

Chapter 2

Synchrotron White-Beam X-ray Microdiffraction at the Advanced Light Source, Berkeley Lab

Abstract The μ SXRD technique is developed at the Advanced Light Source, Berkeley Lab. The technique can provide a local information about the crystal structure of materials in a microscale. This became possible due to the focusing of X-rays into a micron size spot. The numerical analysis of the X-ray diffraction allows to find and quantify not only the crystal structure and lattice parameters, but also the density of geometrically necessary dislocation density, crystal bending, polygonization and rotation, and local stress/strain probing at different conditions. The physical components of the experimental setup and the experimental procedure are also described in details in this chapter.

Keywords ALS • μ XRD • Beamline • Microdiffraction • White-beam • XMAS • Local plasticity • Crystal polygonization • Crystal rotation • Crystal parameter

2.1 Introduction

Traditional X-ray diffraction is a technique that has been used for almost a century for elucidating the structure of materials on the macroscopic scales (0.1–10 mm). As modern electronics, photonics and even biological devices are increasingly made in smaller and smaller scales (submicron and nanometer scales), a thorough understanding of the materials structure-properties-performance relationship at such length scales (0.1–10 μ m) has become critical, and thus the need for high spatial resolution X-ray diffraction. With the recent availability of bright third generation synchrotron sources and progress in X-ray focusing optics, it is now practical to develop an X-ray microdiffraction technique and apply it to characterize materials at such small scales.

2.2 Beamline Components and Layout

The Advanced Light Source (ALS) at the Ernest Orlando Lawrence Berkeley National Laboratory in Berkeley, CA, is a third-generation synchrotron radiation source. It is well known as one of the brightest available sources of extreme ultraviolet and soft X-ray radiation in the world. A wide range of scientific activity, ranging from protein crystallography to semiconductor physics, all the way to pioneering technology development of the Extreme Ultra Violet (EUV) lithography technique critical to the continuing scaling of the microelectronics chips have been supported by ALS. In order to provide a wide range of energy spectra, the ALS uses bend magnet, insertion device, as well as superbend sources. The X-ray microdiffraction beamline described here is located at bend magnet beamline 12.3.2 of the ALS. The beamline provides an extremely bright X-ray beam with a spectral range of approximately 5–22 keV.

Figure 2.1 shows the schematic layout of the X-ray microdiffraction beamline. The X-ray beam from a bending magnet source (1.9 GeV, 400 mA, $250\text{ }\mu\text{m FWHM} \times 40\text{ }\mu\text{m FWHM}$, up to $3 \times 0.2\text{ mrad}$ divergence in horizontal and vertical respectively) is 1:1 refocused at the entrance of the hutch by a 700 mm long platinum coated silicon toroidal mirror operating at a grazing angle of 5.4 mrad [1, 2]. Among few suitable methods for focusing high brightness white-beam X-rays, Kirkpatrick-Baez (KB) mirror pairs has been chosen for producing our X-ray focused beam in the beamline 12.3.2 as it is the only focusing solution to combine both achromaticity and high efficiency. The principle of these KB mirrors has been described in detail elsewhere [3]. This KB mirrors focus the X-ray synchrotron beam into a submicron spot size ($0.8 \times 0.8\text{ }\mu\text{m FWHM}$). Acting as an adjustable size source for the KB demagnifying optics inside the hutch are the water-cooled tungsten slits at the entrance of the hutch. In this way spot size can be traded for flux. As white-beam has been mostly used in the studies described in the following chapters, the 4-crystal monochromator in Fig. 2.1 was not in use.

As we can see from Fig. 2.1, after the X-ray white-beam is focused by the KB mirrors, there remain two main components: the sample stage, and the large area

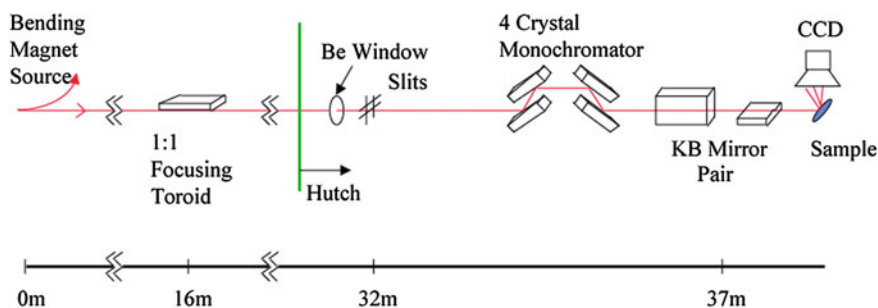


Fig. 2.1 Schematic layout of the beamline 12.3.2 at the advanced light source (ALS), Ernest Orlando Lawrence Berkeley National Laboratory (courtesy of Valek [2])

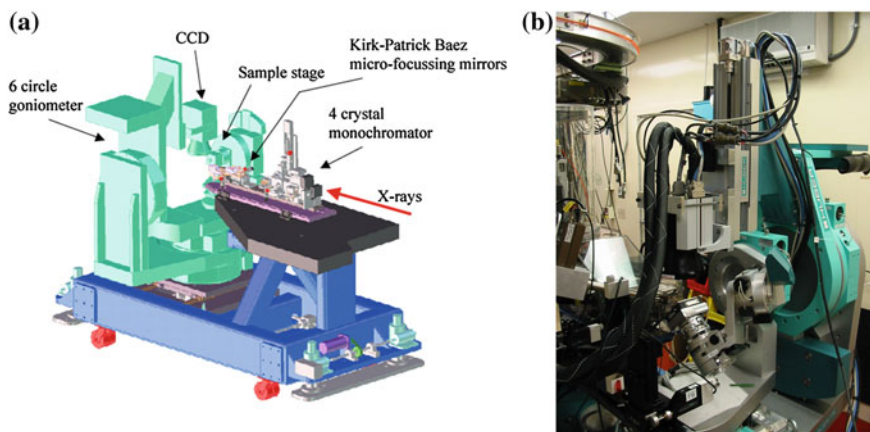
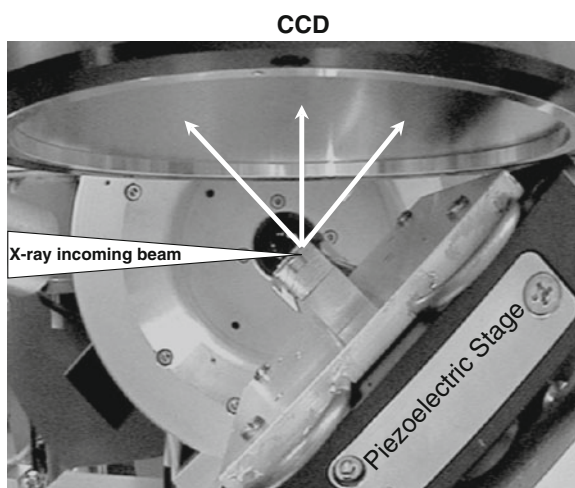


