Three-Dimensional Crystal Structure Mapping by Diffractive Scanning Confocal Electron Microscopy (SCEM)

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Recently a diffracted-probe scanning confocal electron microscopy (SCEM) mode was demonstrated. Analysis of such diffracted-probe images yields the sample height (defocus), thickness and crystal orientation. An extension of this principle for three-dimensional (3D) mapping is described and preliminary bicrystal data presented. Additional experimental criteria are discussed and the 3D resolution of this new diffractive SCEM mapping is derived and was found to be ≈20 nm and is comparable with 3D FIB-EBSD in terms of both field-of-view, spatial resolution and acquisition time.

1. Introduction

Many material properties are highly dependent on the size or morphology of their grains. Examples of this include the yield strength or failure strain of metals and the conductivity of nano-scale films of copper or high-temperature super-conductors. The ability to accurately determine grain size, shape and orientation is essential for modern materials science.

Focused ion-beam milling with electron back-scattered diffraction (3D-FIB EBSD) offers large fields of view (10s of µm) and reasonable spatial resolution (≈ 25 nm) [1]; however this is very time consuming (tens of hours) and necessarily destructive, precluding any further analysis of the specimen.

Non-destructive techniques exist for characterising crystal structures at higher resolution including (scanning) transmission electron microscopy, HR-(S)TEM; offering both imaging and diffraction information for two-dimensional examination of thin samples [2]. Such wide-field STEM can be modified to set up a scanning-confocal geometry (SCEM) [3] ; rejecting out of focus rays and improving depth sensitivity [4].

Wang et al. has demonstrated for a single crystal that raising the specimen well above the confocal plane yields a family of diffracted probe images; yielding information about crystal structure, thickness and height (Δf, Figure 1) of the specimen [5]. The confocal plane is recorded by positioning the CCD in the real-space optically conjugate plane. The intensity and angular distribution of scattered spots will depend on several factors including: the size of the objective aperture, specimen thickness, specimen height and angular proximity to a zone axis.

Here this non-destructive alternative is presented, including example data from a bicrystal; showing the ability to discriminate between two grains across a boundary. Some experimental guidelines are also elaborated on, including deriving the 3D resolution, on-track to developing this as a practical grain mapping technique.
2. Optical Geometry

A geometric consideration shows that the radial distance of the diffracted probes, \( r \), is related to their reciprocal lattice vector, \( g \), the sample height, \( \Delta f \), and the electron wavelength, \( \lambda \) [5].

\[
r = \lambda \cdot \Delta f \cdot g \quad (1)
\]

If the material and its orientation are known, then \( \lambda \), \( r \) and \( g \) are all known and then defocus can be expressed as follows.

\[
\Delta f = \frac{|r|}{|\lambda \cdot |g||} \quad (2)
\]

Equation 2 is valid for each diffracted probe and the the gradient of a \( |r| \) versus \( |g| \) plot yields an accurate value for \( \Delta f \), the sample height.

![Figure 1. Diffractive SCEM optical geometry showing sample-probe intersection volume.](image1)

![Figure 2. Experimental confocal-plane probe image from an YBCO film (\( t \approx 200 \text{ nm} \)).](image2)

In Figure 2 the diffracted probe images are not sharp points, but have finite radial spread, \( s \). Diffraction occurs throughout the thickness of the sample, \( t \), and such spots are expected to be streaked between the solutions to Equation 1 from both the entrance and exit surfaces [5].

\[
t = \Delta f_{\text{ent}} - \Delta f_{\text{ext}} = \frac{|r|_{\text{max}}}{\lambda \cdot |g|} - \frac{|r|_{\text{min}}}{\lambda \cdot |g|} \quad (3)
\]

\[
t = \frac{s}{\lambda \cdot |g|_{\text{hklt}}}
\]

There is occasionally observed some extra detail in the structure of the radial streaks and this is thought to be the effect of multiple scattering and is under investigation.

Equations 2 & 3 then allow a thin crystal’s dimensions to be determined and Wang et al. has shown this thickness and depth resolution to be \( \approx 5 \text{ nm} \) [5]. Repeating a \( \Delta f \) versus \( t \) analysis over an XY raster means that the three dimensional profile of a grain boundary can be mapped.

