Crystal Quality Measurement on Niobium Materials

Xin Zhao, L. Phillips, C. Reece, Jefferson Lab
Qiguang Yang, D.A. Temple, Norfolk State University
M. Krishnan, C. James, Alameda Applied Science Corporation (AASC)

The work at AASC was supported by DOE Grant # DE-FG02-08ER85162. This research is also funded by Jefferson Science Associates, LLC under U.S. DOE Contract No. DE-AC05-06OR23177. The U.S. Government retains a non-exclusive, paid-up, irrevocable, world-wide license to publish or reproduce this manuscript for U.S. Government purposes.
Crystal Quality
– a definition based on crystallography

Crystal Quality

The quality of what is nominally a “single” crystal can vary over an enormous range. At one extreme, the crystal may have undergone gross plastic deformation by bending and/or twisting, such that some portions of it are disoriented from other portions by angles as large as tens of degrees, and the dislocation density is high. At the other extreme, some carefully grown crystals are almost free of dislocations and other line or planar imperfections, and their crystal planes are flat to less than $10^{-4}$ degrees over distances of the order of a centimeter. In general, metal crystals tend to be more imperfect than crystals of covalent or ionic substances.

Various x-ray methods of assessing crystal quality are described below. These methods differ in sensitivity, and we will deal with the least sensitive first.


X.Zhao et al, Talk on 5th SRF Thin Film Workshop, JLab. 2012
Outline

• Crystal Quality Measurement by EBSD
  – “Image Quality” and “Misorientation Angles” as figure-of-merits
  – Surveying AASC Nb Films
  – Surveying bulk Nb and MgB$_2$ Epitaxy film

• Crystal Quality Measurement by XRD
  – Introduction of Pole Figure and Reciprocal Space Mapping (RSM) techniques
  – RSM Experimental Data on film and bulk Nb

• Summary
• Acknowledge
• Questions

X.Zhao et al, Talk on 5th SRF Thin Film Workshop, JLab. 2012
Crystal Quality Measurement by EBSD

Image Quality and Misorientation Angles as Figure-of-Merits
Misorientation Angles - as a caliber of crystal quality

- Misorientation Angles of a survey area could be measured by XRD (Rocking Curve, RSM), or by EBSD

Fig. 8-27 Reflection of white radiation by bent and polygonized lattices (schematic).
The implication of equation (3) is that the quality of a diffraction pattern is dependent on the material being examined. Two other factors affect the quality of the diffraction patterns. The first factor is the degree of deviation from the ideal crystal, due to deformation, impurities etc. Lattice strains due to imperfections cause local deviations in the Bragg reflecting position leading to more diffuse bands in the diffraction pattern as shown in figure 16. The second factor

The factor affecting the quality of diffraction patterns of most interest, from a materials science standpoint, is the perfection of the crystal lattice in the diffracting volume. Any distortions to the crystal lattice within the diffracting volume will produce lower quality (more diffuse) diffraction patterns. This enables the IQ parameter to be used to give a qualitative description of the strain distribution in a microstructure. (A good example in the literature is S.T. Wardle, L. S. Lin, A. Cetel and B.L. Adams, “Orientation Imaging Microscopy: Monitoring Residual Stress Profiles in Single Crystals using an Image-Quality Parameter, IQ” in Proc. 52nd Annual Meeting of the Microscopy Society of America, eds. G. W. Bailey and A.J. Garratt-Reed. San Francisco Press: San Francisco (1994) pp. 680-1.) The IQ

  X.Zhao et al, Talk on 5th SRF Thin Film Workshop, JLab. 2012
Nb Thin Film Samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>CED-47 Thickness</th>
<th>CED-46 Thickness</th>
<th>CED-38 Thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness</td>
<td>~60 nm</td>
<td>~120 nm</td>
<td>~800 nm</td>
</tr>
<tr>
<td>RRR</td>
<td>46</td>
<td>62</td>
<td>136</td>
</tr>
<tr>
<td>$T_c$ (K)</td>
<td>8.95</td>
<td>9.14</td>
<td>9.20</td>
</tr>
</tbody>
</table>