Fig. 2.2 Experimental endstation for beamline 12.3.2 at the ALS: **a** the schematic of the engineering model, and **b** picture of the actual endstation (courtesy of Tamura et al. [1] and Valek [2])

Fig. 2.3 Side view of our typical experimental setup with the 2-D CCD detector on top and the sample mounted in a 45° reflective geometry; X-ray incoming beam and diffracted beams are shown as white arrows, and the sample movement is precisely controlled by the piezoelectric stage (courtesy of Valek [2])



CCD X-ray detector, both of which are mounted on a goniometer as shown in Fig. 2.2. The sample under consideration would sit on a fine XY piezoelectric stage (range of $\pm 50 \mu\text{m}$), which is mounted on a coarse XYZ Huber stage (range of $\pm 5 \text{ mm}$ in XY and $\pm 10 \text{ mm}$ in Z) as shown in Fig. 2.3. The sample can also be mounted on a heating stage for experiments requiring high temperature up to 600°C .

The diffraction patterns are collected with a MAR133 X-ray CCD (active area of $133 \times 133 \text{ mm}$). The sample is usually mounted in a 45° reflective geometry as illustrated in Fig. 2.3, with the CCD detector on a vertical slide at a distance of

approximately 50 mm from the sample area illuminated by the beam. This sample-CCD distance is optimized to give maximum total number of reflections at a reasonable angular resolution. When illuminated with a white beam of 5–22 keV energy range, a (111) oriented Al grain, for example, will give a total of ~ 15 reflections, at an angular resolution of 0.01° (details about the angular resolution has been given by MacDowell et al. [3]).

Compared to electron microscopy techniques, X-rays offer the advantages of characterization of buried grains under overlying cap layers and multilayered films without the need of any sample preparation. In situ measurement under a variety of different conditions (in air, liquid, gas and vacuum, at different temperatures and pressures) thus becomes a possibility and opens opportunities for many experimental applications. The lack of sample preparation is especially important since the sample stress state can be greatly affected by any preparation processes.

2.3 Scanning White-Beam X-ray Microdiffraction

White beam Laue diffraction is a standard crystallographic method used to determine crystal orientation without rotation of the sample. However, Laue diffraction is rarely used to measure strain because the precision of most Laue instruments is low compared to modern diffractometers, and because the unit cell volume cannot be determined with a standard Laue measurement. Nevertheless, with suitable instrumentation, such as used in the experimental setting described above, precise determination of crystal orientation and distortional strain is possible. Laue diffraction might even be extended by measuring the energy of one or more reflections to determine the full strain tensor in polycrystalline samples.

2.3.1 *Experimental Procedure*

The technique at the beamline 12.3.2 that we have used for experimental data collection is known as Scanning white-beam X-ray microdiffraction (μ SXRD). As implied by the name, this technique does not use the monochromatic beam capabilities of the beamline and has significant differences with traditional X-ray diffraction techniques. Instead of the angular scans normally associated with X-ray diffraction, the sample is fixed in the μ SXRD setup (the crystal orientation and information are captured from its white-beam diffraction image). The “scanning” in the name of the technique refers to the manner that we translate the sample in discrete steps in X and Y axes of the sample stage, within the focal plane of the white radiation microbeam and collect the resulting Laue patterns on a CCD frame. This basic illustration of this experiment is shown in Fig. 2.4.

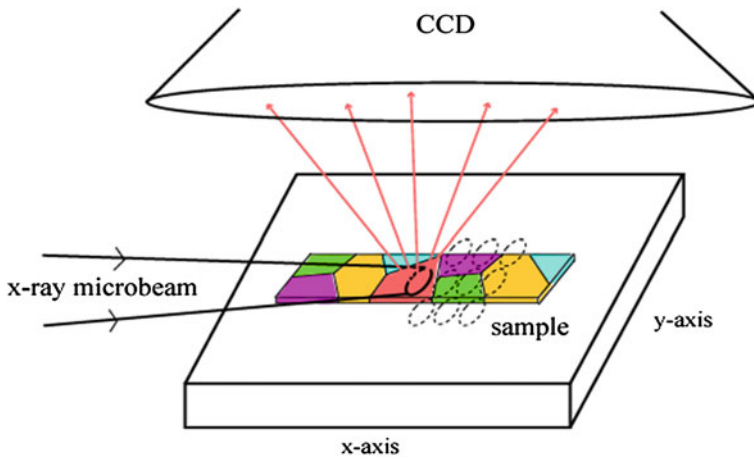


Fig. 2.4 Schematic diagram of a scanning white beam X-ray microdiffraction experiment; Incoming X-ray beam illuminate a volume that may consist of more than one crystal, the diffracted beams from each of the crystal are captured by the CCD detector placed above the sample. Laue patterns are collected from each discrete volume of the sample, followed by the next volume in a discrete-step scanning mode (courtesy of Valek [2])

Any crystal that lies within the illuminated volume will produce a Laue diffraction pattern. A typical white-beam Laue image captured by the CCD X-ray detector, containing of multiple Laue diffraction patterns (from an evidently polycrystalline sample), is given in Fig. 2.5. The Laue patterns can then be analyzed to give information about the complete orientation of individual grains, sample grain structure, deviatoric stress/strain tensors, information on subgrain structures, and crystal deformation/evolution. The methods for analyzing these Laue patterns will be discussed in the coming Sect. 2.3.2.

Prior to that, a rough elemental map of the sample has first to be created using scanning X-ray fluorescence, so that the region of interest can be more precisely pinpointed. For the samples in our experiments, we typically used copper, titanium, platinum and gold fluorescence signals. Subsequently, the area of interest can then be precisely located by using the piezoelectric positioning stage. A typical big-picture elemental map is shown in Fig. 2.6, from which then the exact coordinates to do more precise X-ray microdiffraction scan can be determined, and Laue patterns can thus be collected from each discrete area in the coordinates of interest.

Further references about the experimental approach that we have used could be obtained in a complete manner elsewhere [2].

