Crystal Quality Measurement on Niobium Materials

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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.

- Ref. *"Elements of X-ray Diffraction", B.D. Cullity. 2nd edition, page 260.*

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

Crystal Quality Measurement by EBSD

Image Quality and Misorientation Angles

as Figure-of-Merits

Misorientation Angles

- as a caliber of crystal quality

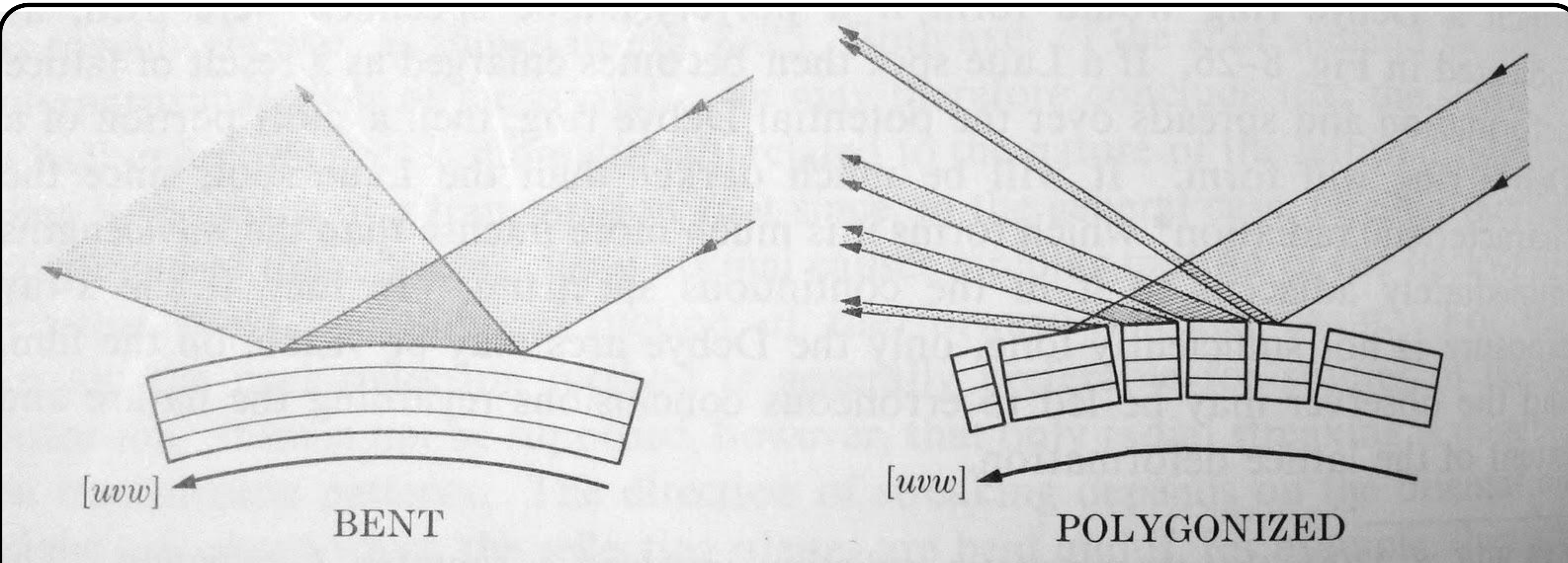

Fig. 8–27 Reflection of white radiation by bent and polygonized lattices (schematic).

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

EBSD **Image Quality** (I.Q.) parameter

- as a caliber of crystal quality

IMAGE QUALITY

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

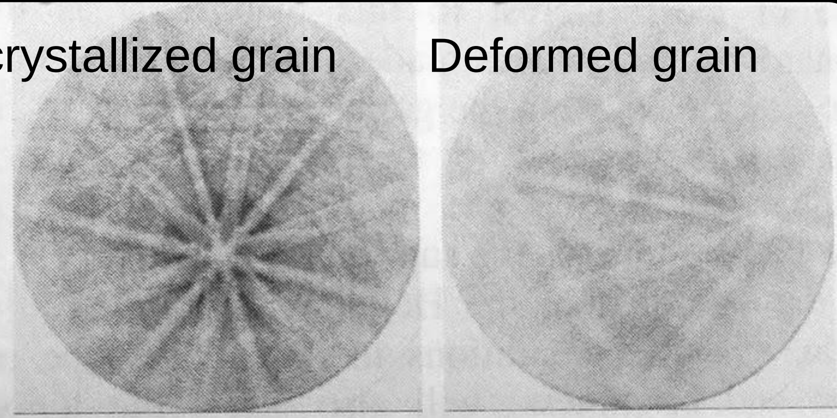

Figure 16. Electron backscatter diffraction patterns from partially recrystallized low carbon steel. The pattern on left is from a recrystallized grain and the pattern at right is from a deformed grain.

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

- Ref. *"EBSD Indexing Tutorial", Lecture Handout from EDAX/TSL company*.

Nb Thin Film Samples

Sample	CED-47	CED-46	CED-38
Thickness	~60 nm	~120 nm	~800 nm
RRR	46	62	136
T_c (K)	8.95	9.14	9.20

- 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^{0}C; The substrate temperate was set at "500^{0}C" during Nb thin film deposition. Note as, "700^{0}C/500^{0}C"
- The films are single crystals with epitaxial relationship, Nb(100)//MgO(100)

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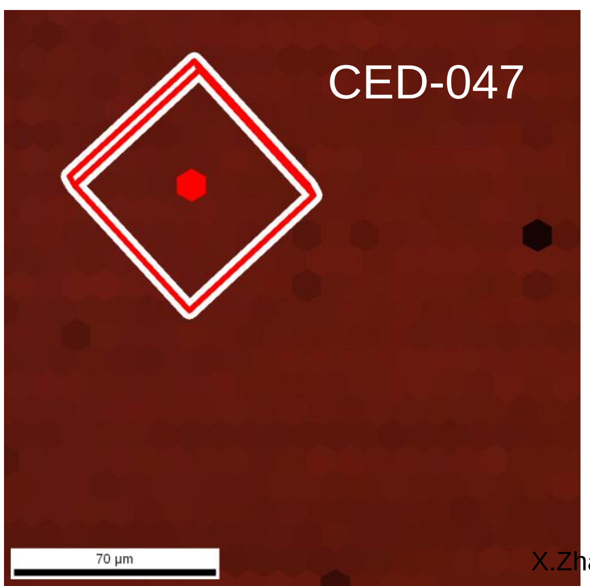
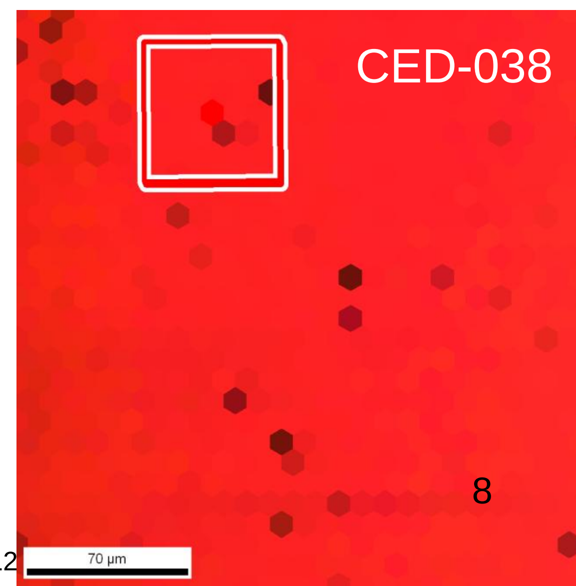
EBSD Measurement (I)

Sample	CED-47	CED-46	CED-38
Avg. C.I.	0.67	0.72	0.90
Avg. I.Q.	1121	1003	**2101**
Avg. Miso. Angle	0.18’	0.20’	0.15’

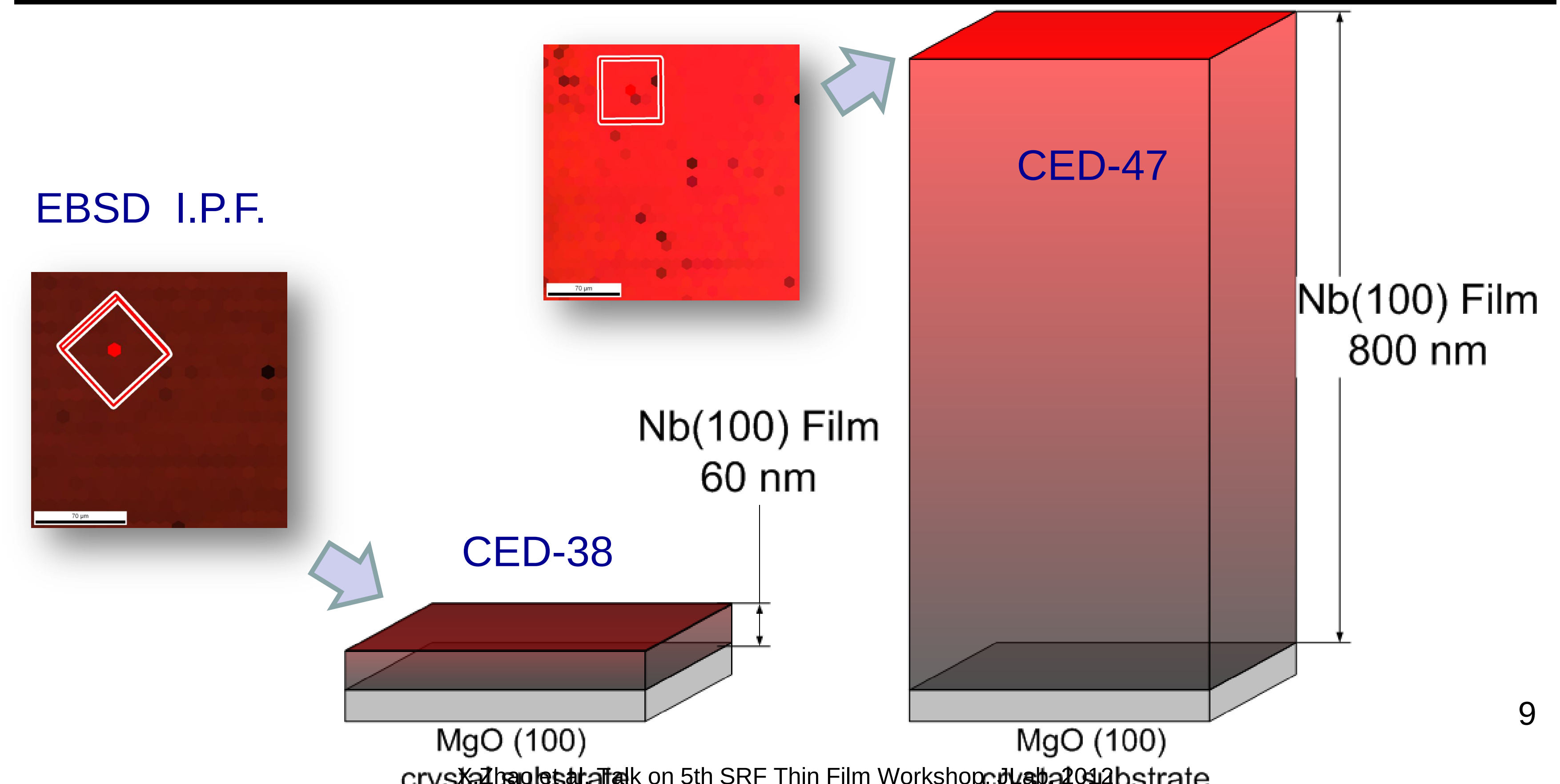
EBSD Survey Area: 250X250 um, Step10 um. The bottom pic. are Inverse Pole Figures.
IPF grayscale are rendered by the same I.Q. value: [min,max] = [500, 2100]





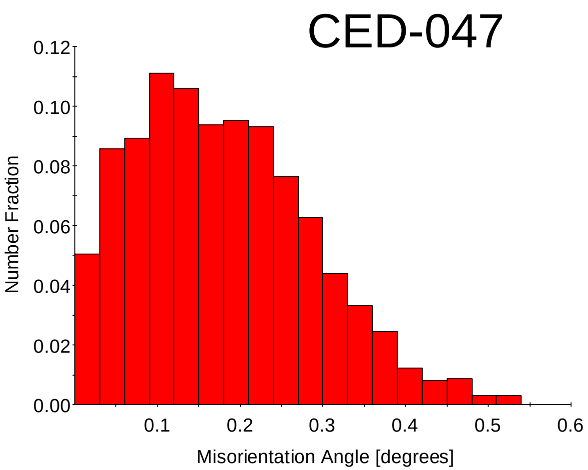
Crystal quality progressively evolves on film thickness

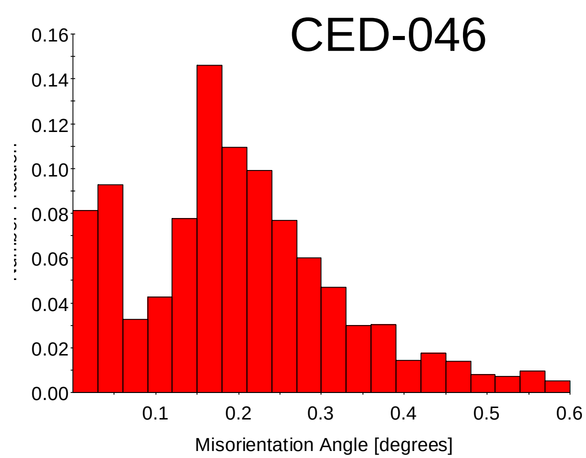
Sample	CED-47		CED-38
Avg. I.Q.	1121		**2101**
Avg. Miso. Angle	0.18’		0.15’
RRR	46		**136**

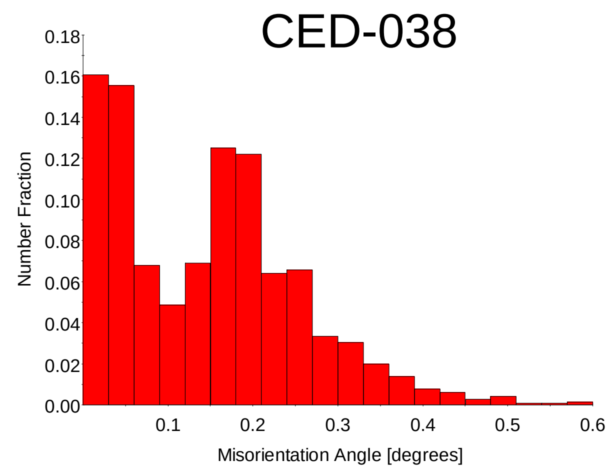


EBSD Measurement (II)