- The samples were coated by cathodic-arc deposition at AASC(CED™).
- Substrates are magnesium-oxide crystal, with MgO(100) in-plane.
- Before coating, the substrates were annealed at 700°C; The substrate temperate was set at “500°C” during Nb thin film deposition. Note as, “700°C/500°C”
- The films are single crystals with epitaxial relationship, Nb(100)//MgO(100)

X.Zhao et al, Talk on 5th SRF Thin Film Workshop, JLab. 2012
EBSD Measurement (I)

<table>
<thead>
<tr>
<th>Sample</th>
<th>CED-47</th>
<th>CED-46</th>
<th>CED-38</th>
</tr>
</thead>
<tbody>
<tr>
<td>Avg. C.I.</td>
<td>0.67</td>
<td>0.72</td>
<td>0.90</td>
</tr>
<tr>
<td>Avg. I.Q.</td>
<td>1121</td>
<td>1003</td>
<td>2101</td>
</tr>
<tr>
<td>Avg. Miso. Angle</td>
<td>0.18’</td>
<td>0.20’</td>
<td>0.15’</td>
</tr>
</tbody>
</table>

EBSD Survey Area: 250X250 μm, Step10 μm. The bottom pic. are Inverse Pole Figures. IPF grayscale are rendered by the same I.Q. value: [min,max] = [500, 2100]
Crystal quality progressively evolves on film thickness

<table>
<thead>
<tr>
<th>Sample</th>
<th>CED-47</th>
<th>CED-38</th>
</tr>
</thead>
<tbody>
<tr>
<td>Avg. I.Q.</td>
<td>1121</td>
<td>2101</td>
</tr>
<tr>
<td>Avg. Miso. Angle</td>
<td>0.18’</td>
<td>0.15’</td>
</tr>
<tr>
<td>RRR</td>
<td>46</td>
<td>136</td>
</tr>
</tbody>
</table>

EBSD I.P.F.

CED-47

MgO (100) crystal substrate

Nb(100) Film 800 nm

CED-38

MgO (100) crystal substrate

Nb(100) Film 60 nm

X. Zhao, Talk on 5th SRF Thin Film Workshop, JLab, 2012


<table>
<thead>
<tr>
<th>Sample</th>
<th>CED-47</th>
<th>CED-46</th>
<th>CED-38</th>
</tr>
</thead>
<tbody>
<tr>
<td>Avg. Miso. Angle</td>
<td>0.18’</td>
<td>0.20’</td>
<td><strong>0.15’</strong></td>
</tr>
</tbody>
</table>

**EBSD Measurement (II)**

<table>
<thead>
<tr>
<th>CED-047</th>
<th>CED-046</th>
<th>CED-038</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Graph" /></td>
<td><img src="image2.png" alt="Graph" /></td>
<td><img src="image3.png" alt="Graph" /></td>
</tr>
</tbody>
</table>

- Average misorientation angles have small change, if compared by Image Quality (I.Q.) index.
- Higher RRR sample has a slightly smaller Avg. Miso. Angle (0.15’)

X.Zhao et al, Talk on 5th SRF Thin Film Workshop, JLab. 2012
Comparison to BCP Nb bulk samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>CED-47</th>
<th>CED-46</th>
<th>CED-38</th>
</tr>
</thead>
<tbody>
<tr>
<td>Avg. Miso. Angle</td>
<td>0.18’</td>
<td>0.20’</td>
<td>0.15’</td>
</tr>
</tbody>
</table>

EBSD survey of 12 bulk Nb samples (BCP’ed and cut from a SRF cavity)

Mean values of the local average misorientation distributions, obtained from the EBSD data on each grain for all the samples (black circles) and average density of pits measured on each grain for six samples (red squares). Samples with more than one grain have multiple points in the plot, corresponding to the different misorientation angle distributions for each grain.