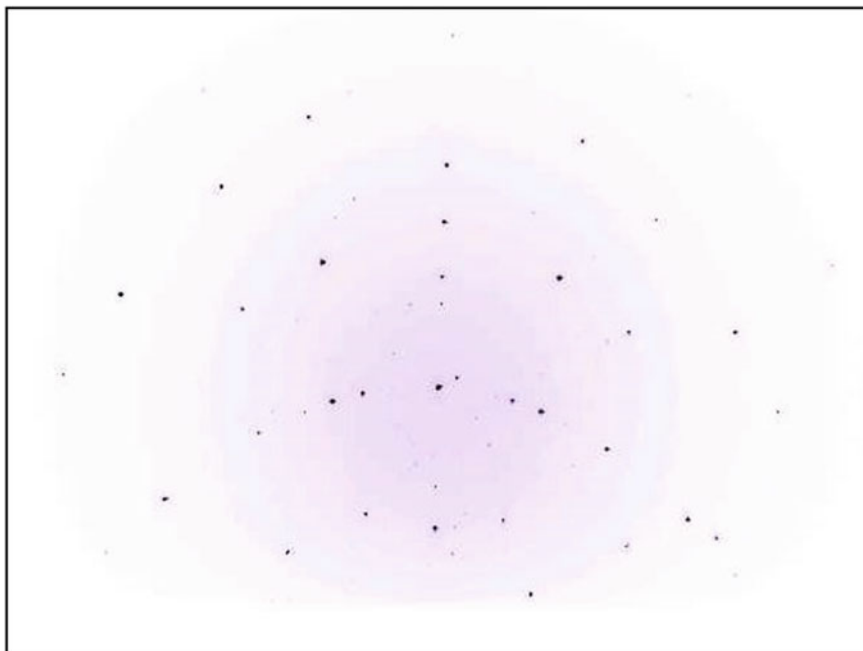


Fig. 2.5 Typical CCD image containing Laue diffraction patterns from copper grains and the underlying silicon substrate; The Si Laue reflections are much brighter than the copper reflections due to silicon substrate's large crystal size relative to copper grains

2.3.2 Data Analysis Using XMAS

A single white-beam Laue diffraction pattern contains a wealth of information about crystallographic orientation, stress/strain and dislocation structure/density in each individual crystal of the typically polycrystalline samples. A typical X-ray microdiffraction scanning of a sample usually yields hundreds to a few thousands of these Laue diffraction patterns. Without a set of software tools that can rapidly analyze the multiple Laue patterns contained in each of the CCD images produced by our experiments, the abundant raw data could not translate to meaningful information about the materials. A computer automated technique developed for crystallographic indexing, orientation, and strain determinations of grains in thin film samples [4–7] has been used, and a specific custom-made software has been developed in the Beamline 12.3.2 by Dr. Nobumichi Tamura of the Advanced Light Source (ALS), Berkeley Lab, and is called XMAS (X-ray Microdiffraction Analysis Software). It is based on an algorithm first described by Chung and Ice [4] as outlined in Fig. 2.7.

The rest of this Sect. 2.3.2 is organized following through the above flow chart, with the exception of energy measurement for the absolute unit cell parameter calculation, which is outside the scope of this book.

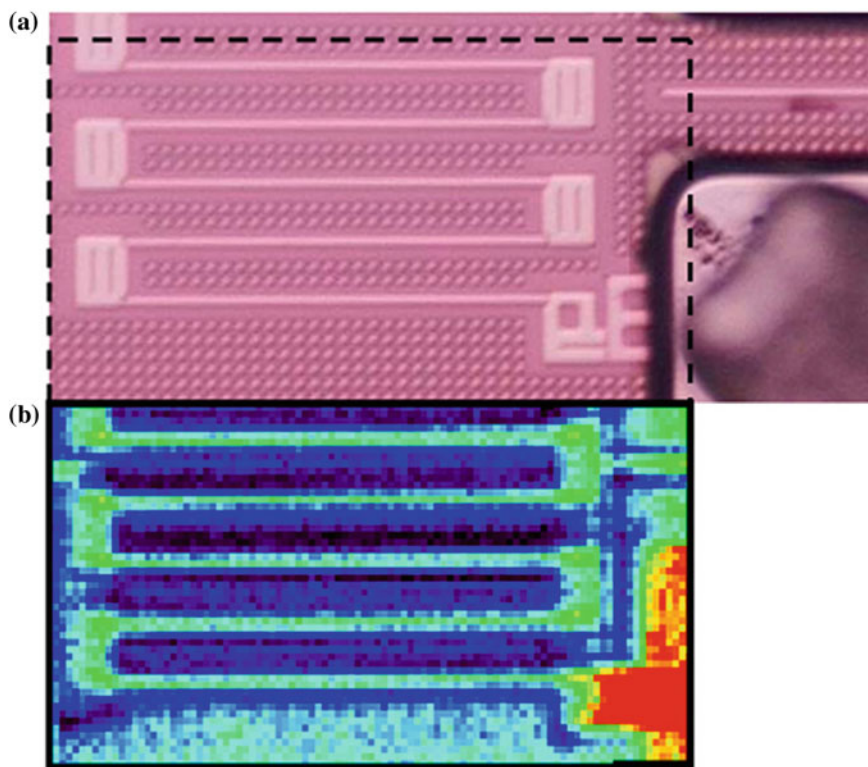


Fig. 2.6 Fluorescence mapping for locating the sample's overall picture; For example **a** shows a series of horizontal copper interconnect lines, and **b** shows the corresponding fluorescence mapping using copper's characteristic radiation wavelength (*red* high intensity of copper fluorescence characteristic radiation, *green* medium, *blue* low). A $0.5\ \mu\text{m}$ step size in x and y was used

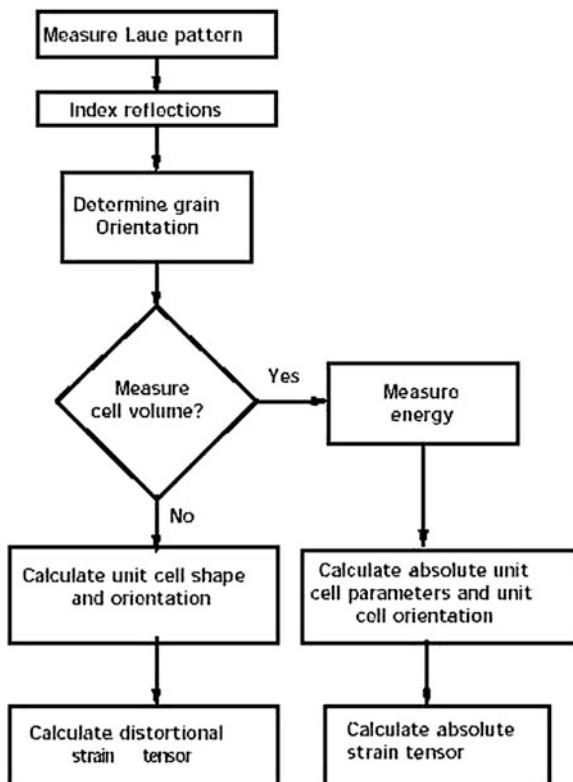
The three key steps for white beam Laue analysis, thus, are:

- (a) Laue peak searching and indexation
- (b) Crystal unit cell parameter determination
- (c) Strain/stress tensor calculation

2.3.2.1 Laue Peak Searching and Indexation

In order to index a Laue pattern, the first step we need to do is to process the image file as captured by the CCD detector. Figure 2.8a shows CCD image collected from a Cu thin film on a single crystal silicon substrate. The XMAS software reads the CCD file and automatically finds peaks using a peak-searching routine. The peaks are classified by their integrated intensity and fit with a 2D Gaussian, Lorentzian, or

Fig. 2.7 Flow chart for Laue reflection data analysis/processing as followed in the XMAS program used in the Beamline 12.3.2. at the ALS, Berkeley Lab (courtesy of Chung and Ice [4])



Pearson VII function, which allows the instrument to achieve subpixel resolution on the position of the peaks on the CCD. This is because each peak illuminates several pixels on the CCD due to the divergence of the beam and long tails of its Lorentzian profile. It has indeed been found that the best fit is usually given by a 2D Lorentzian function. The accuracy of this peak position fitting is one of the key limiting factors for strain accuracy measurement of this technique, thus the importance of having highly, precisely calibrated geometrical setup of the instrumentation.