Sample	CED-47	CED-46	CED-38
Avg. Miso. Angle	0.18’	0.20’	**0.15’**





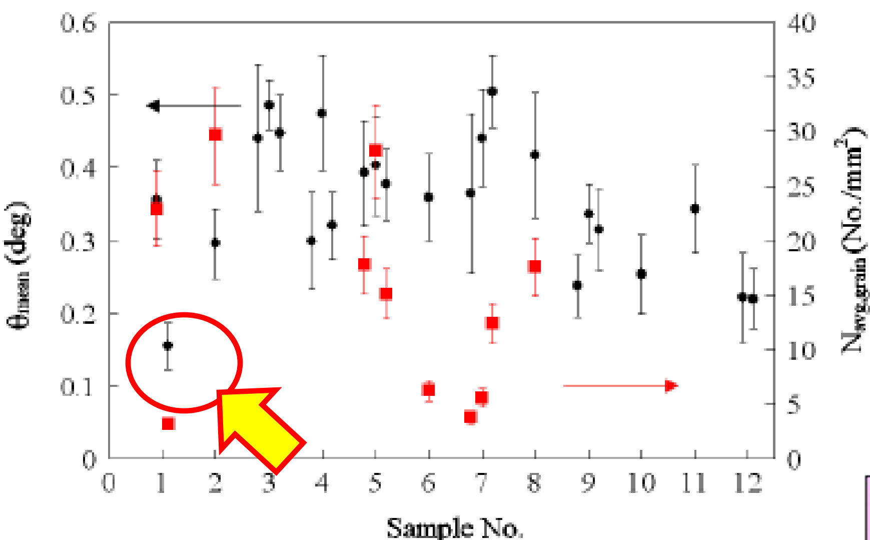


- Average misorientation angles have small change , if compared by Image Quality (I.Q.) index.
- Higher RRR sample has a slightly smaller Avg. Miso. Angle (0.15’)

Comparison to BCP Nb bulk samples

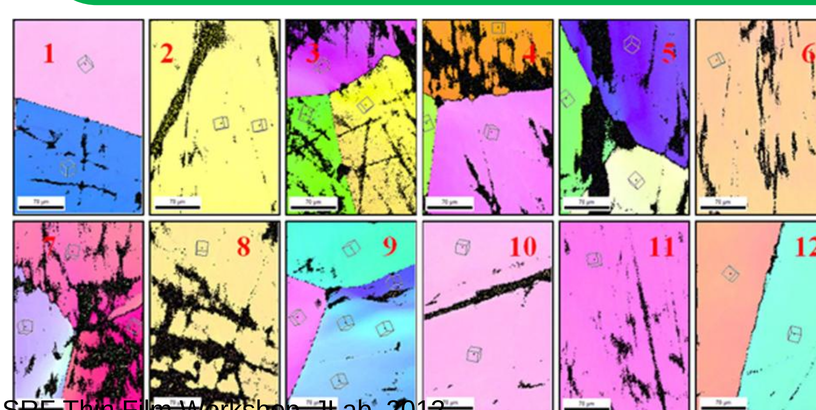
Sample	CED-47	CED-46	CED-38
Avg. Miso. Angle	0.18’	0.20’	**0.15’**

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

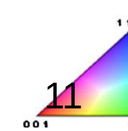


Mean values of the local average misorientation distributions, obtained from the EBSD data on each grain for all the samples (black circles) and average density of pits measured on each grain for six samples (red squares). Samples with more than one grain have multiple points in the plot, corresponding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

Smallest Avg. Miso. Angle is **~0.15^0**

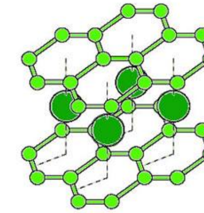


I.P.F. and Legend



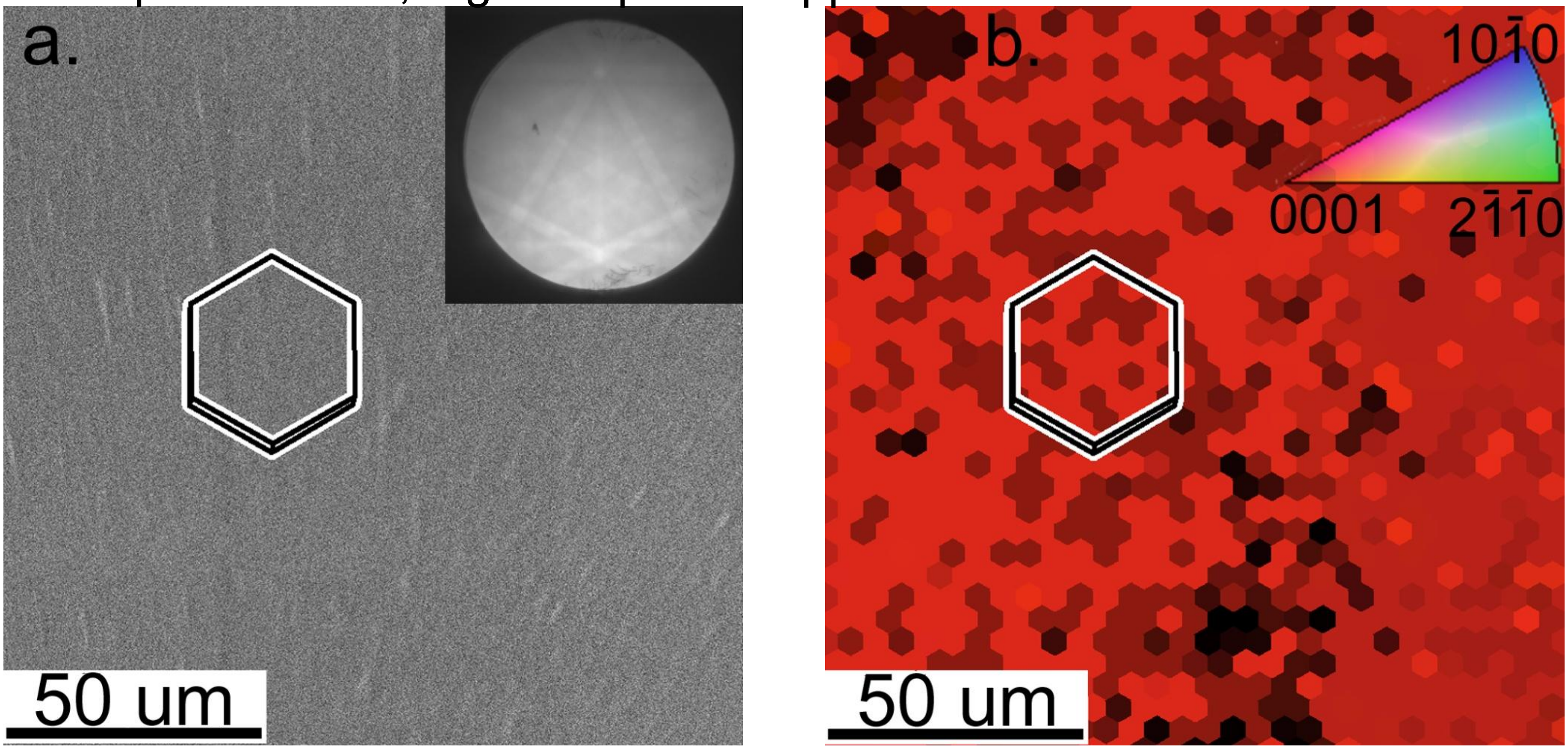
Citation from: Xin Zhao, G. Ciovati, and T. R. Bieler, Phys. Rev. ST Accel. Beams ***13 (12), 124701 (2010).,*** ***“****Characterization of etch pits found on a large-grain bulk niobium superconducting radio-frequency resonant cavity****”***

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: **0.28^0**

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Comparison Chart

- EBSD Survey Area 200X200um.

Sample	MgB_2 CVD Epitaxy Film	Bulk Nb	Nb Film (CED-38)
Avg. Miso. Angle	0.28^0	0.15^0	**0.15^0**

Crystal Quality Measurement by XRD

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

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- 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
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Real Lattice vs. Reciprocal Lattice

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

XRD Diffraction and Reciprocal Lattice

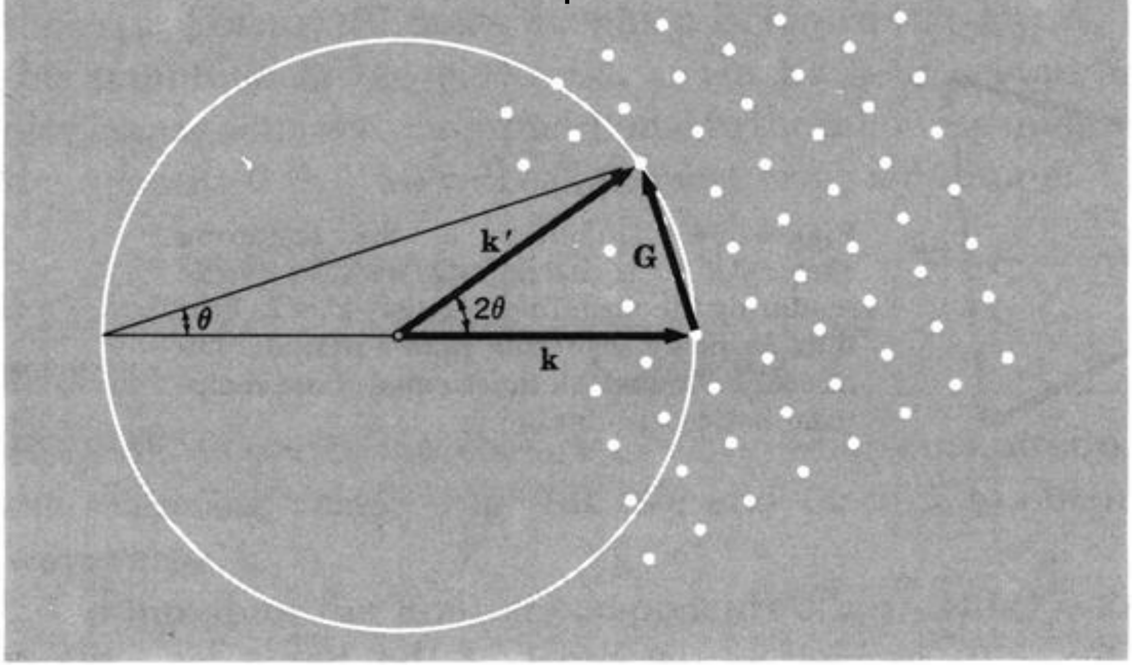


Figure 15 The points on the right-hand side are reciprocal lattice points of the crystal. The vector **k** is drawn in the direction of the incident x-ray beam and it terminates at any reciprocal lattice point. We draw a sphere of radius $k = 2\pi/\lambda$ about the origin of **k**. A diffracted beam 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 $\mathbf{k}' = \mathbf{k} + \mathbf{G}$. This construction is due to P. P. Ewald.

Lattice Transformation:

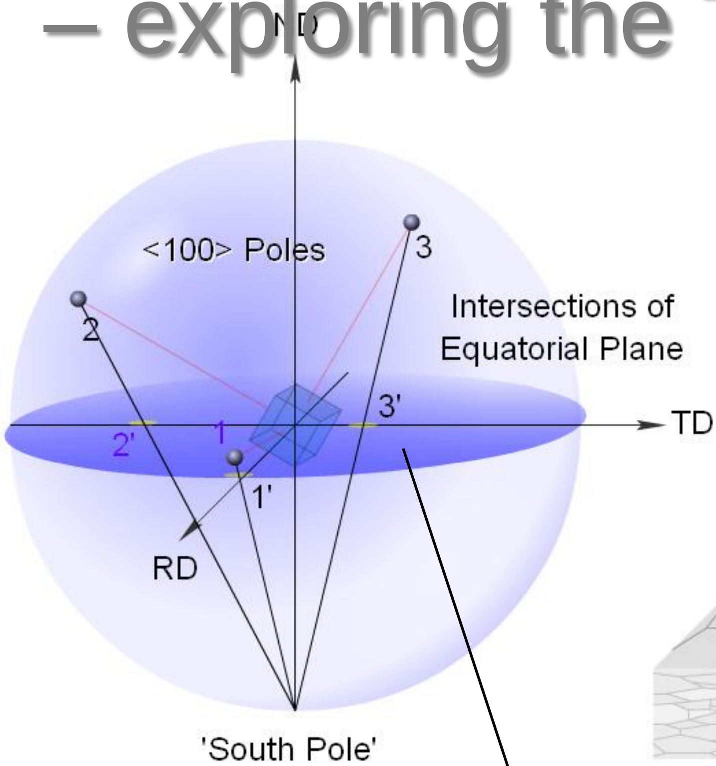
$$\mathbf{a}^* = \mathbf{d}^*_{100} = \frac{1}{\mathbf{d}_{100}} = \frac{\mathbf{b}\times\mathbf{c}}{\mathbf{a}\cdot\mathbf{b}\times\mathbf{c}}$$

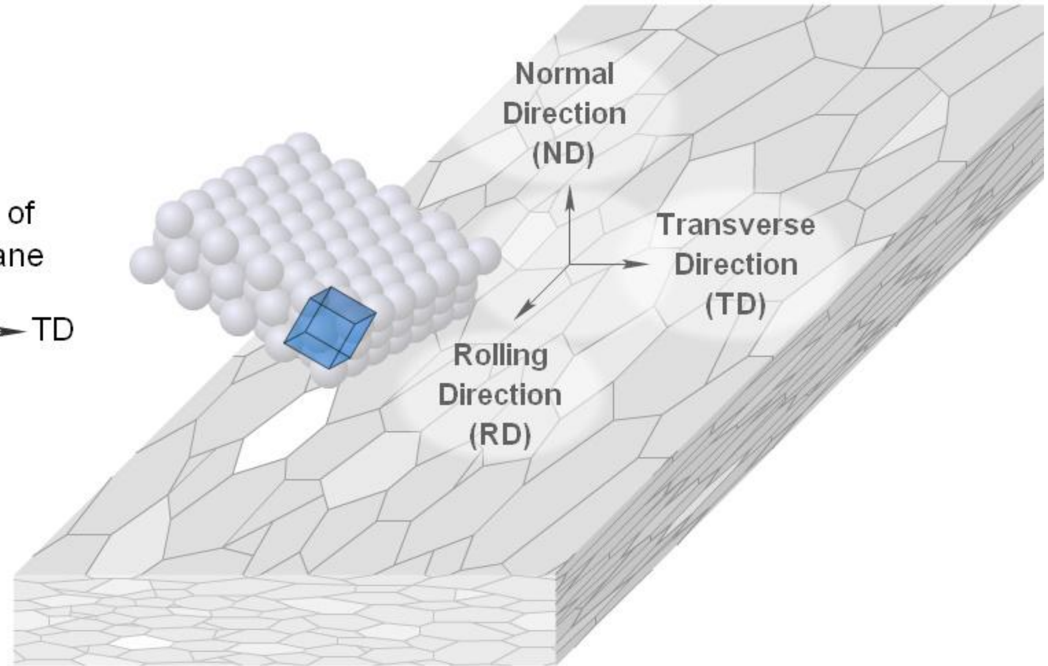
$$\mathbf{b}^* = \mathbf{d}^*_{010} = \frac{1}{\mathbf{d}_{010}} = \frac{\mathbf{c}\times\mathbf{a}}{\mathbf{b}\cdot\mathbf{c}\times\mathbf{a}}$$

$$\mathbf{c}^* = \mathbf{d}^*_{001} = \frac{1}{\mathbf{d}_{001}} = \frac{\mathbf{a}\times\mathbf{b}}{\mathbf{c}\cdot\mathbf{a}\times\mathbf{b}}$$