Smallest Avg. Miso. Angle is ~0.15°


"Characterization of etch pits found on a large-grain bulk niobium superconducting radio-frequency resonant cavity"

X.Zhao et al, Talk on 5th SRF Thin Film Workshop, JLab, 2012
Comparison to a MgB$_2$ Epitaxial Film

- from Temple U. (Prof. Xi’s group)

EBSD Inverse Pole Figure

Sample: “1109C”, MgB2/C-plane sapphire

Average CI is 0.56 (0.086…0.743), Avg IQ=997, Grayscale: [0.1, 0.743]; Avg Misorientation: $0.28^\circ$ 12

X.Zhao et al, Talk on 5th SRF Thin Film Workshop, JLab. 2012
Comparison Chart

- EBSD Survey Area 200X200um.

<table>
<thead>
<tr>
<th>Sample</th>
<th>MgB₂ CVD Epitaxy Film</th>
<th>Bulk Nb</th>
<th>Nb Film (CED-38)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Avg. Miso. Angle</td>
<td>0.28°</td>
<td>0.15°</td>
<td>0.15°</td>
</tr>
</tbody>
</table>

X.Zhao et al, Talk on 5th SRF Thin Film Workshop, JLab. 2012
Crystal Quality Measurement by XRD

Introduction of Pole Figure and Reciprocal Space Mapping (RSM) techniques
Outline

• Crystal Quality Measurement by EBSD

• Crystal Quality Measurement by XRD
  – Introduction of Pole Figure and Reciprocal Space Mapping (RSM) techniques
  – RSM Experimental Data
    • Probing a Nb Film
    • Probing a Single Crystal Bulk Nb
    • Probing a Polycrystalline Bulk Nb

• Summary
• Acknowledge
• Questions
Real Lattice vs. Reciprocal Lattice

R space is also known as *momentum space* or *k-space*

---

**Figure 15** The points on the right-hand side are reciprocal lattice points of the crystal. The vector \( k \) is drawn in the direction of the incident x-ray beam and it terminates at any reciprocal lattice point. We draw a sphere of radius \( k = 2\pi/\lambda \) about the origin of \( k \). A diffracted beam will be formed if this sphere intersects any other point in the reciprocal lattice. The sphere as drawn intercepts a point connected with the end of \( k \) by a reciprocal lattice vector \( G \). The diffracted x-ray beam is in the direction \( k' = k + G \). This construction is due to P. P. Ewald.

Lattice Transformation:

\[
\begin{align*}
\mathbf{a}^* &= \mathbf{d}_{100}^* = \frac{1}{d_{100}} = \frac{\mathbf{b} \times \mathbf{c}}{\mathbf{a} \cdot \mathbf{b} \times \mathbf{c}} \\
\mathbf{b}^* &= \mathbf{d}_{010}^* = \frac{1}{d_{010}} = \frac{\mathbf{c} \times \mathbf{a}}{\mathbf{b} \cdot \mathbf{c} \times \mathbf{a}} \\
\mathbf{c}^* &= \mathbf{d}_{001}^* = \frac{1}{d_{001}} = \frac{\mathbf{a} \times \mathbf{b}}{\mathbf{c} \cdot \mathbf{a} \times \mathbf{b}}
\end{align*}
\]

**Notes:**

- http://leung.uwaterloo.ca/CHEM/750/Lectures%202007/SSNT-3-Surface%20Structure%20II.htm

X. Zhao et al, Talk on 5th SRF Thin Film Workshop, JLab. 2012
Pole Figure – exploring the Texture of crystallites

Points 1', 2' and 3' are drawn where these connecting lines intersect the equatorial plane. These are the 100 poles and uniquely represent the orientation of the unit cell in 3D space on a 2D plane.