Once the peak positions are established, we can index the Laue pattern with Miller indices. An indexed Cu Laue pattern is shown in Fig. 2.8b. Using the instrument geometry calibration procedure described below, we can calculate the scattering vector attached to each Laue reflection found during the peak fitting routine. The vector $\mathbf{k}_{in}$ describes the direction of the incident beam, while a vector $\mathbf{k}_{out}$ describes the outgoing diffracted beam directions. If we assume elastic scattering ($|\mathbf{k}_{in}| = |\mathbf{k}_{out}|$), then $\mathbf{q}_{exp}$ describes the directions of the experimental scattering vectors:

$$\mathbf{q}_{exp} = \mathbf{k}_{out} - \mathbf{k}_{in}. \quad (2.1)$$

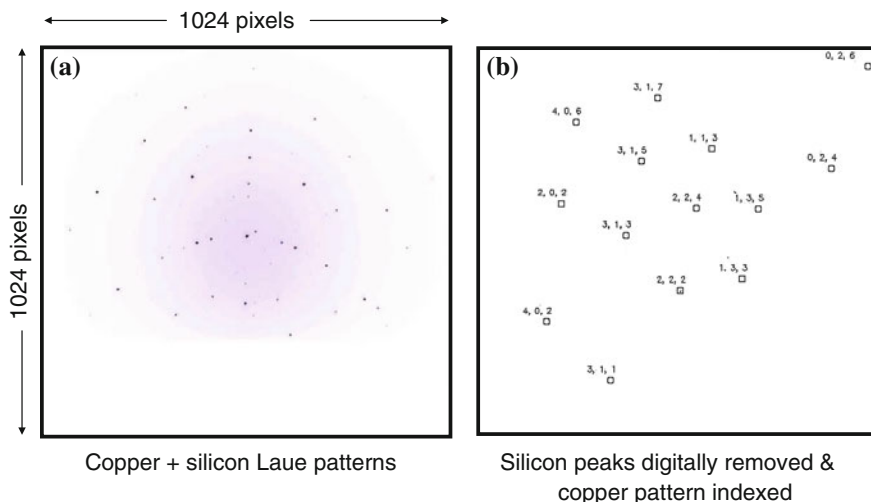


Fig. 2.8 Laue diffraction patterns are indexed by comparing the angles between triplets of experimental diffraction vectors with a list of theoretical angles for the crystal structure; **a** a CCD image consisting of bright silicon peaks as well as copper peaks, **b** indexed copper peaks belonging to a single grain of Cu (there may be other grain/crystal) after the bright silicon peaks are digitally removed

To index the pattern, the code uses a subset N of the brightest Laue reflections. The angles between these $\mathbf{q}_{exp}$ vectors for this set of N reflections are tabulated in an ‘experimental’ list of $(N(N - 1)/2)$ items. This experimental list is then compared to a reference list of angles between the theoretical scattering vectors that have been computed for the crystal structure of interest. The number of theoretical scattering vectors is limited by the energy bandpass of the polychromatic beam. To index the peaks, the code looks for angular matches between triplets of reflections within an adjustable angular tolerance. For each triplet and their corresponding (hkl) indices, the code calculates a complete list of reflections that should be visible on the CCD based on the considered energy bandpass, CCD dimensions, and geometry. The best match is the triplet that matches the largest number of experimental reflections. To limit the number of possible matches, many considerations such as structure factor and crystal symmetry are used.

In the indexing algorithm, the value of N is important. For instance, for a Laue pattern taken on a single-crystal region, a small value of N is used because the most intense reflections will all originate from the same grain. However in the case of a pattern taken in a polycrystalline region, this N value should be increased such that the algorithm can index overlapping Laue patterns. This ability to index multiple Laue patterns in a single CCD frame is key in analyzing microdiffraction data with incident X-ray spot size on the order of the grain size. More than ten overlapping grains in a single CCD frame can be differentiated and indexed with this algorithm.

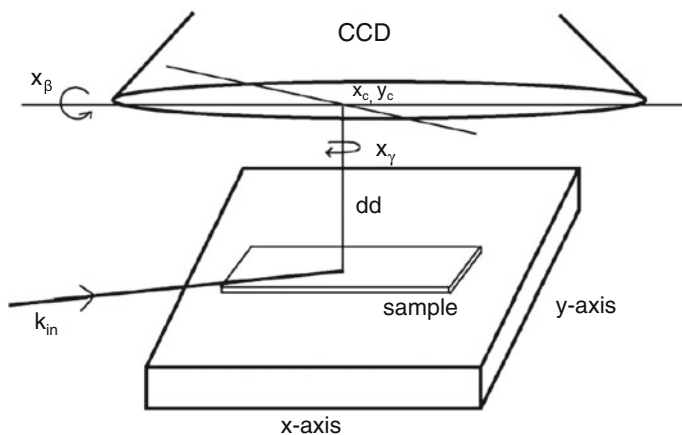


Fig. 2.9 Schematic drawing of the spatial calibration parameters for the CCD detector relative to the sample. These parameters include the sample to detector distance (dd), the pitch (x_β) and the yaw (x_γ) of the CCD, and the pixel coordinates of the CCD center channel (x_c, y_c). The vector $\mathbf{k}_{in}$ represents the direction of the incident X-ray beam (courtesy of Valek [2])

Once we know the positions of the reflections on the CCD, we can calculate their Bragg angle, θ , if the exact geometry of the instrumentation systems is defined with high precision (i.e. if the exact position of the CCD with respect to the incoming beam and the point of “impact” on the sample are known precisely). The number of the independent geometrical parameters is five: the X and Y “center channel” coordinates of the CCD, the distance between the CCD center channel and “point of impact” of the incident X-ray beam on the sample, and the two angles describing the tilt orientation of the detector relative to the incident beam (the pitch, x_β , and the yaw, x_γ). The center channel is defined as the X and Y pixel coordinates (x_c and y_c) of the position on the CCD at which the distance between the CCD and point of impact of the incident beam on the sample is minimized. The parameters are shown schematically in Fig. 2.9.

