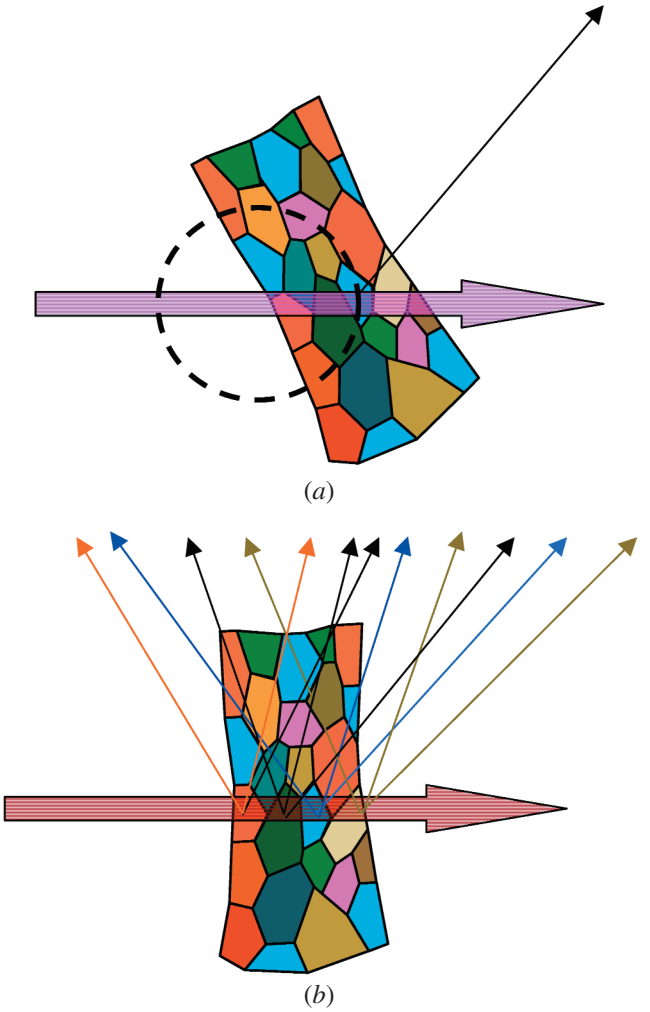


Fig. 1—(*a*) As an X-ray beam penetrates a polycrystalline sample, it intercepts a number of grains or subgrains. As the sample rotates, the grains/subgrains rotate into or out of the beam. The problem of determining the origin of each reflection is complicated by the motion of the grains relative to the beam, by sphere-of-confusion errors in any goniometer, and by elastic strain that confuses the scattering angle (*d* spacing). (*b*) With a polychromatic X-ray beam, a Laue spot is generated at each subgrain intercepted by the beam.

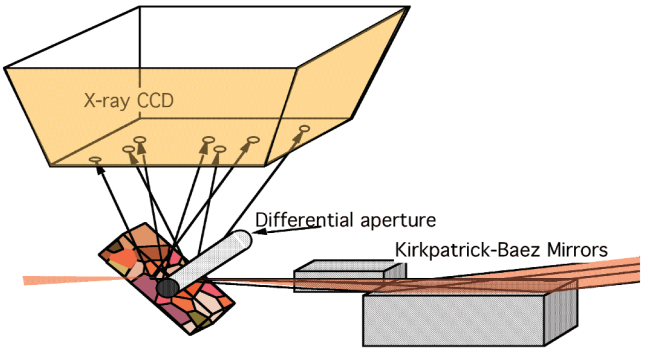


Fig. 2—Schematic of the polychromatic 3-D X-ray crystal microscope. The incident X-ray beam can be selected to have either a monochromatic or a polychromatic spectra. The beam is focused by nondispersive total-external-reflection K–B mirrors onto the sample, which is translated relative to the beam by precision stages. A precision 50-μm-diameter wire is translated near the sample surface to decode the origin of the overlapping Laue patterns. By subtracting CCD images taken before and after small movements of the wire, a pixel by pixel mapping of intensity can be made back to the incident beam path. After scanning across the surface of the sample, a series of single-crystal Laue patterns associated with each location along the beam can be recovered.

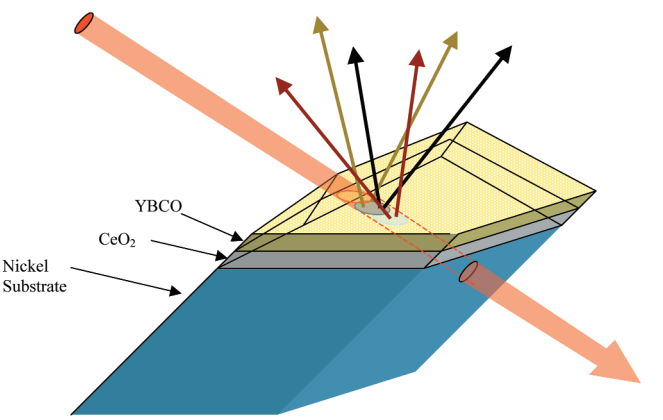


Fig. 3—Schematic showing the measurement of grain orientations in a bilayer thin film on a polycrystalline substrate. If the probe size is small with respect to the substrate grain size, and if the film thicknesses are small, then the orientation of the substrate grain directly underneath the film does not change relative to the volume sampled by the penetrating X-ray beam.