Equatorial Plane is viewed from top to form stereographic projection (Pole Figures)

Source:
http://aluminium.matter.org.uk/content/html/eng/0210-0010-swf.htm

X.Zhao et al, Talk on 5th SRF Thin Film Workshop, JLab. 2012
XRD Pole Figure Experimental Setup and Standard Nb (110) Pole Figure

• Nb (110) Pole Figure

Experimental Steps:
• Fixed 2θ of a \{hkl\} crystal plane. (Bragg Law \(2d_{\{hkl\}} \sin(\theta) = \lambda\))
• Rotated around Normal Direction (Azimuthal \(\phi\), from 0-360°)
• Titled off-angle from Normal Direction (\(\psi\), 0-90°)

P.F. is to visualize **Reciprocal Lattice Space**
One **Crystal Plane** in real lattice space is a **Pole** in reciprocal space

<table>
<thead>
<tr>
<th>Crystal Plane</th>
<th>(\psi^{(\circ)})</th>
<th>(\phi^{(\circ)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(110)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>(011)</td>
<td>60</td>
<td>54.74</td>
</tr>
<tr>
<td>(101)</td>
<td>60</td>
<td>125.26</td>
</tr>
<tr>
<td>(1,0,-1)</td>
<td>60</td>
<td>234.74</td>
</tr>
<tr>
<td>(0,1,-1)</td>
<td>60</td>
<td>305.26</td>
</tr>
<tr>
<td>(1,-1,0)</td>
<td>90</td>
<td>180</td>
</tr>
<tr>
<td>(-1,1,0)</td>
<td>90</td>
<td>0</td>
</tr>
</tbody>
</table>

X.Zhao et al, Talk on 5th SRF Thin Film Workshop, JLab. 2012
Reciprocal Space Mapping (RSM)

RSM is a well established XRD technique.

Reciprocal Space Mapping
- XRD Experimental Setup

WORK STAGES:
1. Set $\omega^0, 2\theta_{hkl}$
2. Run $\theta/2\theta$ mode scan,
3. Slightly change $\omega^0$. Set $\omega^1, 2\theta_{hkl}$
4. Run $\theta/2\theta$ mode scan
n. ...Plot $\text{diff}(\omega)$ vs. $\text{diff}(\theta)$

\[
2d_{hkl} \sin(\theta_{hkl}) = \lambda_{cu}
\]

\[
\Delta d_{Nb(110)} = -1.871 \times \Delta \theta_{Nb(110)}
\]

*For $\Delta \theta_{Nb(110)} = 0.1^0$*

\[
\Delta d/d_{Nb(110)} \times 100\% = 8\%
\]
XRD Bragg-Brentano Scan

Typical application configurations

Thin film analysis and/or reflectometry

Time/Step 0.20 sec; Step size: 0.03°
X.Zhao et al, Talk on 5th SRF Thin Film Workshop, JLab. 2012
XRD RSM Experimental Data

Samples:
A High RRR Nb Film
CMP’ed Bulk Nb Coupons
Outline

• Crystal Quality Measurement by EBSD
• Crystal Quality Measurement by XRD
  – RSM Experimental Data
    I. Probing a Nb Film
    II. Probing a Single Crystal Bulk Nb
    III. Probing a Polycrystalline Bulk Nb

• Summary
• Acknowledge
• Questions

X.Zhao et al, Talk on 5th SRF Thin Film Workshop, JLab. 2012
RSM Data I. Survey a Nb Film

- AASC Nb Thin Films “CED-34”, on MgO crystal substrate. MgO(100) in-plane.
- Thickness: ~ 1.6 um (3000 arc-pulse)
- Epitaxial Relationship (“O_p” - type), Nb(100)//MgO(100), Nb[100]//MgO[110]
- RRR = 277, Tc=9.21-9.25K
- Pre-coating Substrate Heat-Treatment T=700°C
- Substrate temperature in coating T=500°C
Preparation Before RSM

Through Pole Figure Simulation and $k$-space Analysis, Select Pole (231) for RMS

Theta(123) = 60.85°

Psi = 55.49°
Incident Angle is 5.4°

Psi = 74.54°
For incident Angle is -13°, it is not observable

Psi = 36.72°
Incident Angle is 29.13°
I. Probing Different Film Thickness by Varying X-ray Incident Angle