There are two methods can be used to refine the geometrical parameters. The first, triangulation, requires several images are collected at different CCD distances from the sample. Ray-tracing the reflective beams back to the origin is then used to define the geometrical parameters. Moving the CCD, however, introduces a sixth parameter that must be used to describe the angular deviation of the CCD translation stage with respect to the incident beam, which adds additional undesirable complications and errors. The second technique collects a Laue pattern from a calibration sample and uses a non-linear least square refinement to define the necessary geometrical parameters. The ideal calibration sample should be an unstrained large single crystal with no defects (short extinction length) and have a lattice parameter that produces a large enough number of reflections for the energy bandpass of the incident beam. For instance, in the typical thin film materials studies, the reflections from the relatively unstrained silicon wafer substrate can be used as calibration. We can then refine these geometrical parameters by minimizing the function

$$\alpha_0 = \frac{\sum_i w_i (\alpha_i^{th} - \alpha_i^{exp})^2}{\sum_i w_i}, \quad (2.2)$$

where α_i^{th} and α_i^{exp} are the differences in angle between pairs of the theoretical and experimental scattering vectors, respectively, and w_i is a weighting factor. This minimization of course presupposes that the reference Laue pattern is indexed properly and sums over all pairs of reflections visible on the CCD.

2.3.2.2 Crystal Unit Cell Parameter Determination

In the case of strained crystal where unit-cell parameters are unknown, it is still possible to determine the orientation and distortion strain of the unit cell if four independent broad-bandpass reflections are observed. Here we seek to find a matrix U that simultaneously satisfies four observed normal directions. Matrix U is a 3×3 matrix that transforms experimental scattering vectors in the reciprocal space (q_{hkl}) into a real space laboratory coordinate system (q_{xyz}).

$$q_{xyz} = U q_{hkl}. \quad (2.3)$$

Hence, matrix U defines a crystal system, and its 9 unknowns are the parameters of the crystal unit cell (3 crystal rotations, 6 unit cell parameters). They are basically the unit cell parameters $a, b, c, \alpha, \beta, \gamma$ such as shown in Fig. 2.10, and the 3 crystal rotations.

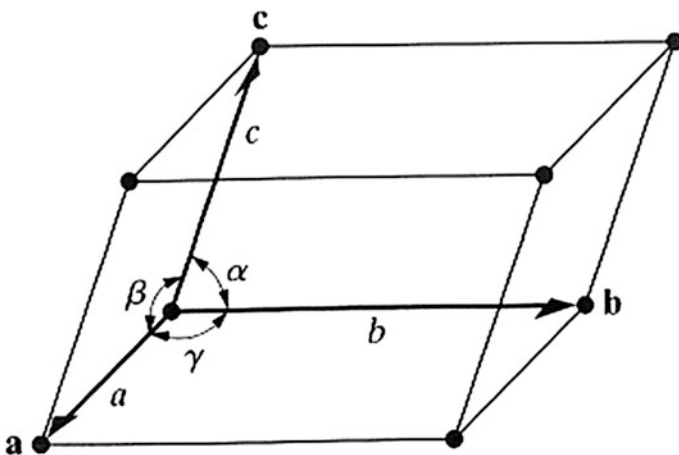


Fig. 2.10 The basic parameters of a unit cell: $a, b, c, \alpha, \beta, \gamma$

With four observed normal directions of scattering vectors, each normal has two direction angles, so altogether there are a total of eight independent equations to solve for the 9 unknowns. However, since the dilatation term cannot be determined without an energy measurement, we restrict ourselves to the determination of the orientation and distortional strain. If dilatation is ignored, there are, therefore, a total of 8 unknowns about the crystal orientation and the unit cell parameters. The one missing unknown is the absolute value of lattice parameters, and thus only the relative magnitude between a , b , and c can be identified, i.e. b/a and c/a .

We can then calculate the unit cell parameters for a single crystalline grain using the same minimization procedure used to calibrate the geometrical parameters of the instrumentation system. Similarly, the differences in angle between pairs of experimental and theoretical scattering vectors are minimized—in this case, Eq. 2.2 is used to calculate the lattice parameter ratios (b/a , c/a) and lattice angles, rather than the geometrical parameters. The instrumentation geometrical parameters (x_c , y_c , dd , x_β , and x_γ) have been fixed from the earlier calibration step.

2.3.2.3 Strain/Stress Tensor Calculation

Upon finding the relative lattice parameters a , b , and c and the lattice angles α , β , and γ , we can use this information to calculate the strain tensor. Here, we follow the procedure outlined by Chung and Ice [4]. Consider for example a unit cell with lattice parameters a_i and α_i , and a Cartesian coordinate system u_i attached to the crystal, such that a_i and u_i are coincident, a_2 is in the u_1u_2 plane and u_3 is perpendicular to the u_1u_2 plane, as modeled in Fig. 2.11.

We specify a position in the crystal using either a vector in the crystal coordinates, $\mathbf{v}_a$, or a vector in the Cartesian coordinates, $\mathbf{v}_u$. To transform from unit cell coordinates to Cartesian coordinates, we use the equation

$$\mathbf{v}_u = A\mathbf{v}_a, \quad (2.4)$$

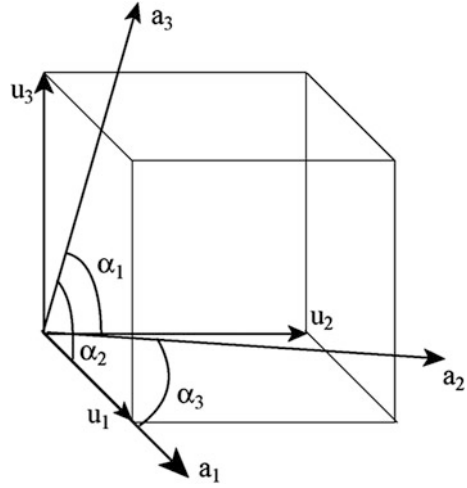
where

$$A = \begin{pmatrix} a_1 & a_2 \cos \alpha_3 & a_3 \cos \alpha_2 \\ 0 & a_2 \sin \alpha_3 & -a_3 \sin \alpha_2 \cos \beta_1 \\ 0 & 0 & 1/b_3 \end{pmatrix}. \quad (2.5)$$

Here the b_i and β_i are the reciprocal lattice parameters for the unit cell.