III. FUTURE DIRECTIONS

Recent progress in the fabrication of high-precision X-ray optics at the ESRF (European Synchrotron Radiation Facility, Grenoble, France) and at Spring-8 (Tsukuba, Japan) have demonstrated that nanoscale X-ray probes are possible.[19,20] Already, X-ray probes below 80 nm in diameter have been demonstrated, and the theoretical limit for a hard X-ray probe with K–B total-external-reflection mirrors is around 25 nm.[19] The availability of nanoscale beams[21] will not only extend the 3-D X-ray crystal microscope to materials with nanoscale crystalline grains, but will allow for measurements of 3-D nanoscale inhomogeneities and for precision measurements of morphological details in materials with micron-sized or larger grains. Of course, a smaller probe size will also limit the depth of field of the probe. Typically, total-external-reflection K–B optics, designed to pass 22 keV X-rays, have a critical angle of about 3 mrad, which allows for a full-width, half-maximum convergence on the sample of about 0.5 to 1 mrad. The depth of field is, therefore, on the order of 1000 times the focal spot size: as the focal spot size decreases, there will be a proportionate loss in the depth of field along the beam direction. Although a smaller depth of field decreases the number of resolvable elements along the beam path, the number of resolvable volume elements transverse to the beam scales inversely with spot area. Hence, the total number of resolvable volume elements will scale inversely with the probe transverse dimension, so that very fast methods are required to survey even small volumes of the sample with very high resolution. Better X-ray mirrors will also extend the critical X-ray energy of focusing mirrors to allow for measurements deeper within a specimen.

In addition to better X-ray focusing optics, new detectors will greatly extend the range of experiments that can be undertaken with the 3-D X-ray crystal microscope. New X-ray-sensitive detectors are emerging with an orders-of-magnitude

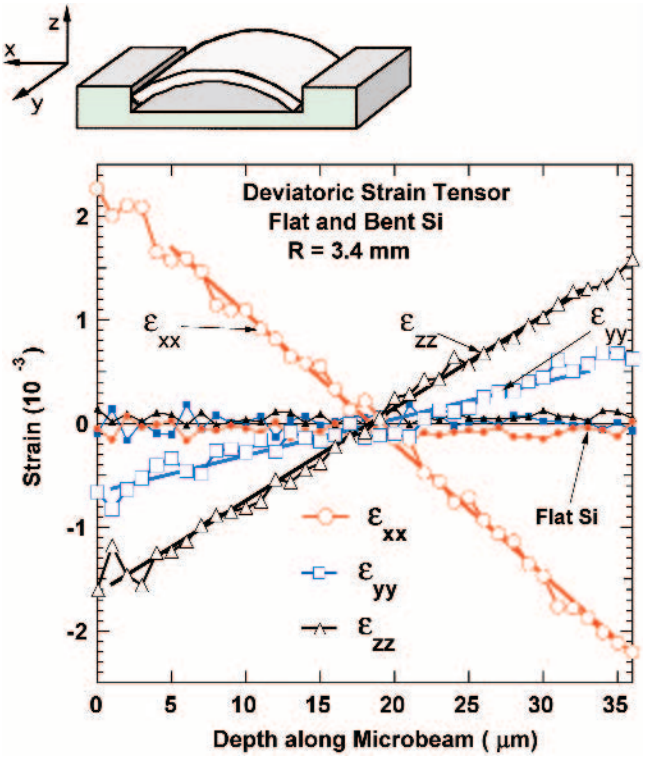


Fig. 4—The strain tensor in a flat single crystal of elastically bent Si can be estimated from the radius of curvature and the position within the thickness of the crystal. Even within a single crystal, the strain tensor elements can be quantitatively measured through the volume of a bent Si beam. Although the overall elastic behavior of the bent Si can be estimated from simple beam theory, the Si is actually a plate and exhibits complex elastic behavior during bending.