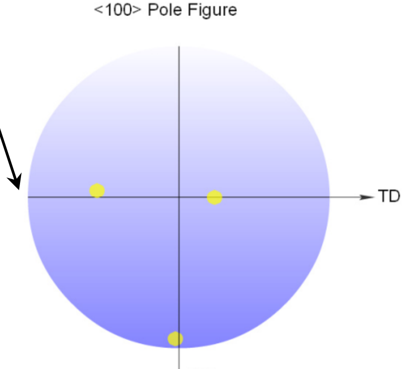
http://leung.uwaterloo.ca/CHEM/750/Lectures%202007/SSNT-3-Surface%20Structure%20II.htm

Pole Figure
– exploring the **Texture** of crystallites





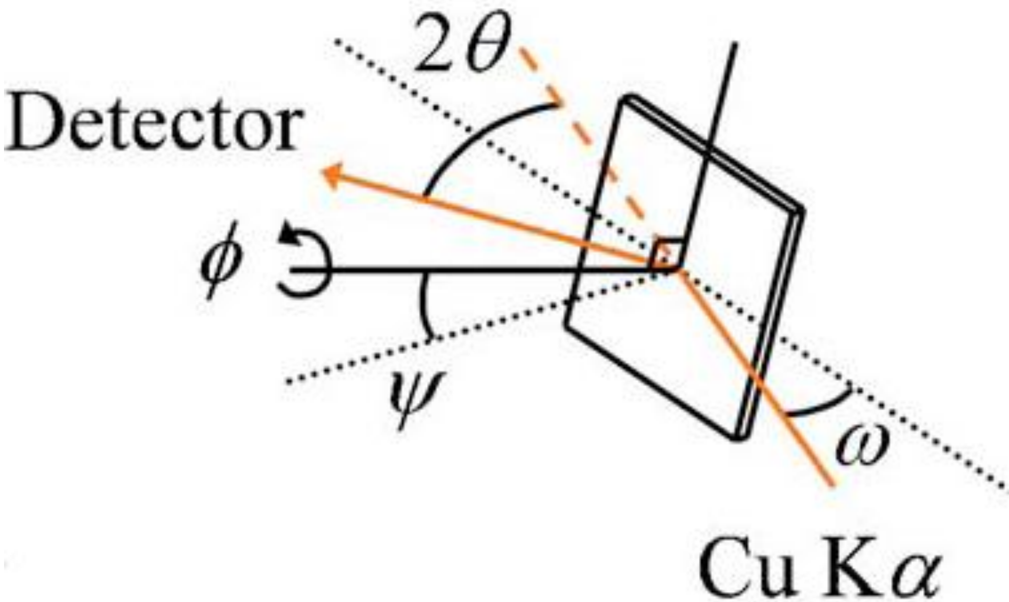
Points 1', 2' and 3' are drawn where these connecting lines intersect the equatorial plane. These are the 100 poles and uniquely represent the orientation of the unit cell in 3D space on a 2D plane.



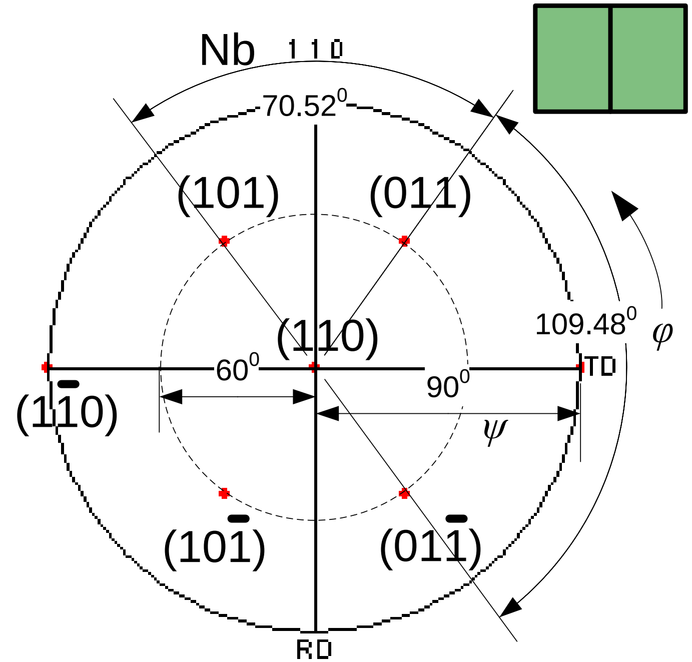
Equatorial Plane is viewed from top to form stereographic projection (Pole Figures)

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

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 φ, from 0-360^0)
- Titled off-angle from Normal Direction (ψ, 0-90^0)

Crystal Plane	ψ (^{0})	φ (^{0})
(110)	0	0
(011)	60	54.74
(101)	60	125.26
(1,0,-1)	60	234.74
(0,1,-1)	60	305.26
(1,-1,0)	90	180
(-1,1,0)	90	0

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

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Reciprocal Space Mapping (RSM)

RSM is a well established XRD technique.

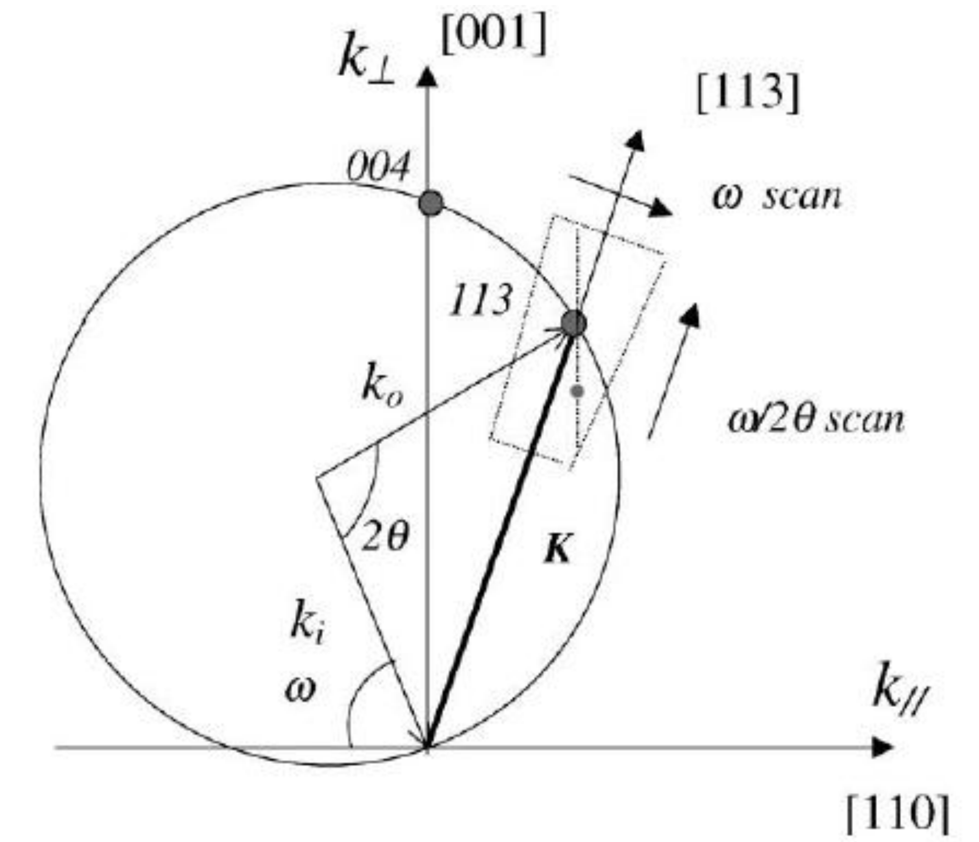
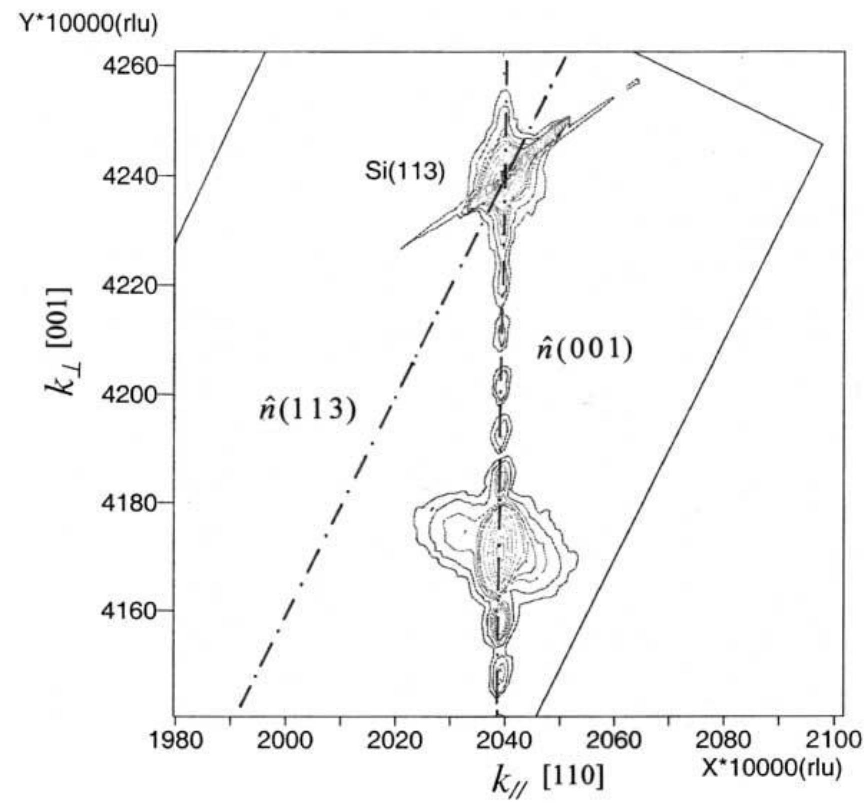


Fig. 1. Presentation of Ewald sphere and the scan directions of the XRD mapping.

RSM Experimental Results



Ref. Ni *et al* "*X-ray reciprocal space mapping studies of strain relaxation in thin SiGe layers", J. Crystal Growth 227-228 (2001), 756-760*.

Reciprocal Space Mapping

- XRD Experimental Setup

WORK STAGES:

1. Set ω^0, $2\theta_{hkl}$
2. Run $\theta/2\theta$ mode scan,
3. Slightly change ω^0 . Set $\omega^1, 2\theta_{hkl}$
4. Run $\theta/2\theta$ mode scan

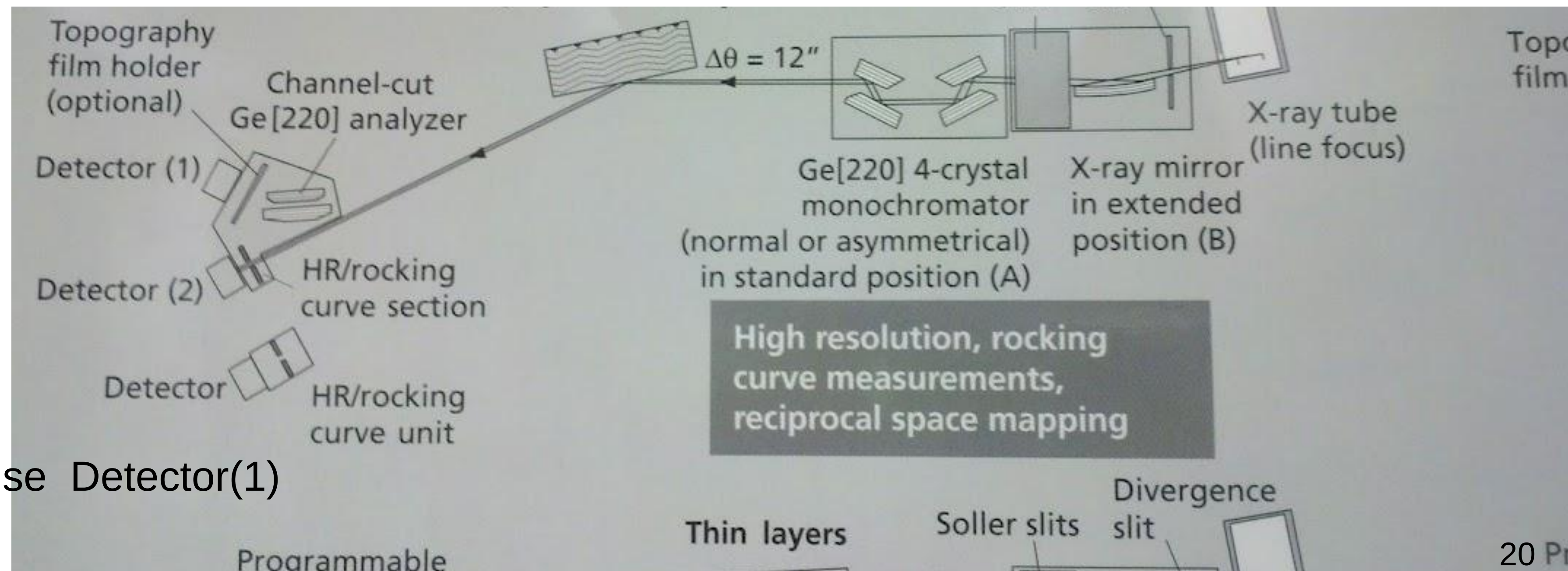
n. …Plot *diff(ω) vs. diff(θ)*

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

$$\Delta d_{Nb(110)} = -1.871 * \Delta\theta_{Nb(110)}$$

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

$$\Delta d/d_{Nb(110)} \ *100\% = 8\%$$



Use Detector(1)