Rigid body translation, rotation, and crystal distortion can transform a vector position $\mathbf{v}$ attached to a crystal. Let A_{meas} be the matrix that converts a measured vector $\mathbf{v}$ into the measured crystal Cartesian coordinates, calculated from the refined lattice parameters found using Eq. 2.5. Let A_o be the matrix for an unstrained unit cell that converts $\mathbf{v}$ into the measured Cartesian crystal coordinates, calculated from the unstrained crystal lattice parameters and angles. Within this definition, there is a transformation matrix T that maps unstrained vectors to strained vectors:

Fig. 2.11 A cartesian coordinate system (u_i) attached to a real space unit cell (a_i , α_i). Note that we define $u_1 = a_1/|a_1|$; $u_3 = a_1 \times a_2/|a_1 \times a_2|$; and $u_2 = a_3 \times a_1/|a_3 \times a_1|$ (based on Chung and Ice [4], figure courtesy of Valek [2])



$$A_{meas} = TA_o. \quad (2.6)$$

T can contain both distortional components and rigid body rotation terms. Rigid body translation has been eliminated by defining the crystal and Cartesian coordinate systems to have a common origin. By using the definition of the strain tensor, ε_{ij} :

$$\varepsilon'_{ij} = (T_{ij} + T_{ji})/2 - I_{ij} \quad (2.7)$$

where I is the identity matrix, we can thus eliminate the antisymmetric rotational component.

Finally, the deviatoric stress tensor can be derived from the deviatoric strain tensor by applying the anisotropic stiffness coefficients C_{ijkl} for the material:

$$\sigma'_{ij} = C_{ijkl} \varepsilon'_{kl} \quad (2.8)$$

We have described the data analysis process behind the XMAS program which will be used heavily in the following chapters. Overlapping Laue patterns from multiple grains can be indexed by an iterative process which compares possible indices for several reflections with the observed angles between the reflections. Once the reflections are indexed, the unit cell parameters and crystal orientations can be determined. From the deviation between the observed Laue pattern and that of the unstrained crystal, deviatoric strain tensor, and thus deviatoric stress tensor can be calculated. These methods allow for rapid data analysis which makes mechanical probing of polycrystalline materials practical.

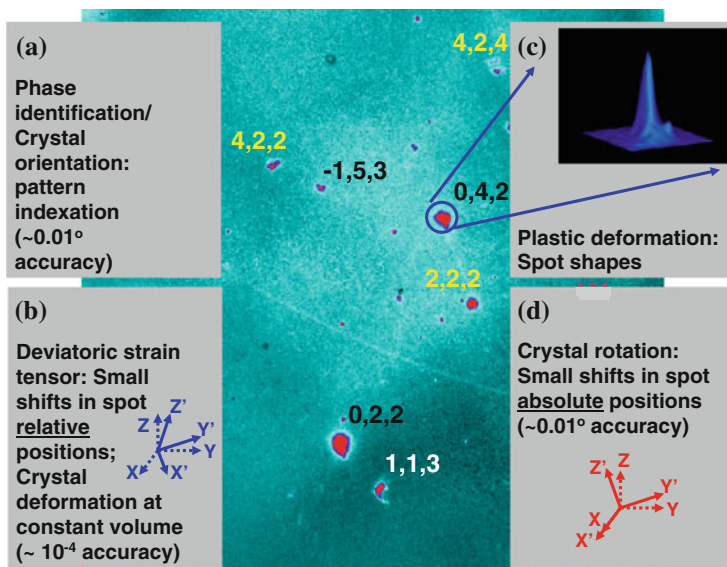


Fig. 2.12 A single white-beam CCD image consisting of multiple sets of Laue diffraction peaks (three colors: *black*, *yellow* and *white*) from a Cu polycrystalline sample; The determination of **a** and **b** have been described in Sect. 2.3, while the determination of **c** and **d** will be discussed in this section

2.4 Local Plasticity Probing Using Whitebeam μ XRD

The determination of the crystallographic orientation and stress/strain (deviatoric) in each of the individual crystal has been discussed (Sect. 2.3.2). It is basically done using the position and change in the relative position of the Laue diffraction peaks on the CCD image. Having done extensive experiments using the technique [8–18], we now realize another source of wealth of information that the technique gives is the shape of the Laue diffraction peak itself, as well as the change in the absolute position of the peak. Figure 2.12 shows features in Laue diffraction patterns and their associated structural and mechanical information that they contain about the material/sample.

First, the shape of the Laue peak itself provides information about plastic deformation in the crystal, especially the one involving the Geometrically Necessary Dislocations (GNDs), and then secondly, the change in the absolute position of the Laue peak gives us the rotational deformation of the crystal body. This Section will describe and discuss about the data analysis procedure for the determination of plastic and rotational deformation in crystals that will be used again and again throughout the chapters in this book.

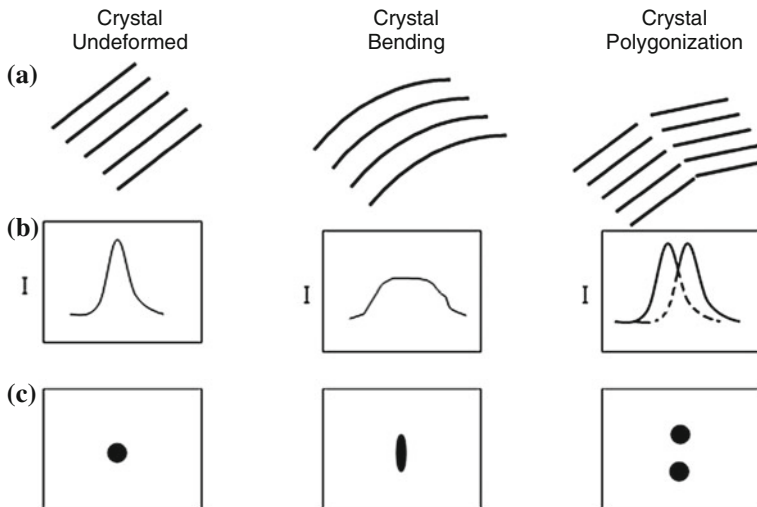


Fig. 2.13 Schematic diagrams comparing a set of crystal planes in their undeformed, bent/curved and polygonized states (a), while their expected Laue diffraction peaks corresponding to each of the crystal states are shown in (b), in intensity scanning over angle consisting of the Bragg angle/s, and (c), in CCD detector space (courtesy of Spolenak et al. [11])