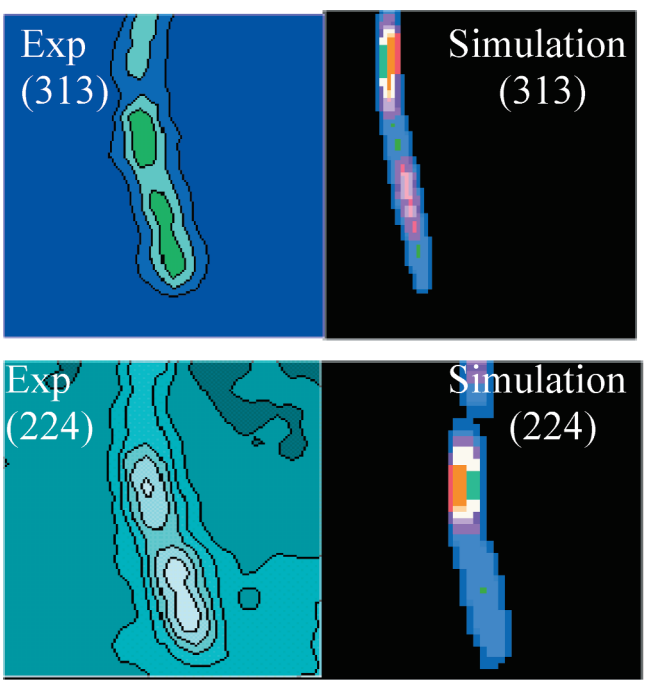
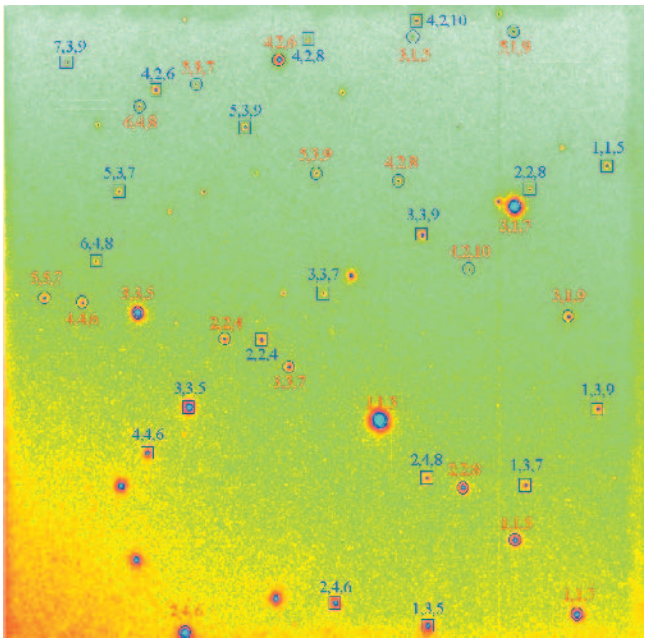
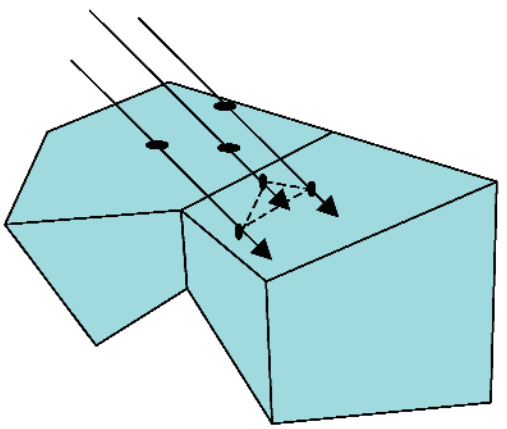


Fig. 5—Plastic deformation rotates Bragg planes within the volume sampled by the X-ray beam. Here, several reflections are isolated from the complete Laue pattern to illustrate the fine structure arising from rotated crystal planes. The measured rotations can be modeled to estimate the unpaired dislocation density.



(*a*)



(*b*)

Fig. 6—(*a*) Near a grain boundary, the Laue patterns from two grains are observed. The patterns can be indexed to precisely determine the orientation of each grain. As shown in the indexed patterns from two nickel grains, many reflections are recovered even from this simple fcc metal. (*b*) With differential aperture microscopy, the 3-D position of the grain boundary/X-ray beam intersect can be determined. Assuming a locally planar grain boundary, three non-colinear (linearly independent) intersects determine a grain boundary normal.

faster readout that will allow for the collection of real-time 3-D images to study mesoscale evolution in materials. Whereas about 15 s/voxel is our current limit, fast detectors and improved techniques should improve data collection rates to ~10 to 100 Hz. At 100 Hz, volumes with 50 × 50 × 50 elements could be measured every 15 minutes for *in-situ* real-time studies of mesoscale evolution. Similarly, emerging X-ray area detectors with energy sensitivity will greatly increase the signal-to-noise ratio of the 3-D X-ray crystal microscope and will obviate the complexity of monochromatic X-ray measurements. Ongoing efforts to develop a neutron analog suggest that an energy-sensitive 3-D neutron crystal microscope will have the ability to study materials very far

below the sample surface, although with lower spatial resolution and slower data collection speed.

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