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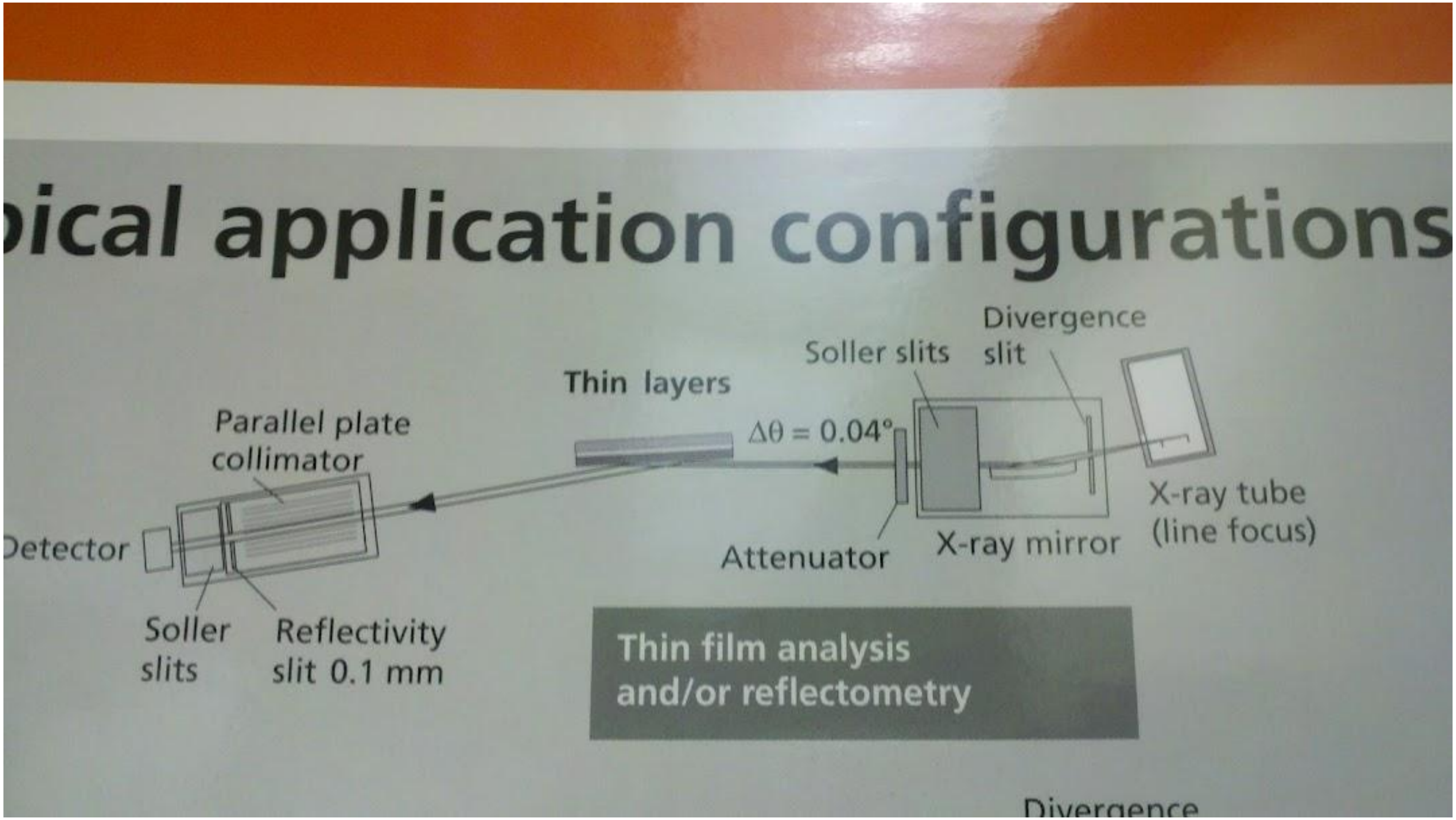
XRD Bragg-Brentano Scan



Time/Step 0.20 sec; Step size: 0.03^0

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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
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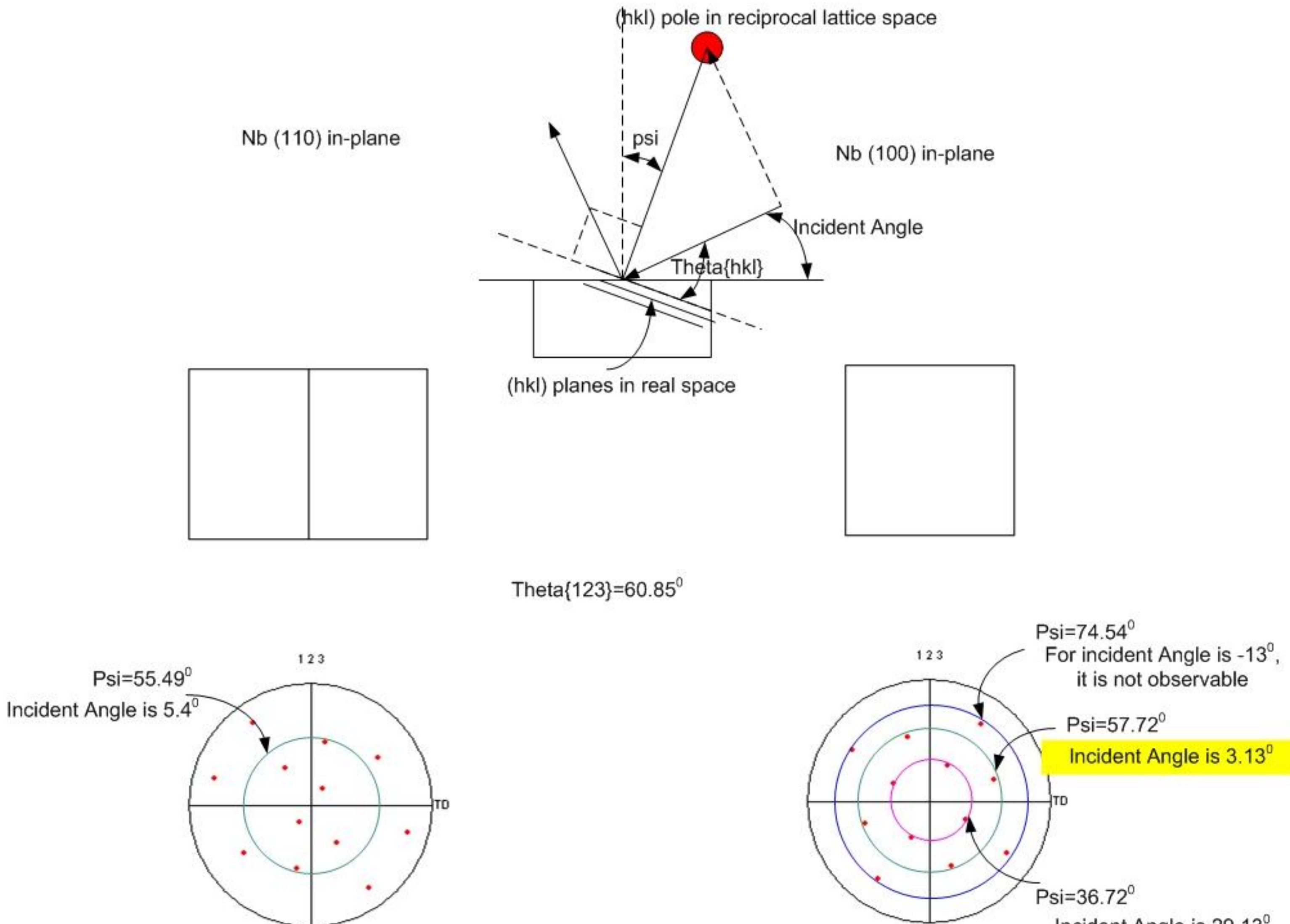
RSM Data I. Survey a Nb Film

- 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^{0}C
- Substrate temperature in coating T=500^{0}C

Preparation Before RSM

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



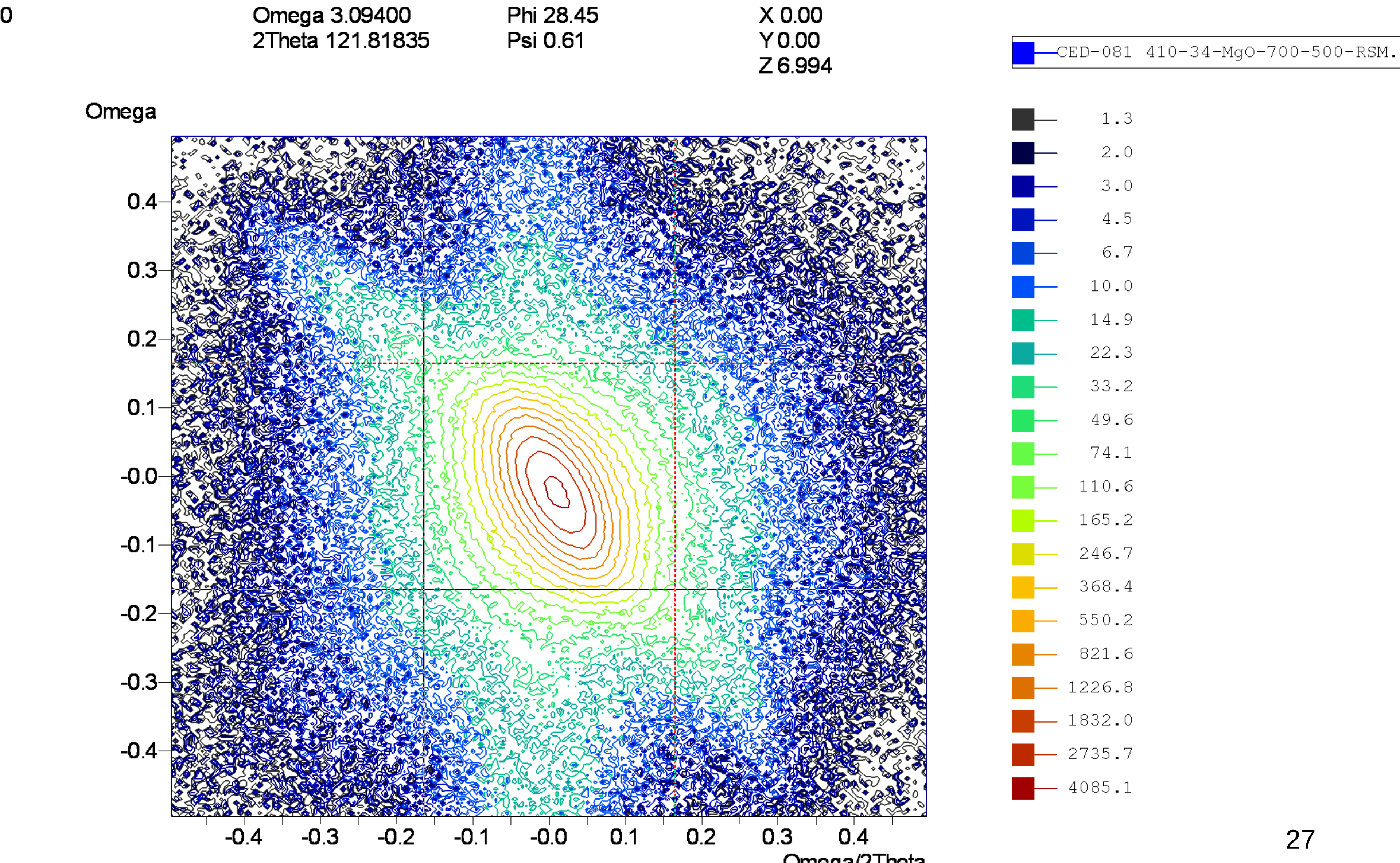
[Cont.] I.Probing Different Film Thickness by Varying X-ray Incident Angle

- High Incident Angle (**ω = 60.9^0**):
  - Probing Depth (if for a bulk Nb, **3645 nm**): **entire film (1.6 um)**
- Low Incident Angle:(**ω = 3.09^0**):
  - Probing Depth: **430 nm**
- Definition of penetration depth

$$t = \sin\alpha/\mu$$

With α the incident angle and $\mu = 1259$ is the absorption coefficient of Nb at 0.154 nm.

RSM Probing Film's Top-layer



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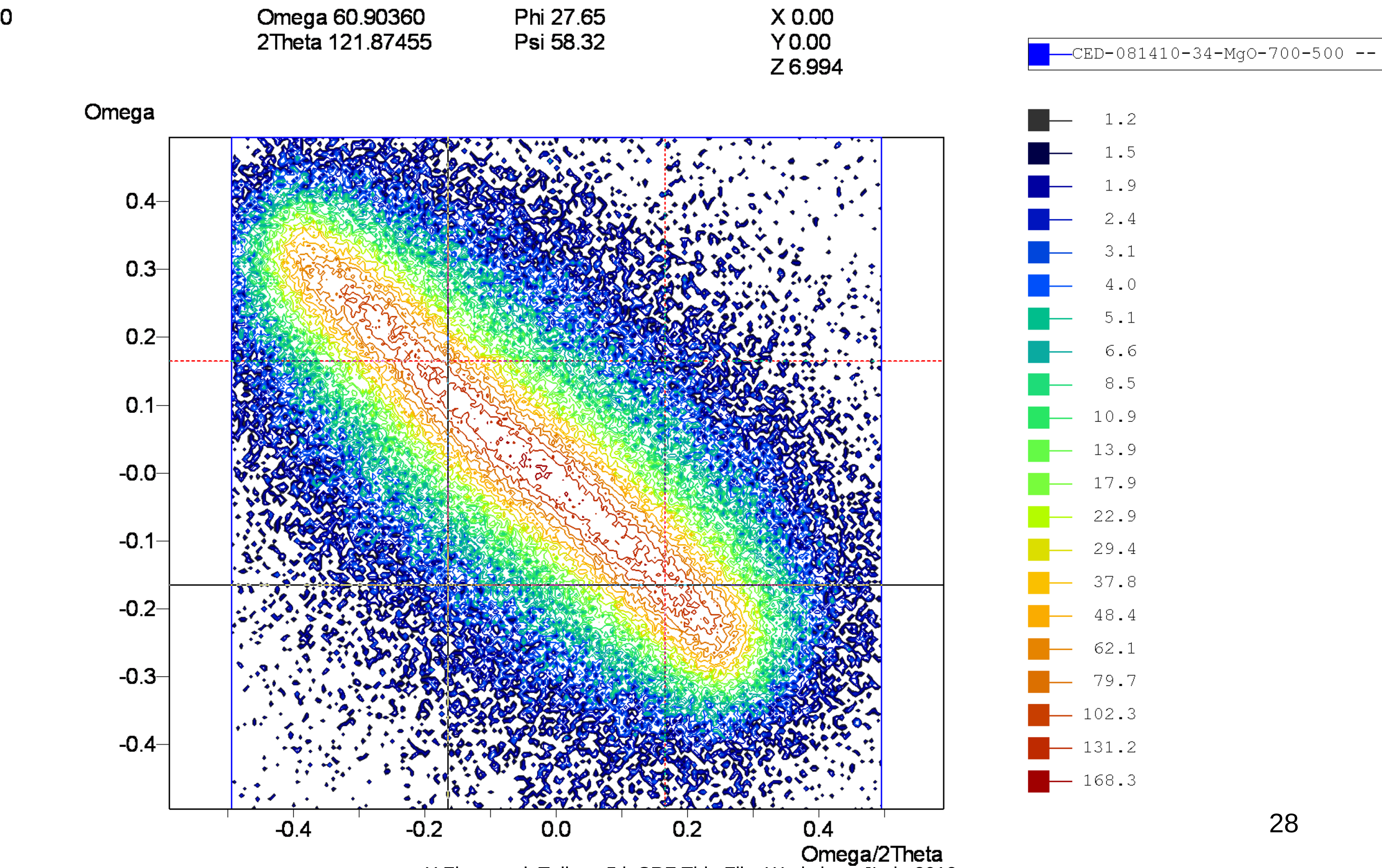
RSM Probing Entire Film