3. Experimental Results & Discussion

The specimen studied in this work was an YBCO thin film prepared on a MgO substrate similar to those in reference [2]. Optical microscopy, Figure 3, shows many grains are visible sized 20-50 µm. The rough surface of these grains remain visible in the dual beam FIB-SEM and a Zeiss NVision was used to mill a specimen 10µm by 5µm with a thickness \( \approx 200 \text{ nm} \).
SEM imaging of both sample faces allowed for various types of grain interface to be identified (Figure 5). An edge-view bicrystal was investigated using the Oxford-JEOL 2200MCO with pre and post specimen spherical aberration correction. Confocal plane images were recorded along a 400 nm line at 20 nm intervals, Figure 6.

Figure 3. Optical micrograph of polycrystalline YBCO thin film between electrical contacts.

Figure 4. SEM image of one face of the prepared specimen (field of view ≈15x20 µm).

Figure 5. Various potential grain interfaces: a) plan-view bicrystal, b) edge-view bicrystal, c) inclined bicrystal, d) tricrystal and e) tortuous bicrystal boundary.

Figure 6. False-colour (online) ADF image showing two grains separated by a G.B. (dashed line). Solid line shows a 400 nm long measurement location path. Insets show confocal plane images corresponding to a) a hole, b) grain 1 and c) grain 2.

Inset a) shows no diffracted probes when the beam is at a hole in the specimen. Insets b) and c) show the patterns recorded either side of the grain boundary and how the two grains can be discriminated.

When the sample is placed well above the confocal plane the probe exhibits a finite width at the specimen. This probe spread limits the lateral resolution to much poorer than the atomic resolution of ADF STEM. To estimate the lateral resolution achievable we must first consider the types of specimens technologically relevant for such grain mapping where thicknesses up to 200 nm may be
needed. At such thicknesses the first order diffraction spots will become heavily elongated. If the second order spots are also to be used for thickness/defocus determination then the defocus will need to be large enough to sufficiently separate the two orders. This criterion is comfortably met when the defocus is at least equal to the thickness. The lateral resolution then is limited by the width of the intersection volume, $\delta$ (Figure 1). Geometrically $\delta$ is found to be proportional to the defocus and the semi-angle of probe convergence.

\[ \delta = 2 \cdot \Delta f_{\text{ent}} \cdot \alpha \quad (4) \]

For the imaging conditions used in reference [5] ($\Delta f_{\text{ent}} = 186$ nm, $\alpha = 22$ mrad) this would correspond to a lateral resolution of 8.2 nm. However for the imaging of more realistic thicker specimens:

\[ \Delta f_{\text{ent}} = 2 \cdot t \quad (5) \]

\[ \delta = 2 \cdot (2 \cdot t) \cdot \alpha \]

\[ \delta = 4 \cdot t \cdot \alpha \]

For $t = 200$ nm and $\alpha = 22$ mrad this gives a lateral resolution limit of $\approx 18$ nm. In Figure 6 inset c) a weak contribution from grain 1 is seen. This arises from the probe-specimen intersection volume containing more than one grain. As the radial distance of the spots remains unchanged from inset b), the originating crystals for the two patterns evident in inset c) must be at the same height (edge-view bicrystal, Figure 5 B.). This is consistent with the predicted lateral resolution and an intersection volume being probed near the grain boundary.

This thickness dependence of the resolution requires the user to balance lateral resolution and mapable volume similar to EBSD. Additionally Wang et al. has shown that for specimens much thicker than 40 nm, and oriented to a strongly diffracting condition, dynamical diffraction imparts additional fine structure to the diffracted probe images making analysis of such patterns very difficult. This condition can be avoided by slightly tilting the sample to a more kinematical condition. In the case where this is not possible, data interoperability may impose a thickness limit.

4. Conclusions

A practical extension of the previously reported technique is described, with a bicrystal test sample prepared and explored. A line across the grain boundary was investigated at intervals using diffractive SCEM and the associated confocal plane images were used to demonstrate the ability to clearly discriminate between different grains, or holes, in the specimen. Some new practical considerations and criterion were discussed relating to sample thickness and a practical limit to 3D resolution of around 20 nm was derived. Extending such an analysis to an XY raster and incorporating determination of the specimen height and thickness is expected to yield a non-destructive three-dimensional grain mapping technique.

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