- High Incident Angle ($\omega = 60.9^0$):
  - Probing Depth (if for a bulk Nb, $3645 \text{ nm}$): entire film (1.6 um)

- Low Incident Angle: ($\omega = 3.09^0$):
  - Probing Depth: 430 nm

- Definition of penetration depth
  \[ t = \frac{\sin \alpha}{\mu} \]
  With $\alpha$ the incident angle and $\mu = 1259$ is the absorption coefficient of Nb at 0.154 nm.
RSM Probing Film’s Top-layer

Omega 3.09400  Phi 28.45  X 0.00
2Theta 121.81835  Psi 0.61  Y 0.00
               Z 6.994

X.Zhao et al, Talk on 5th SRF Thin Film Workshop, JLab. 2012
RSM Probing Entire Film

Omega 60.90360
2Theta 121.87455

Phi 27.65
Psi 58.32

X 0.00
Y 0.00
Z 6.994

X.Zhao et al, Talk on 5th SRF Thin Film Workshop, JLab. 2012
Sample: CED-34

RSM Survey on Plane/Pole (231)

#1. High Incident Angle
RSM probes entire film thickness (1.6 um)
(Probing Depth 3.6um if bulk Nb)
\( \Delta \omega = \sim 0.6^{0} \)
\( \Delta \theta = \sim 0.2^{0} \)

#2. Low Incident Angle
RSM probes film top-layer
(Probing Depth 430nm)
\( \Delta \omega = \sim 0.1^{0} \)
\( \Delta \theta = \sim 0.1^{0} \)

X.Zhao et al, Talk on 5th SRF Thin Film Workshop, JLab. 2012
Crystal Quality Evolution of Epitaxy Growth

Sample “CED-34”

RSM of Top-layer

Top-layer ~400 nm

Nb(100) Film 1600 nm

RSM probing interface?

MgO (100) crystal substrate

X.Zhao et al, Talk on 5th SRF Thin Film Workshop, JLab. 2012
RSM Data II. Survey a Nb Single Crystal Bulk Material

• A Single Crystal Bulk Nb Coupon Sample
• Chemical-Mechanical Polished (CMP’ed) by *ATI Wah Chang*™, then Buffered Chemical Polished (BCP’ed) ~2micron. Mirror Finished ($R_q \sim 40$nm)
• Orientation: Nb(110) *in-plane*. 

X.Zhao et al, Talk on 5th SRF Thin Film Workshop, JLab. 2012
Pole Figure of the Single Crystal Nb

- Nb {110} Pole Figure
RSM Probing a Bulk Nb from top to 4 um deep layer
RSM Probing a Bulk Nb Top-layer

X.Zhao et al, Talk on 5th SRF Thin Film Workshop, JLab. 2012
Sample: CMP’ed Nb Single Crystal Bulk Material

RSM Survey on Plane/Pole \{110\}

Probing Top&Deep Layer (High Incident Angle, \(\sim 20^\circ\))
\[
\Delta \omega = \sim 0.1^\circ \\
\Delta \theta = \sim 0.1^\circ
\]

Probing Top-Layer only (Low Incident Angle, \(\sim 8^\circ\))
\[
\Delta \omega = \sim 0.6^\circ \\
\Delta \theta = \sim 0.2^\circ
\]

X.Zhao et al, Talk on 5th SRF Thin Film Workshop, JLab. 2012
Crystal Quality Evolution of a Bulk Nb sample

X.Zhao et al, Talk on 5th SRF Thin Film Workshop, JLab. 2012
A Fine-grain Polycrystal Nb
Grain size ~50 microns
CMP’ed, then BCP’ed ~2micron.
No preferred Orientations
Sample:
CMP+2 um BCP’ed
Nb Fine-grain polycrystal Bulk Material