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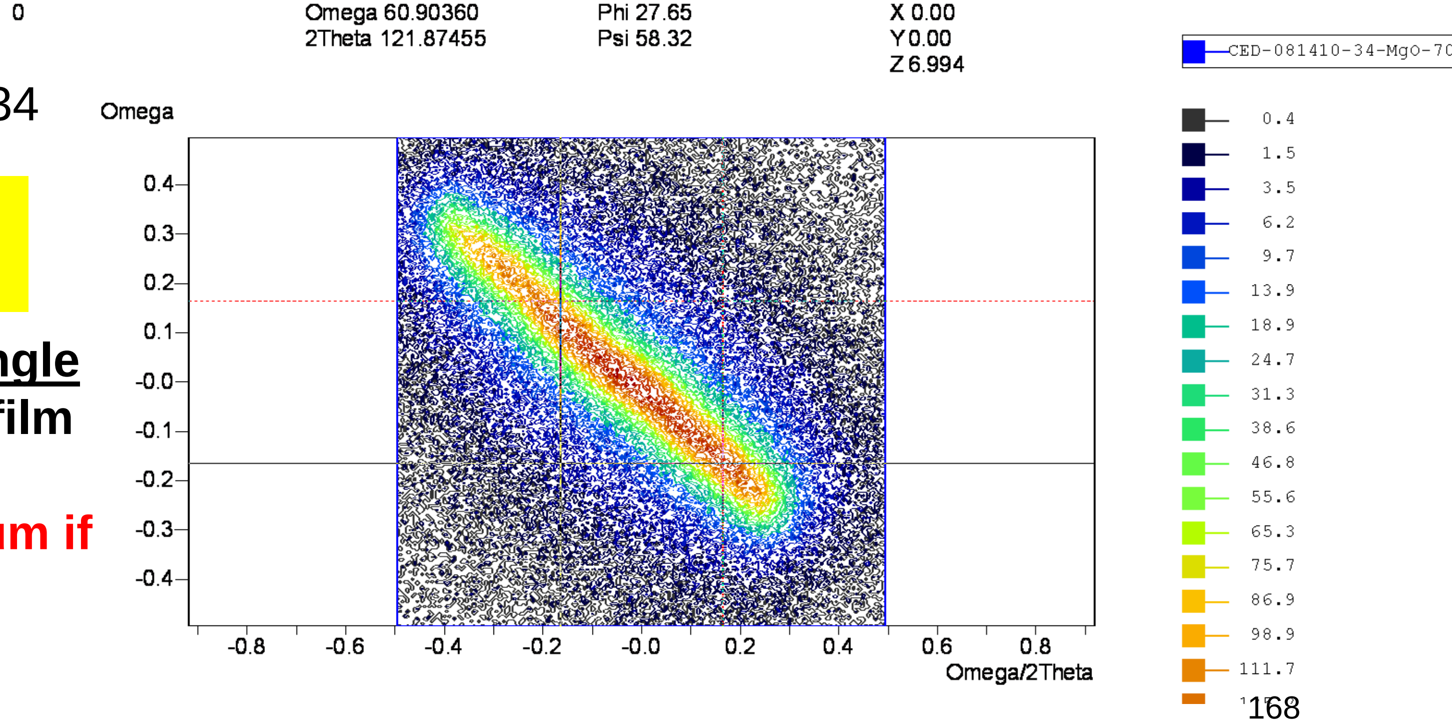
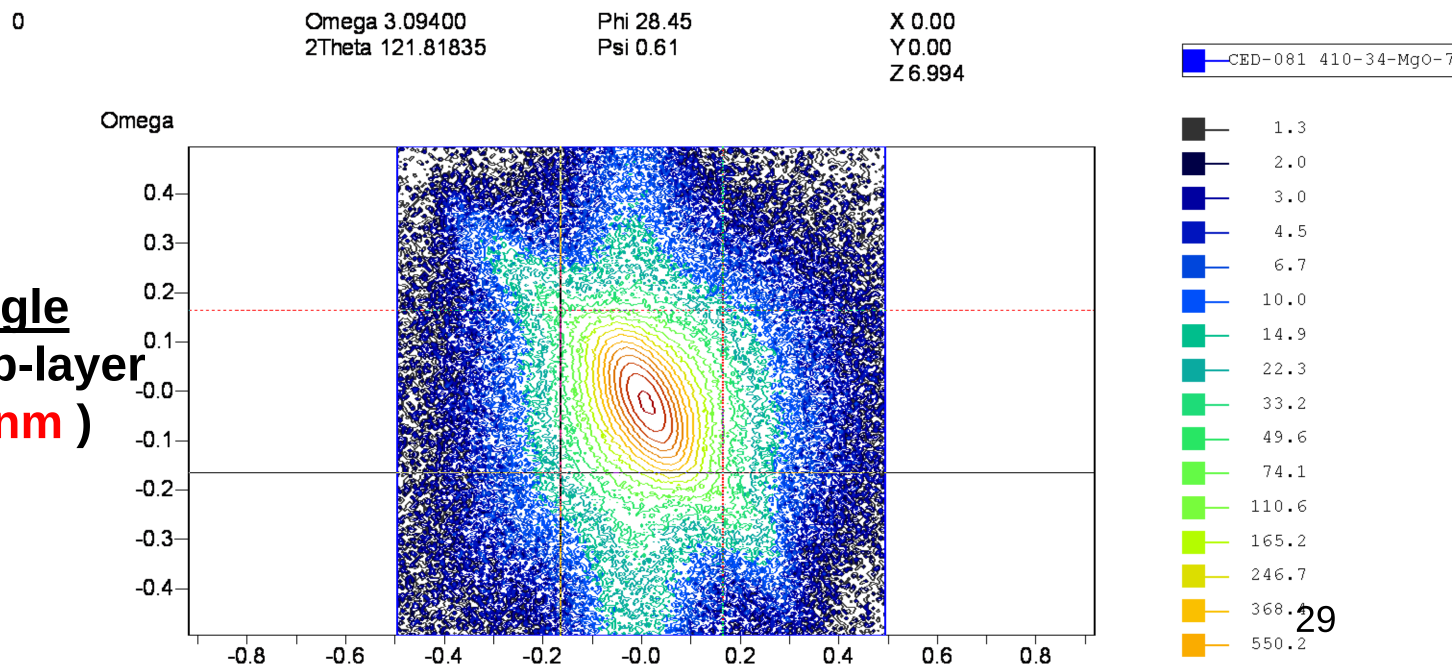
Sample: CED-34

RSM Survey
on Plane/Pole (231)

#1. <u>High Incident Angle</u>
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. <u>Low Incident Angle</u>
RSM probes film top-layer
(Probing Depth 430nm)
$\Delta\omega = \sim 0.1^0$
$\Delta\,\theta = \sim 0.1^0$



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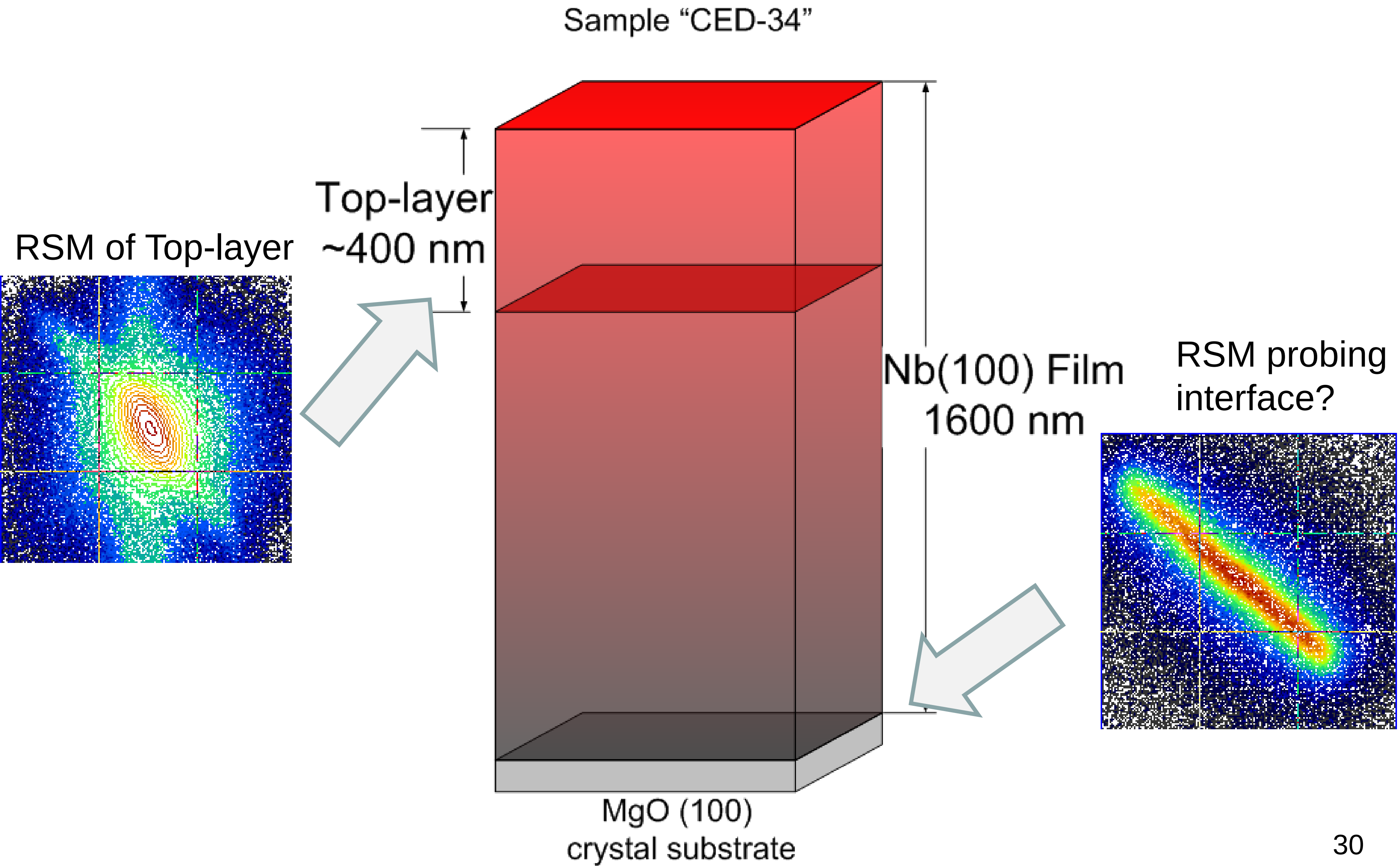
Crystal Quality Evolution of Epitaxy Growth



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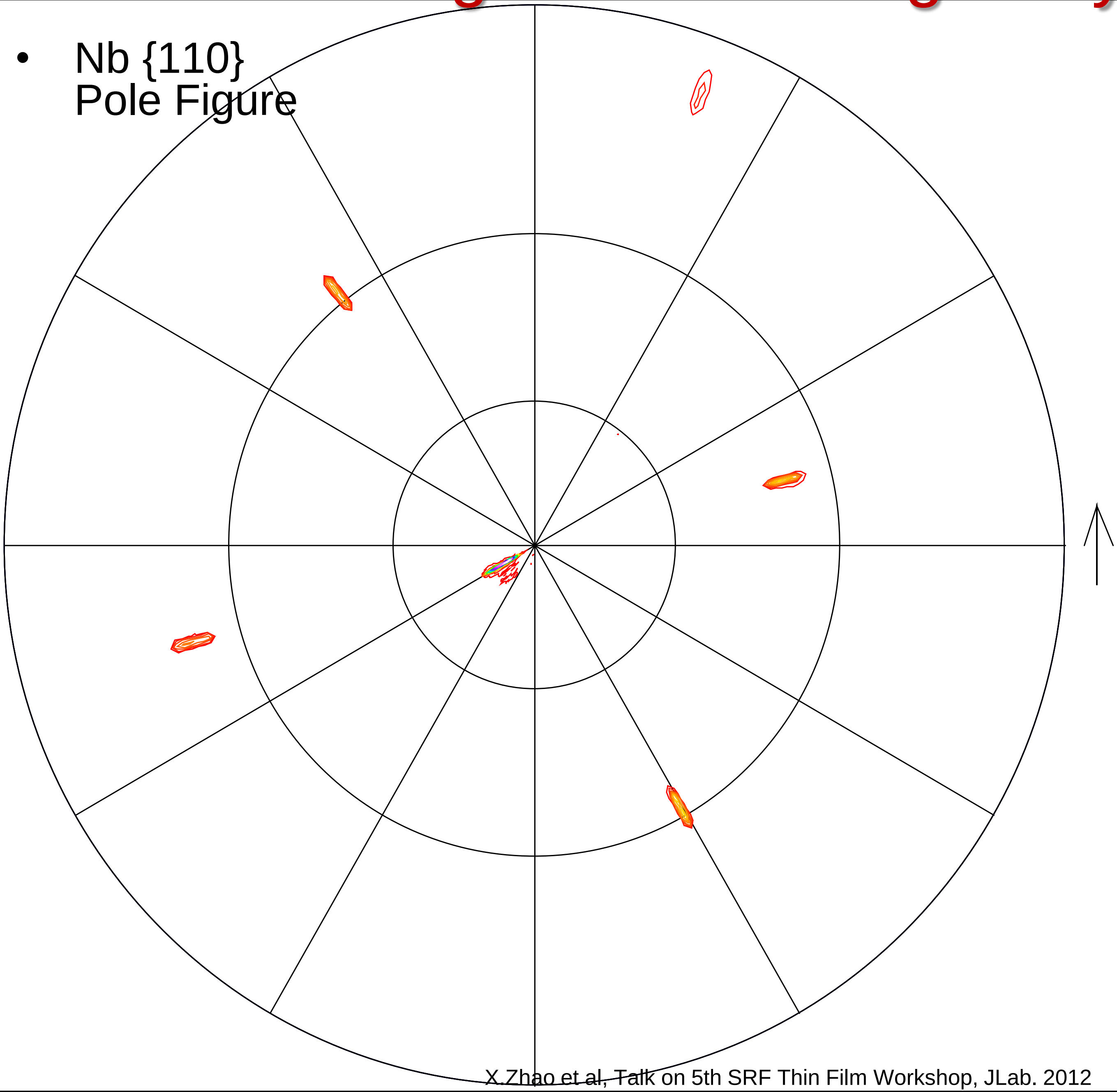
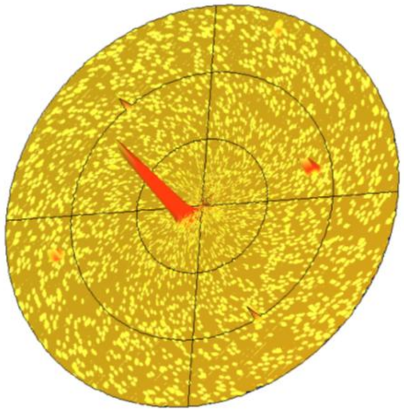
RSM Data II. Survey a Nb Single Crystal Bulk Material