2.4.1 Crystal Bending, Polygonization and Rotation

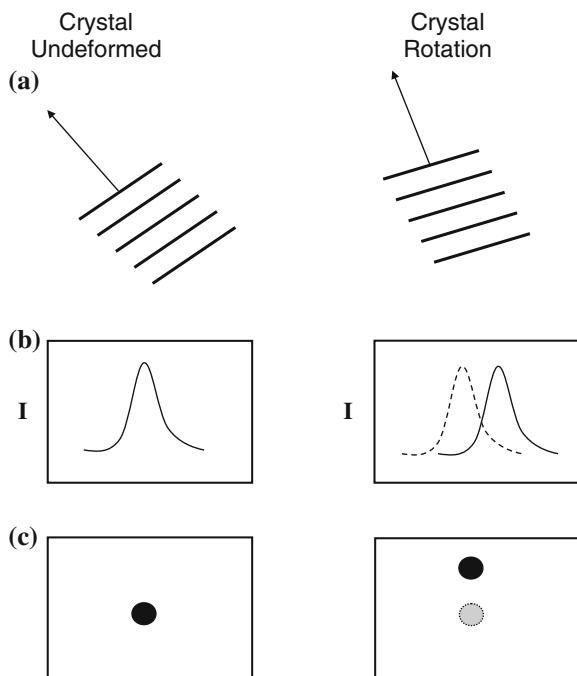
In traditional X-ray Diffraction (XRD) experiments, a peak at a certain θ angle means a particular (hkl) plane is detected, i.e. the particular θ angle, d_{hkl} interplanar distance and $\lambda_{Cu,k\alpha}$ wavelength (for instance) conspire such as to satisfy Bragg's Law:

$$n\lambda_{Cu,k\alpha} = 2d_{hkl} \sin \theta. \quad (2.9)$$

Using this methodology, only elastic deformation of crystal can be determined, where strain can simply be computed from the difference of interplanar distances between atomic planes, before and after the deformation. In contrast, plastic deformation may involve curved and polygonized crystal planes, such as shown in Fig. 2.13. In such configuration, a particular crystal plane (with a fixed d_{hkl} interplanar distance) may have a range of values of θ angle. This lattice curvature information will be lost in a traditional XRD (using a single wavelength and no tilt). However, using a white-beam X-ray, which also has a range of wavelengths, Bragg's law can still be satisfied even though the θ angle varies. This means that with white-beam, a presence of lattice curvature can still be detected and even measured.

In the case of a curved crystal plane (crystal bending), a broadened Laue diffraction peak in a certain direction would be observed (Fig. 2.13) instead of a single, sharp, rounded peak typical of an undeformed crystal plane. The Laue peak

Fig. 2.14 Schematic diagrams comparing two bodies of crystal in their undeformed/unrotated and rotated states (a), while their expected Laue diffraction peaks corresponding to each state are shown in (b), in intensity scanning over angle consisting of the Bragg angle (there is a shift in the absolute angular position of the peak), and (c), in CCD detector space (again, a shift in the position of the peak on the CCD detector space)



broadening (also called “peak streaking”) is continuous representing the continuum of θ values involved in the curved crystal. Crystal polygonization, in contrast, involves a multiple, discrete peaks coming from slightly misoriented sub-crystal structures (such as shown, again, in Fig. 2.13). Such polygonization often occurs following bending of crystal where more and more dislocations are piling up, and thus become unstable with respect to glide and eventually climb to form a low-angle boundary [19–22].

This is the unique capability of our white-beam X-ray diffraction technique. Using this white-beam methodology, we can start to directly and quantitatively study the plastic deformation in crystals. This technique is especially sensitive towards the crystal bending or polygonization in their simplest geometries, where a net density of parallel same-sign Geometrically Necessary Dislocations (GND's) is formed.

Furthermore, in traditional XRD, when a body of crystal rotates, the θ angle changes and without rotating the sample, Bragg's law (Eq. 2.9) can no longer be satisfied. In contrast, using a white-beam X-ray, another wavelength would simply be available to satisfy diffraction condition, and thus would give a constructive interference in the diffracted intensity (a Laue diffraction peak) instead on a slightly different position in the CCD camera, such as shown in Fig. 2.14. In other words, a crystal rotation would appear as a shift in the absolute positions of each of the Laue peaks belonging to the same crystal (it is to be noted that a change in the *relative* position of the Laue peaks—relative to other peaks belonging to the same

crystal—in contrast, does not mean crystal rotation, but instead, shear deformation or in other words, deviatoric strains, as has been discussed in the Sect. 2.3).

2.4.2 Quantitative Peak Study

Our technique of White-beam X-ray Microdiffraction can detect and measure the curvature of the lattice, or in the case of polygonized subgrain structure, the low-angle subgrain boundary. From how much the crystal under consideration curved, or bent, or polygonized, we can obtain quantitative data related to the plastic deformation the crystal must have undergone. The width of a Laue diffraction peak contains information on the dislocation density within a grain and the splitting of Laue diffraction peak into multiple individual spots can be used to measure the formation of low angle grain boundaries.

The X-ray Microdiffraction Analysis Software (XMAS) program allows us to select an individual Laue diffraction peak from a CCD image and study it quantitatively. The peak can be plotted in 2-D or 3-D using the detector coordinates. More meaningfully, as far as the crystal is concerned, is the ability to convert the peak into either theta-chi (θ - χ) space or reciprocal space. In θ - χ space, the Bragg angle, θ , can be calculated using the equation:

$$\theta = \frac{\cos^{-1}[\mathbf{k}_{in} \cdot \mathbf{k}_{out}]}{2}, \quad (2.10)$$

where $\mathbf{k}_{in}$ and $\mathbf{k}_{out}$ are the incident beam and diffracted beam. The χ angle is defined as the angle of the diffracted beam within the plane perpendicular to the incident beam. The χ angle can be found by projecting the diffracted beam into the XZ_{lab} plane, and then finding its angle relative to the Z_{lab} axis. The distortion of the θ - χ space on the CCD frame typical for our experimental geometry is shown in Fig. 2.15. The XMAS program allows conversion to remove the distortion caused by using a flat CCD to detect the Laue patterns in three dimensional space.

Once the peaks are in θ - χ coordinates, we have the real rotation of the crystal planes associated with the plastic deformation. This angular change in the geometry of our crystals can thus be further converted into the change in the geometrically necessary dislocation structures (plasticity) that the crystal must have undergone during the deformation. For illustration purposes, we use our real experimental results (Fig. 2.16), in the form of Laue peak intensity contour on a θ - χ space, its intensity trace along a certain χ angle, and the Full Width Half Maximum (FWHM) measurements from each of the peak, to give examples of the methodology to determine the extent of plastic deformation from the peak study.