Nb \{110\} Pole Figure

X. Zhao et al, Talk on 5th SRF Thin Film Workshop, JLab. 2012
Sample: CMP+2 um BCP’ed
Nb Fine-grain polycrystal Bulk Material

Probing Top&Deep Layer

(High Incident Angle Omega 19.27°)

Probing Top Layer only
( Low Incident Angle Omega 1.5°)
Summary

1. Crystal quality of epitaxy film progressively evolves on Growth Thickness (Verified by EBSD and XRD-RSM).

2. Reciprocal Space Mapping (RSM) is an non-destructive technique to probe crystal quality of film or bulk Nb, via 2-D mapping of crystal misorientation angle (ω) & crystal plane distance (d_{hkl}).

3. Besides ω, RSM discerns d_{hkl}.

4. Top-layer and deep-layer Nb film/bulk have obvious crystal quality difference.
Implication to Structure Zone Model - microstructure evolution along thickness

Grayscale mask renders Anders’ SZM to visualize crystal quality
“Top-down” vs “Bottom-up” - Crystal Etching vs Growth - Bulk vs Film

- CMP’ed Bulk Nb Sample
  - Top-layer ~400 nm
  - Bulk Nb(110) ~4000 nm

- Sample “CED-34”
  - Top-layer ~400 nm
  - Nb(100) Film 1600 nm

X. Zhao et al, Talk on 5th SRF Thin Film Workshop, JLab. 2012
Acknowledge

• Colleagues of Jefferson Lab, who provided the samples, enlightening advices and critical thoughts: Hui Tian, Anna-Marie, Josh …..

• Collaborators from FSU, Zuhawn et al
• Collaborators from NCSU, Fred, et al
• Collaborators from WM
Questions to You

1. Why crystal quality progressively evolves on growth thickness (for Epitaxy Energetic Condensation Film) ? strain/stress relaxation, “Subplantation” outward growth…?

2. Will crystal quality of Fiber-Columnar Film also evolves along growth thickness?

3. What is the optimal thickness for Fiber Growth Film?

4. Besides Crystal Quality, Is a way to measure “Grain Boundary Quality”?
Appendix
Energetic Condensation – Deposition of “Hyperthermal Ions”

SRIM simulation shows penetration depth: 0 - 0.2 nm

X.Zhao et al, Talk on 5th SRF Thin Film Workshop, JLab. 2012
Three-dimensional epitaxy relationship of Nb/MgO(100)*

Table I. Tabulation of the lattice misfit parameters for the observed orientation (O), (001)_{Nb}/(001)_{MgO} with [010]_{Nb}/[010]_{MgO}, a more favored orientation (F), (101)_{Nb}/(001)_{MgO} with [011]_{Nb}/[100]_{MgO}, and a second possible orientation O_p (001)_{MgO} with [110]_{Nb}/[010]_{MgO}.

<table>
<thead>
<tr>
<th>Orientation</th>
<th>Parallel directions</th>
<th>% misfit</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>[100]<em>{Nb}/[100]</em>{MgO}</td>
<td>19.4</td>
</tr>
<tr>
<td></td>
<td>[010]<em>{Nb}/[010]</em>{MgO}</td>
<td>19.4</td>
</tr>
<tr>
<td>O_p</td>
<td>[100]<em>{Nb}/[010]</em>{MgO}</td>
<td>8.0</td>
</tr>
<tr>
<td></td>
<td>[100]<em>{Nb}/[110]</em>{MgO}</td>
<td>56.5</td>
</tr>
<tr>
<td>F</td>
<td>[011]<em>{Nb}/[100]</em>{MgO}</td>
<td>8.0</td>
</tr>
<tr>
<td></td>
<td>[010]<em>{Nb}/[010]</em>{MgO}</td>
<td>19.4</td>
</tr>
</tbody>
</table>

Illustration of three types Nb/MgO(100) epitaxial relationship, as proposed by Hutchinson et al.*.

3. X. Zhao et al, Talk on 5th SRF Thin Film Workshop, JLab. 2012