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

Pole Figure of the Single Crystal Nb

- Nb {110} Pole Figure





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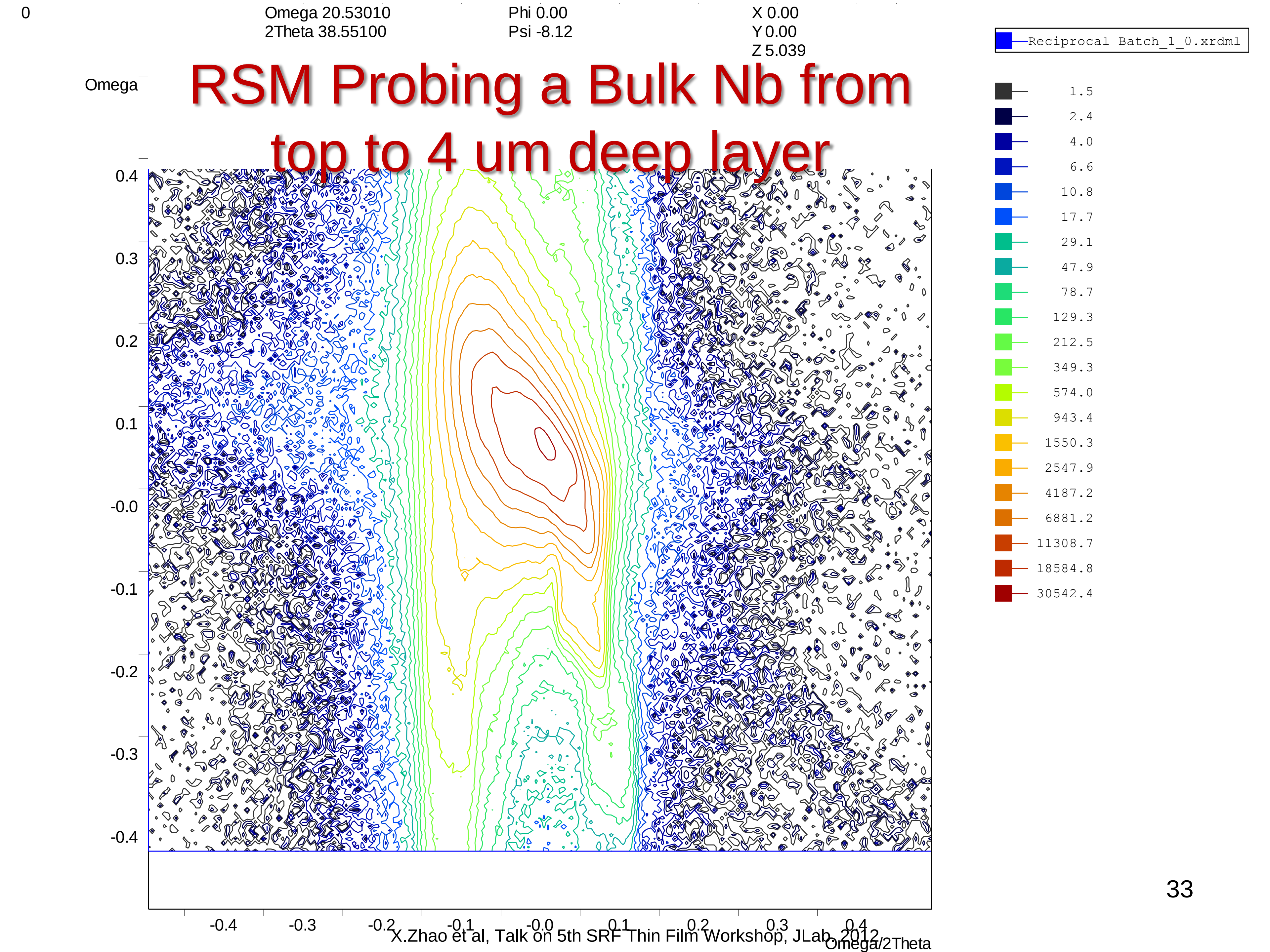
RSM Probing a Bulk Nb from top to 4 um deep layer



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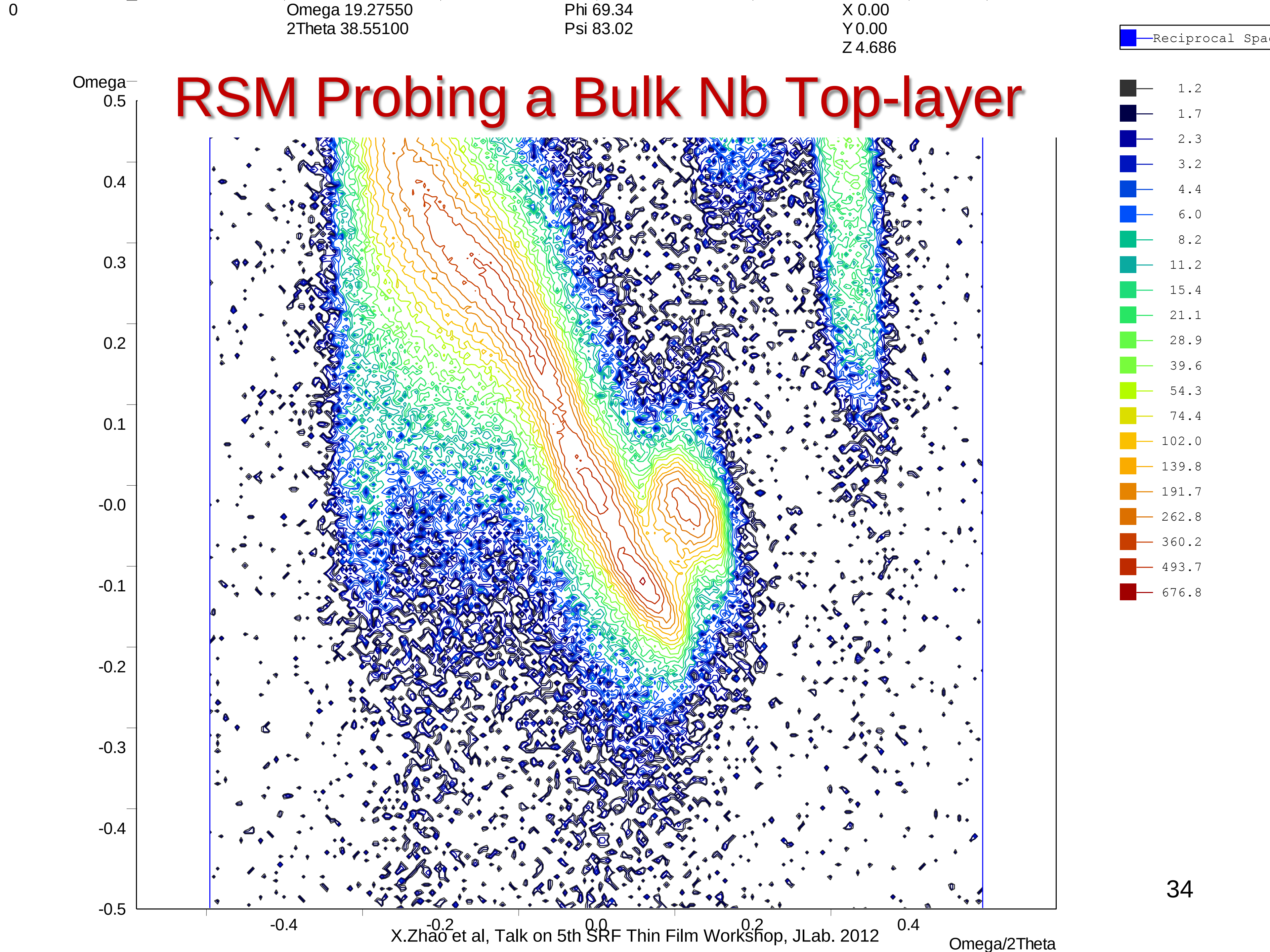
RSM Probing a Bulk Nb Top-layer



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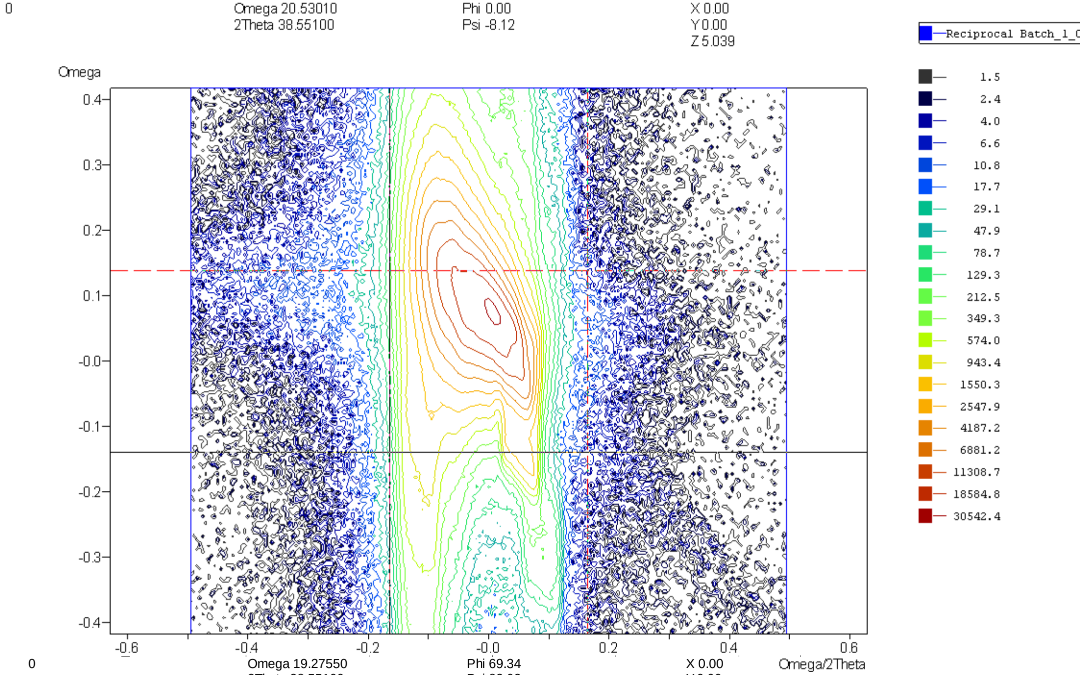
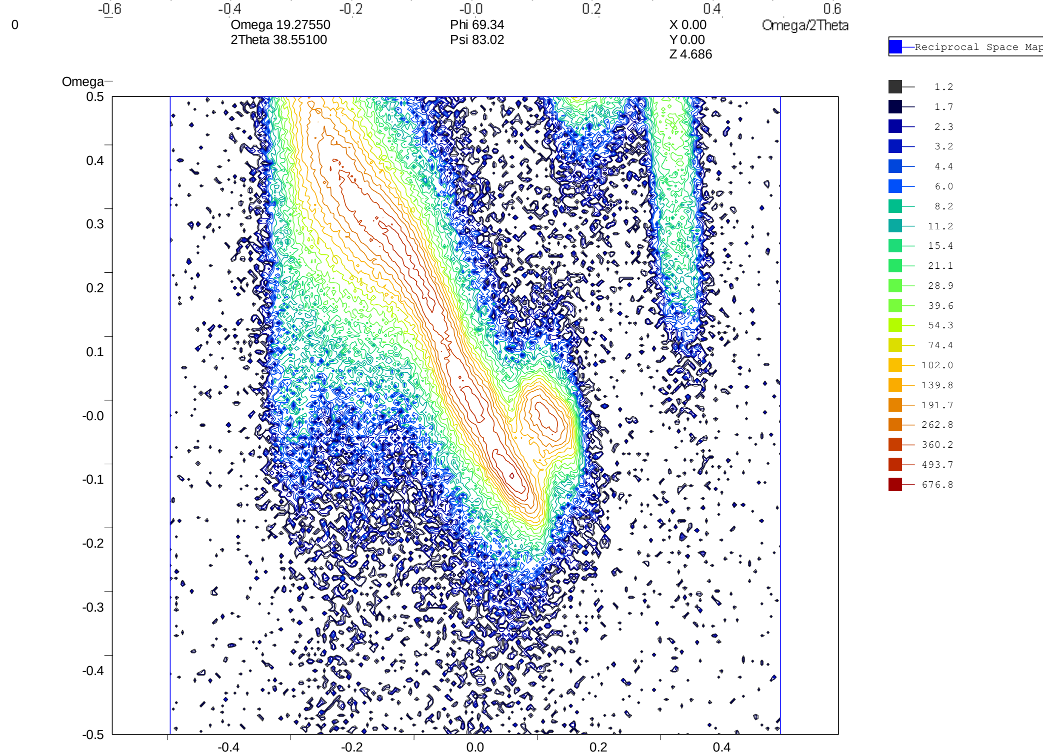
Sample: CMP'ed Nb Single Crystal Bulk Material

RSM Survey
on Plane/Pole {110}

Probing Top&Deep Layer
(High Incident Angle, ~20^0)
$\Delta\omega$ = ~ 0.1^0
$\Delta\theta$ = ~ 0.1^0



Probing Top-Layer only
(Low Incident Angle, ~8^0)
$\Delta\omega$ = ~ 0.6^0
$\Delta\theta$ = ~ 0.2^0



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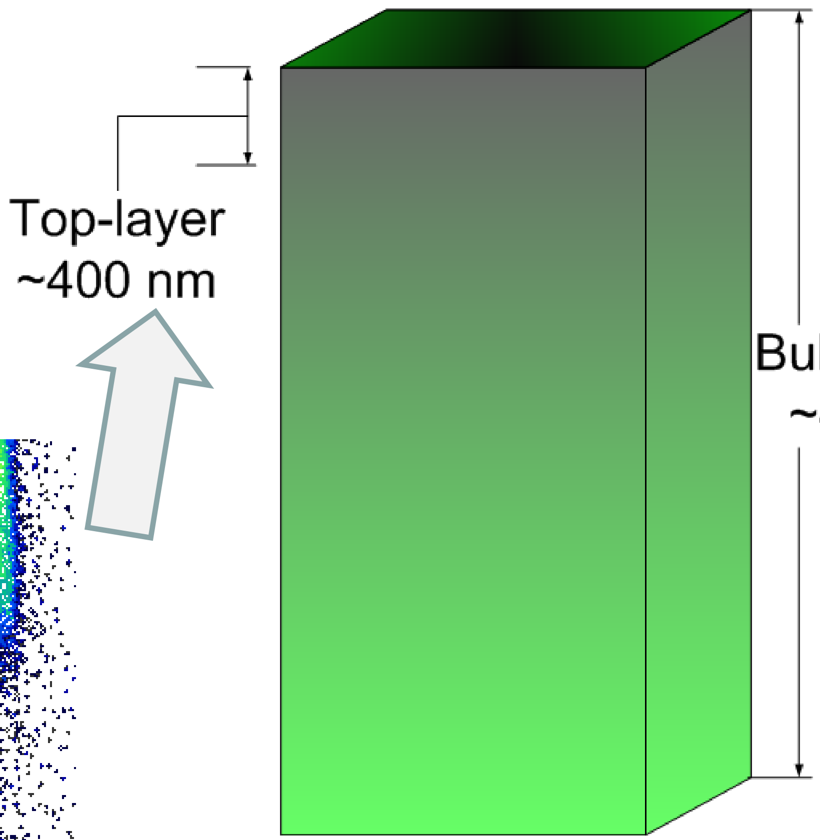
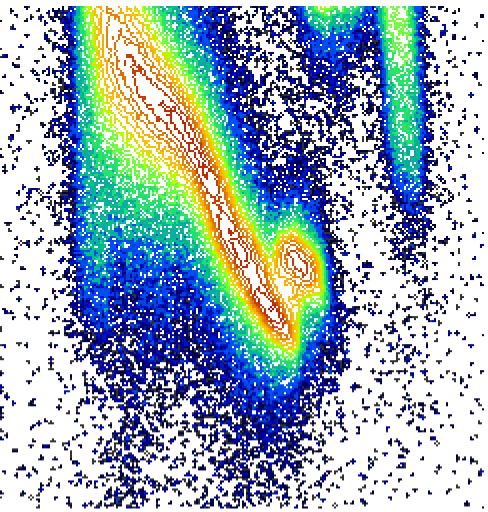
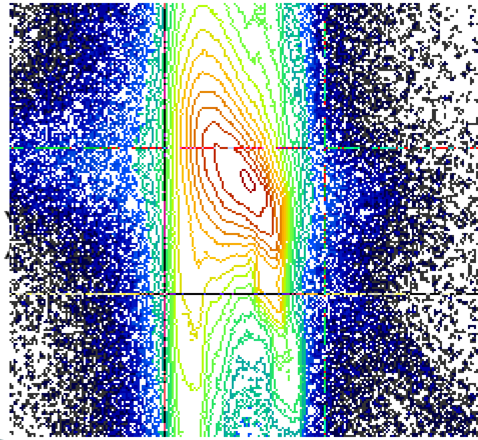
Crystal Quality Evolution of a Bulk Nb sample