Figure 2.16 shows typical Laue diffraction peaks (in θ - χ coordinates) coming from an undeformed crystal, a plastically bent/curved crystal and a polygonized crystal into two low-angle subgrain structures. Peak broadening and split occur primarily across the theta direction in this particular experiment. The peak

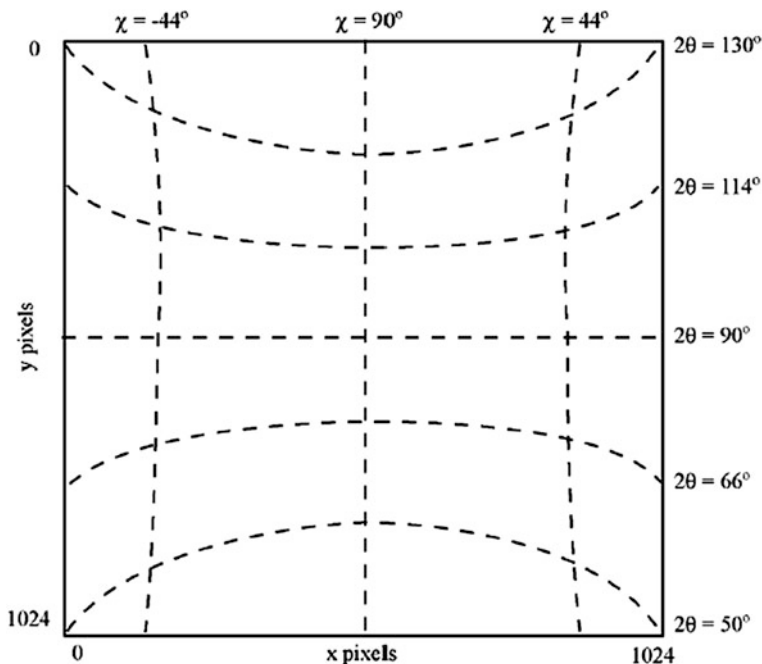


Fig. 2.15 The distortion of 2θ - χ space on the CCD detector typical for our experimental geometry; lines of constant 2θ and constant χ are shown, as well as the orientation of the CCD pixels (courtesy of Valek [2])

broadening can be quantified by defining $\Delta\theta_{FWHM}$ as the difference between the full width at half maximum (FWHM) of the peaks plotted in the θ - χ space along the θ direction at a constant value of χ , chosen to divide the peak in half. These intensity traces are plotted in Fig. 2.16 (in the column next to the Laue peaks) and are subsequently fit using a Lorentzian function as shown in the figure. Clearly from the FWHM measurements, we see peak broadening from (a) to (b) which represents plastic bending of crystal such as illustrated in (d). Similarly, the measurement of the θ angle difference between the two peaks in (c) suggests polygonization of the crystal across the theta direction as illustrated again in (d). Data can also be quantified within the reciprocal space, as an alternative to the θ - χ space.

Knowing the relevant geometrical dimensions of the crystal in the experiment, and the calibrated CCD-detector-to-sample distance, the peak broadening ($\Delta\theta_{FWHM}$) can be converted into the radius of the curvature of the crystal bending, Cahn [23] and Nye [24] further suggested that from the curvature of the crystal bending, we can determine the amount of Geometrically Necessary Dislocations (GND's) that have to be in the crystal to accommodate such a change in the geometrical shape of the crystal:

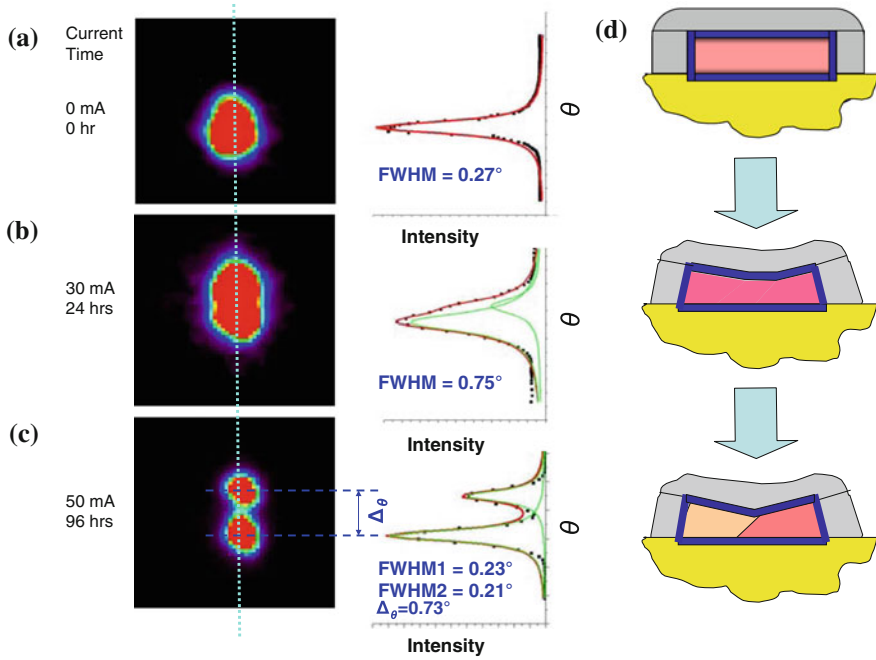


Fig. 2.16 Quantitative measurement of the evolution of a Laue diffraction peak (Peak 002) of a copper grain/crystal in an interconnect line under high current density electrical loading (electromigration) [16], and will be described again in Chap. 3; broadening is shown as the peak evolves from (a) to (b), while peak splitting, signifying the formation of low-angle grain boundaries, is evident in (c); (d) is an illustration of the evolution of the grain/crystal that the Laue peak evolution indicates

$$\rho = \frac{1}{Rb}, \quad (2.11)$$

where ρ is the dislocation density of GND's, R is the radius of curvature, and b is the component of the Burgers vector on the neutral axis. This is illustrated in Fig. 2.17a.

The peak split intensity profiles (Fig. 2.16) show clearly resolvable peaks indicating that the initial grain (a) breaks up into crystal segments with their own well-defined orientation (c). From the splitting of the Laue peaks, $\Delta\theta$, the misorientation between adjacent subgrains can be measured. Using the measured misorientation, the spacing between dislocations in the boundary can be derived using the Burgers relation for a small angle grain boundary:

$$\Delta\theta = \frac{b}{L}, \quad (2.12)$$

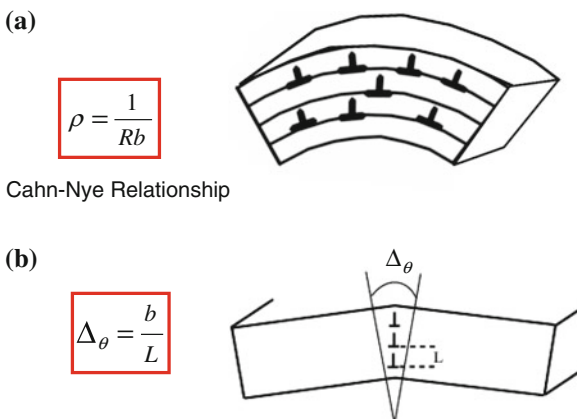


Fig. 2.17 Determinations of densities of GND's from geometrical shape of the crystals; **a** crystal bending/curvature, using Cahn-Nye [23, 24] relationship, and **b** crystal polygonization, using Burgers relation for a low-angle grain boundary

where Δ_{θ} is the measured misorientation angle, b is the Burgers vector and L the spacing between dislocations in the boundary, as illustrated in Fig. 2.17b.

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