CMP'ed Bulk Nb Sample



RSM of Top-layer





RSM of bulk

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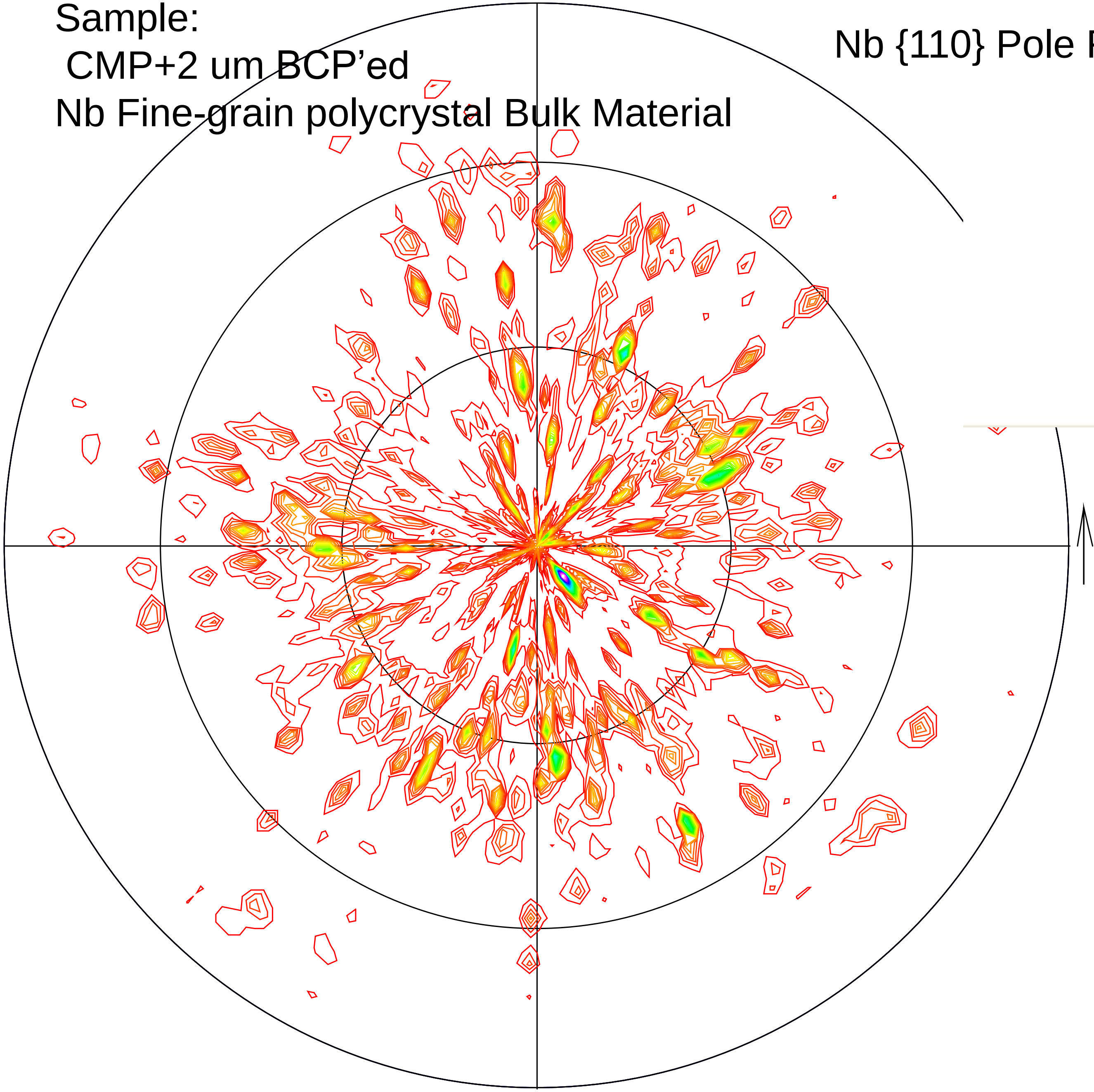
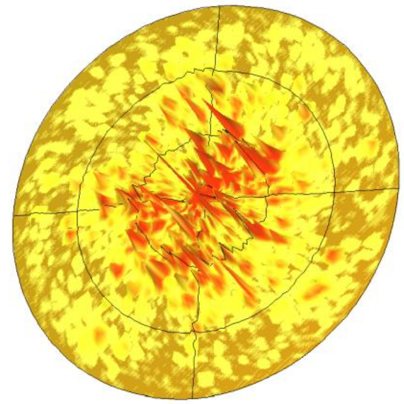
RSM Data III. Survey a Nb Polycrystalline Bulk Material

- 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





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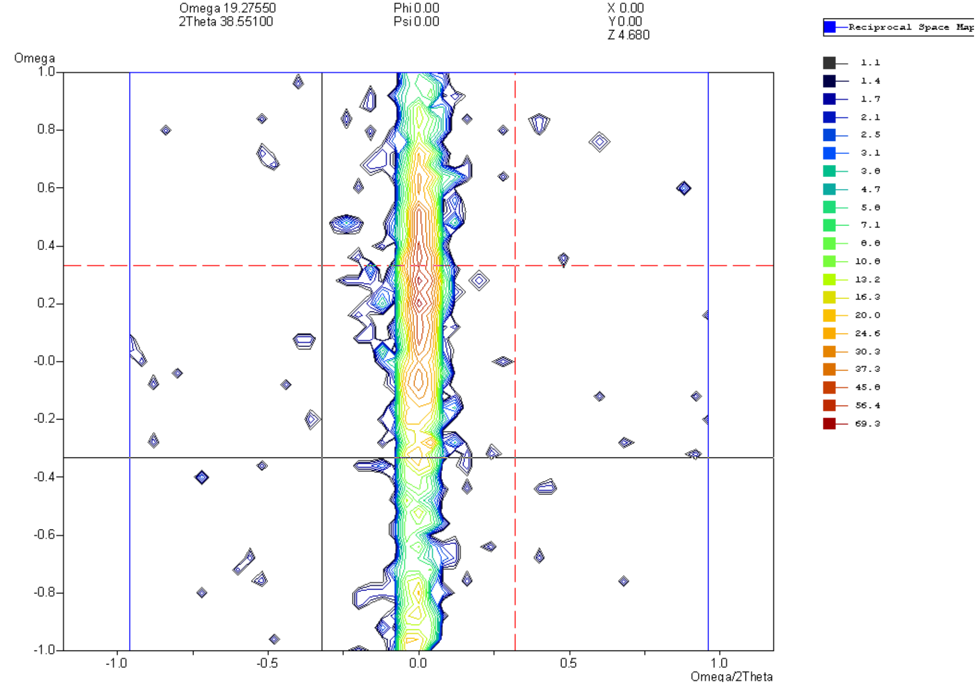
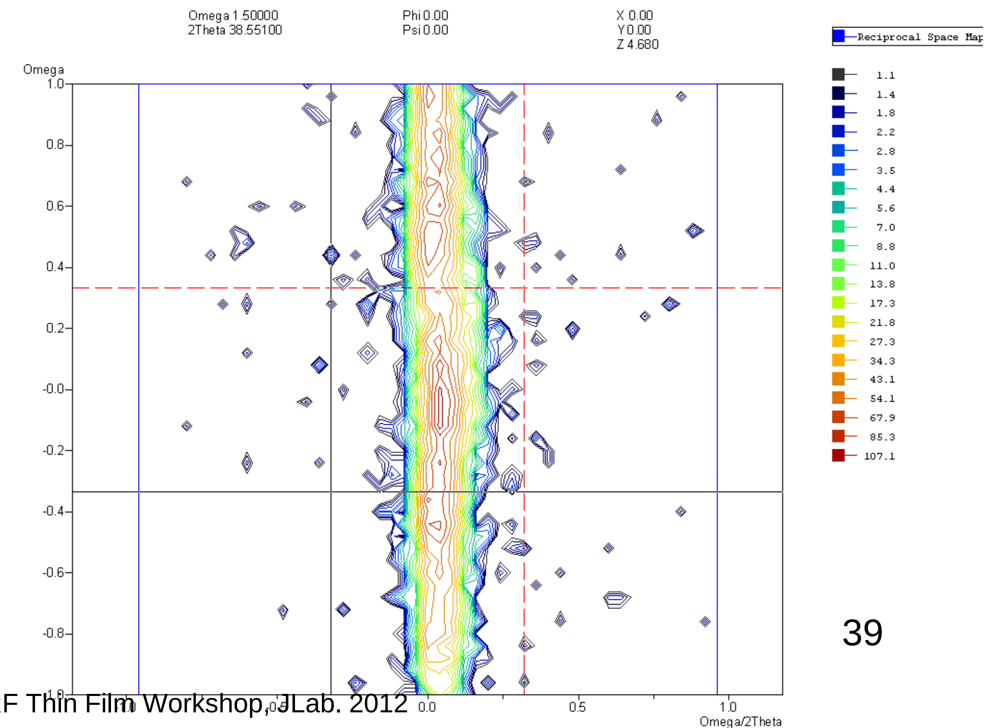
Sample:
CMP+2 um BCP'ed
Nb Fine-grain polycrystal Bulk Material

Probing Top&Deep Layer

(High Incident Angle Omega 19.27^{0})



Probing Top Layer only (Low Incident Angle Omega 1.5^{0})



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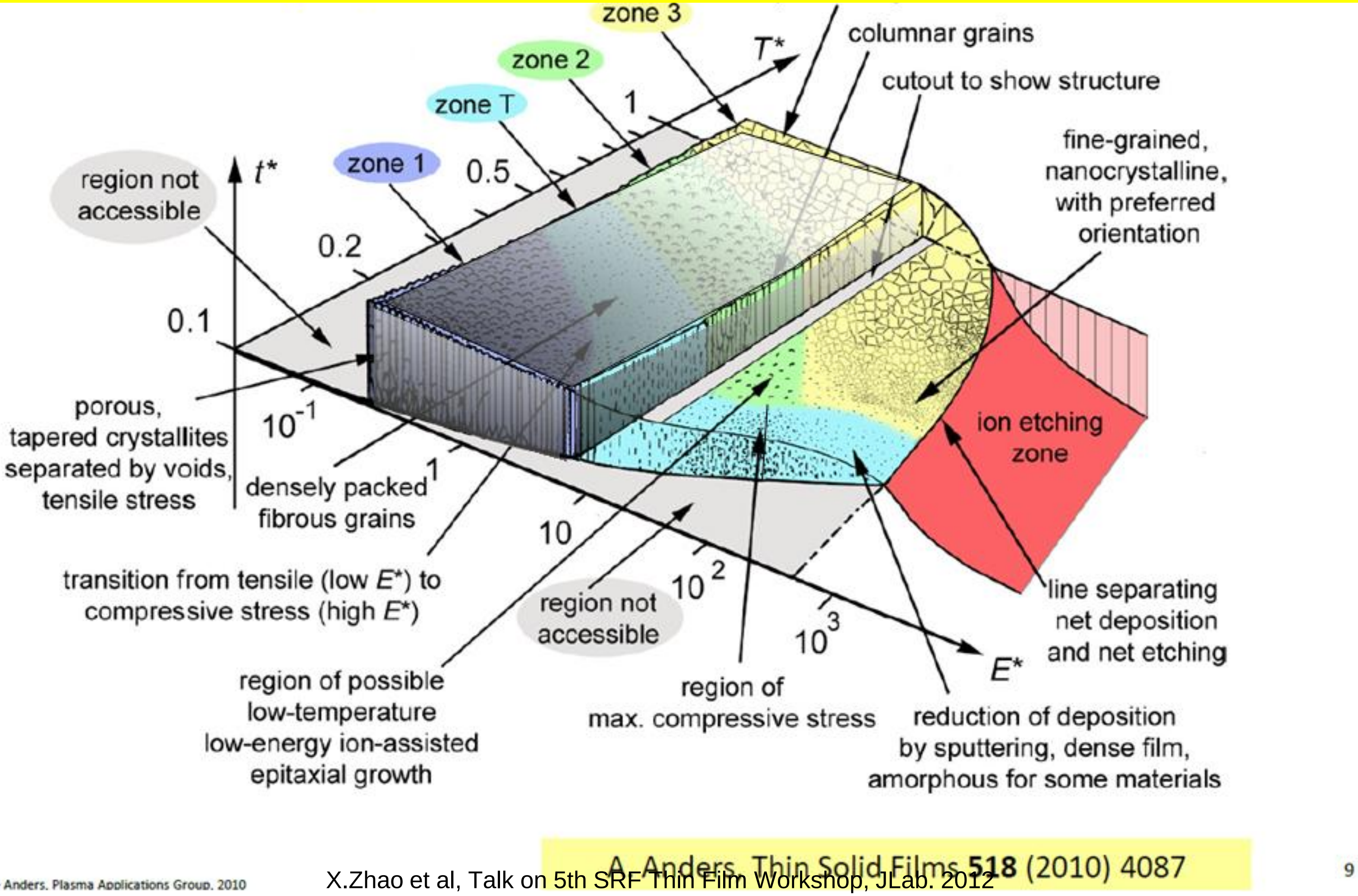
Summary

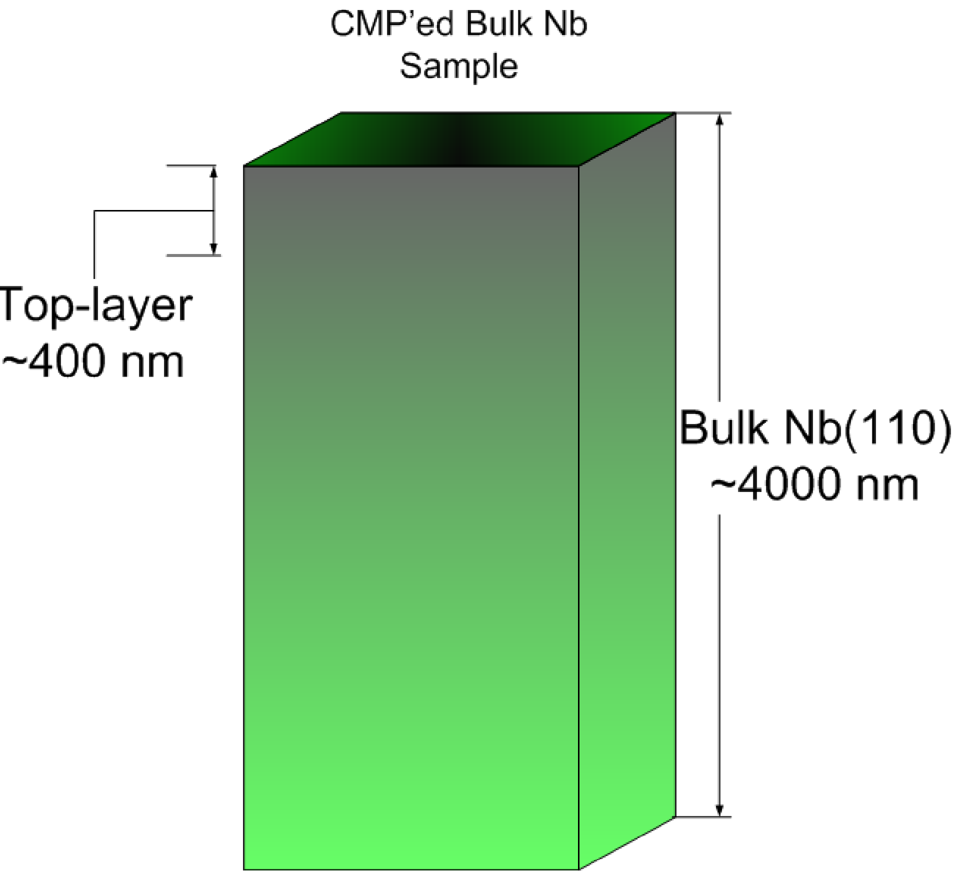
- 1. Crystal quality of epitaxy film progressively evolves on Growth Thickness (Verified by EBSD and XRD-RSM).
- 2. Reciprocal Space Mapping (RSM) is an non-destructive technique to probe crystal quality of film or bulk Nb, via 2-D mapping of crystal mis-orientation angle (ω) & crystal plane distance (d_{hkl})
- Besides ω, RSM discerns d_{hkl}
- 4. Top-layer and deep-layer Nb film/bulk have obvious crystal quality difference.

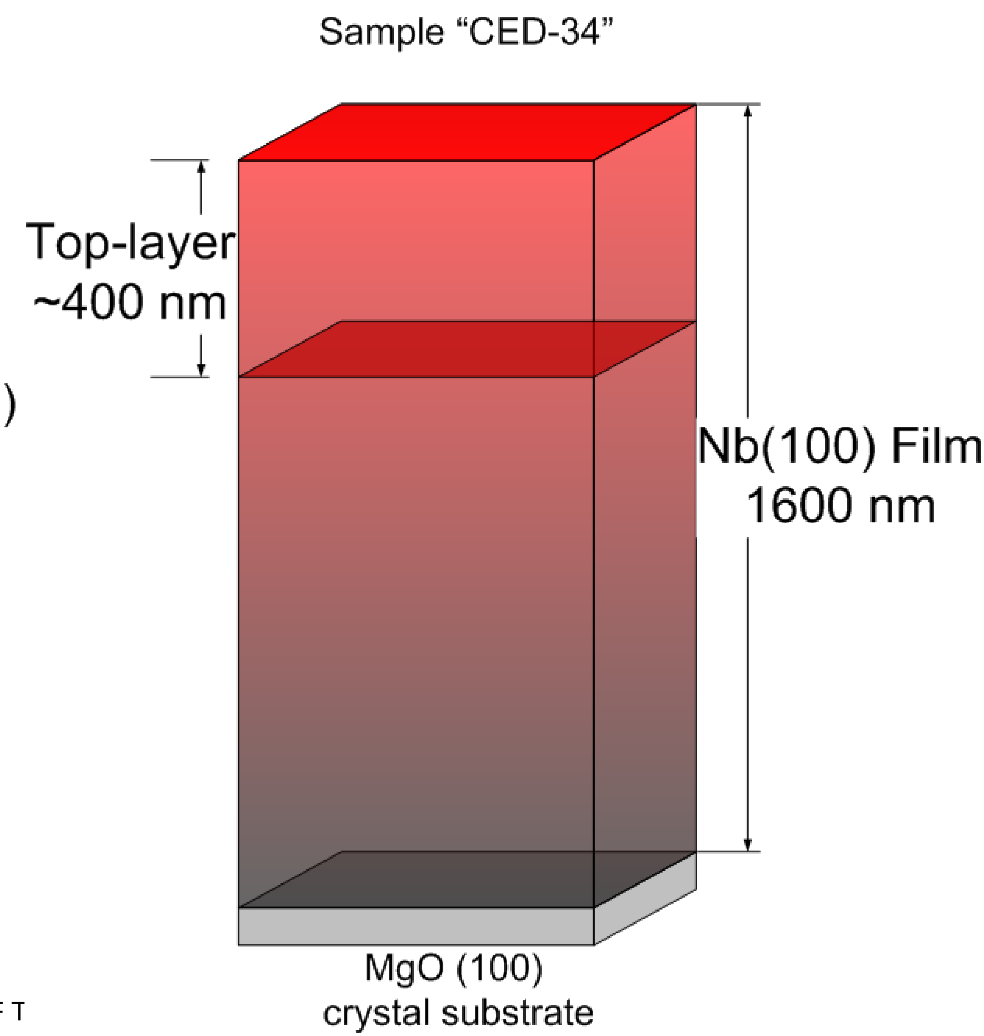
Implication to Structure Zone Model - microstructure evolution along thickness

Grayscale mask renders Anders' SZM to visualize crystal quality



“Top-down” vs “Bottom-up”
- Crystal Etching vs Growth
- Bulk vs Film





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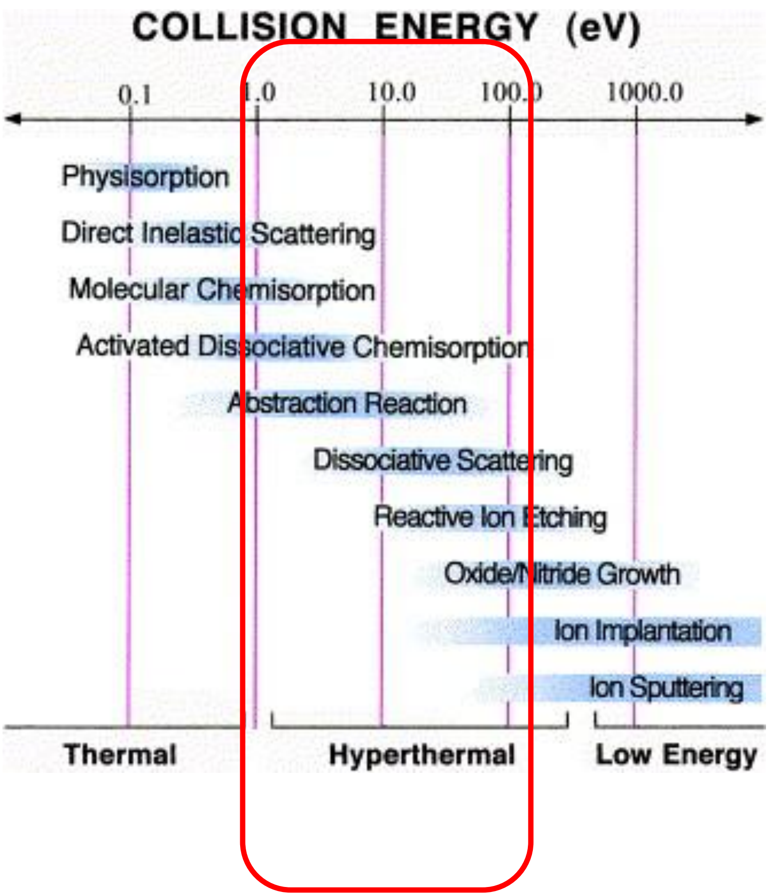
- Colleagues of Jefferson Lab, who provided the samples, enlightening advices and critical thoughts: Hui Tian, Anna-Marie, Josh ……
- Collaborators from FSU, Zuhawn et al
- Collaborators from NCSU, Fred, et al
- Collaborators from WM

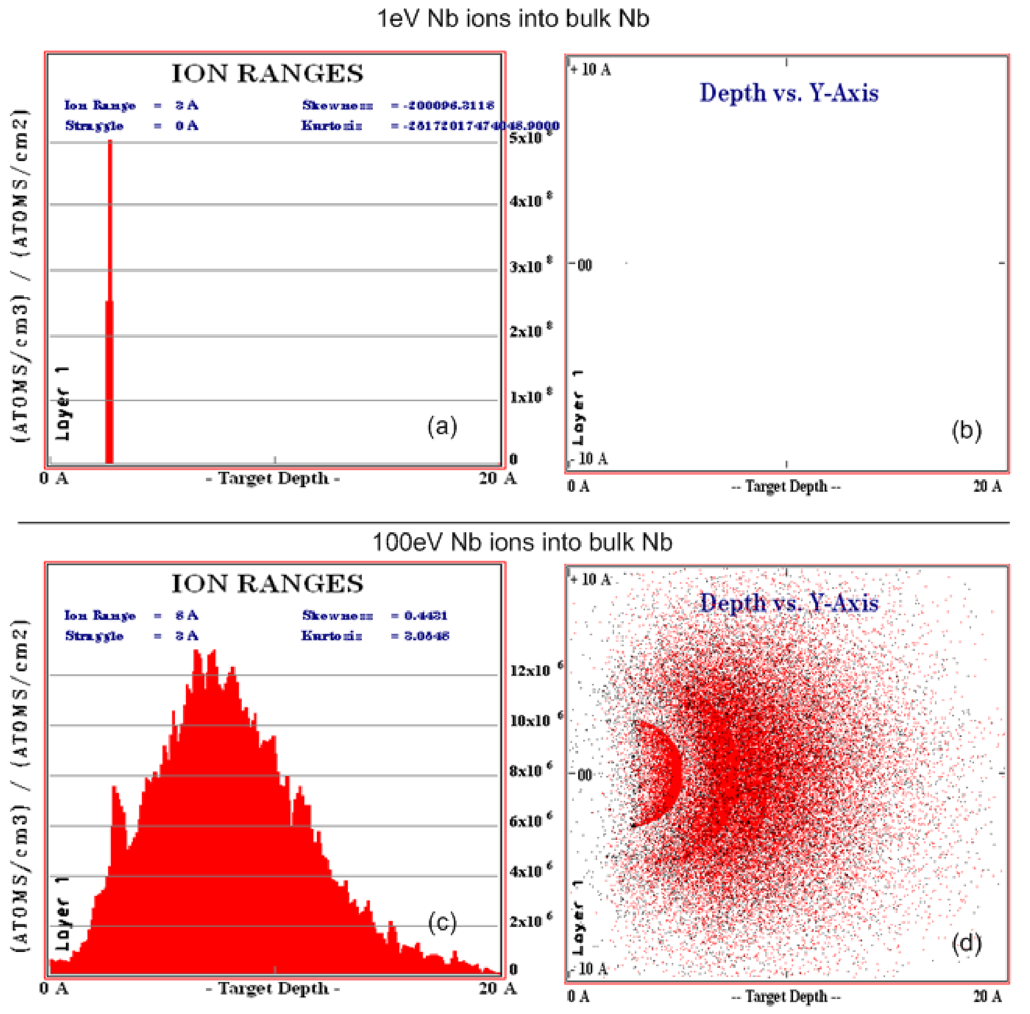
Questions to You

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

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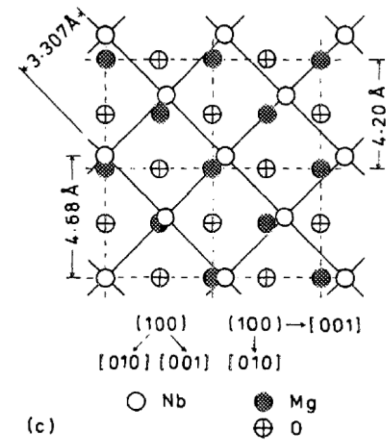
Three-dimensional epitaxy relationship of Nb/MgO(100)*

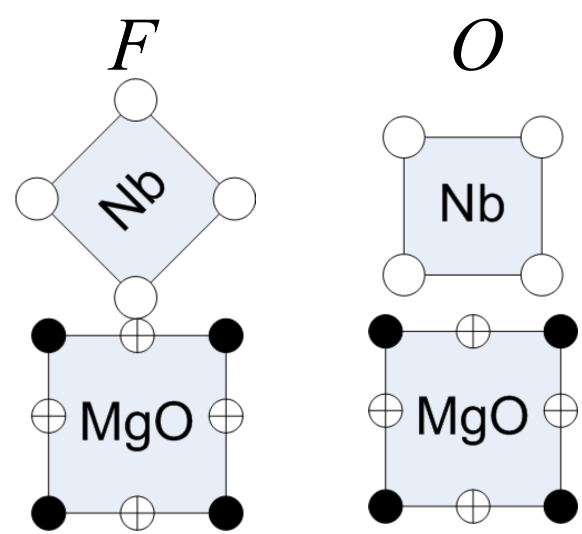
TABLE I. Tabulation of the lattice misfit parameters for the observed orientation (O), $(001)_{Nb}//(001)_{MgO}$ with $[010]_{Nb}//[010]_{MgO}$, a more favored orientation (F), $(101)_{Nb}//(001)_{MgO}$ with $[01\bar{1}]_{Nb}//[100]_{MgO}$, and a second possible orientation O_p, $(001)_{MgO}$ with $[110]_{Nb}//[010]_{MgO}$.

Orientation	Parallel directions	% misfit
O	$[100]_{Nb}//[100]_{MgO}$	19.4
	$[010]_{Nb}//[010]_{MgO}$	19.4
O_p	$[100]_{Nb}//[010]_{MgO}$	8.0
	$[100]_{Nb}//[110]_{MgO}$	56.5
F	$[01\bar{1}]_{Nb}//[100]_{MgO}$	8.0
	$[010]_{Nb}//[010]_{MgO}$	19.4

Orientation: O_p



Top View



Cross-section View

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

1. *E. Hutchinson and K. H. Olsen, "Substrate Condensate Chemical Interaction and the Vapor Deposition of Epitaxial Nb Films", J. Appl. Phys. 38, 4933 (1967).
2. J. E. Mattson, Eric E. Fullerton, C. H. Sowers, and S. D. Bader, "Epitaxial growth of body-centered-cubic transition metal films and superlattices onto MgO (111), (011), and (001) substrates", J. Vac. Sci. Technol. A 13, 276 (1995).