Surface Characterization for SRF

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USPAS Course:

SRF Technology: Practices and Hands-On Measurements

January 2015

SRF Surfaces

SRF cavity surfaces must be "pure", "clean", and "smooth"

- **"Ideal" surface is defect-free Nb crystals** with only Nb_2O_5 ~4 nm capping layer and planar surface topography.
- After practical cavity fabrication, the real surface is "disturbed" and "polluted."
- Empirically found that >100 μm removal is typically required to reliably expose "good" bulk Nb material, i.e. predictable SRF performance.
- SRF cavity performance limitations always result from particular details of the surface.
  - Multipacting, field emission, quench, "*Q*-slope", "*Q*-drop", "*Q*-rise", Q_0
- A lot of detailed attention is required to understand how to "grow" excellent SRF thin film surfaces.

SRF Surfaces

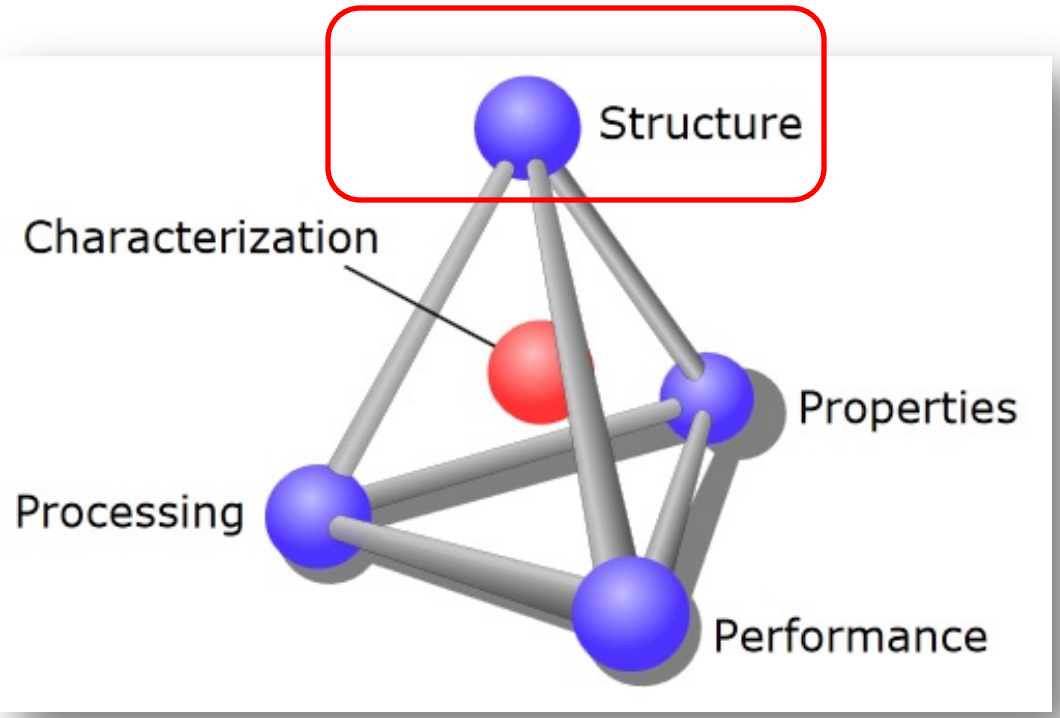
SRF is inherently a surface phenomenon

- **RF Supercurrents flow only within a very shallow depth: penetration depth - λ ~40 nm for Nb**

  e.g., for a 9-cell Tesla-style cavity **< 0.1 cm^3** of Nb actually matters for SRF

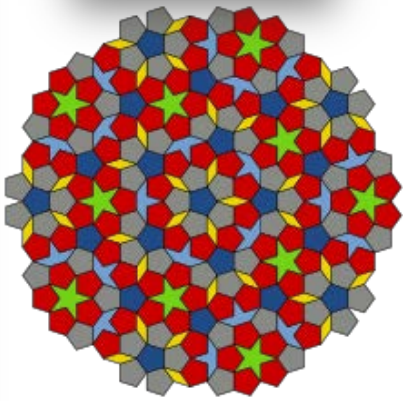
- **To understand and control the desirable properties of SRF cavities requires knowledge and control of this thin layer of material over large surfaces**
  - **Composition – elemental, structure, interstitials**
  - **Morphology – pits, scratches, edges, topography**
  - **External contamination – particulates, condensed gases**

Structure Determines Properties

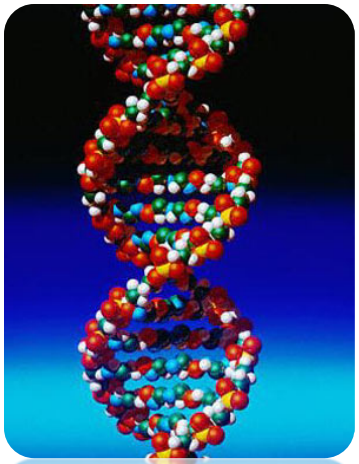


Standard set of relationships in Materials Science

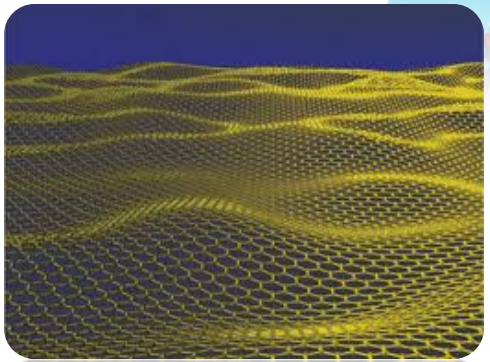
Glass,
Random close-packed-sphere model.



Quasi-crystal



DNA
double-helix



2D Crystal
Graphene

Material Science of Thin Films, Tutorials at JLab, Xin Zhao

Microscopy & Microanalysis

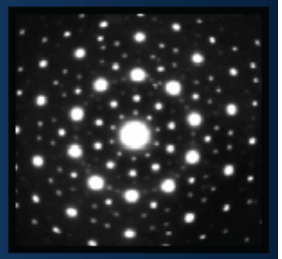
Experimental methodologies which employs (electron-optical) instrumentation to spatially characterize matter on scales which range from tenths of a millimeter to tenths of a nanometer. The principle modalities employed are:

Imaging

- Scanning Electron Microscopy
- Transmission Electron Microscopy
- Scanning Transmission Electron Microscopy
- Focussed Ion Beam

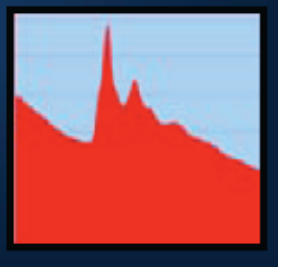
Diffraction

- Electron Backscattered Difrraction
- Selected Area Electron Diffraction
- Convergent Beam Electron Diffraction
- Reflection High Energy Electron Diffraction



Spectroscopy

- X-ray Energy Dispersive
- Electron Energy Loss
- Auger Electron

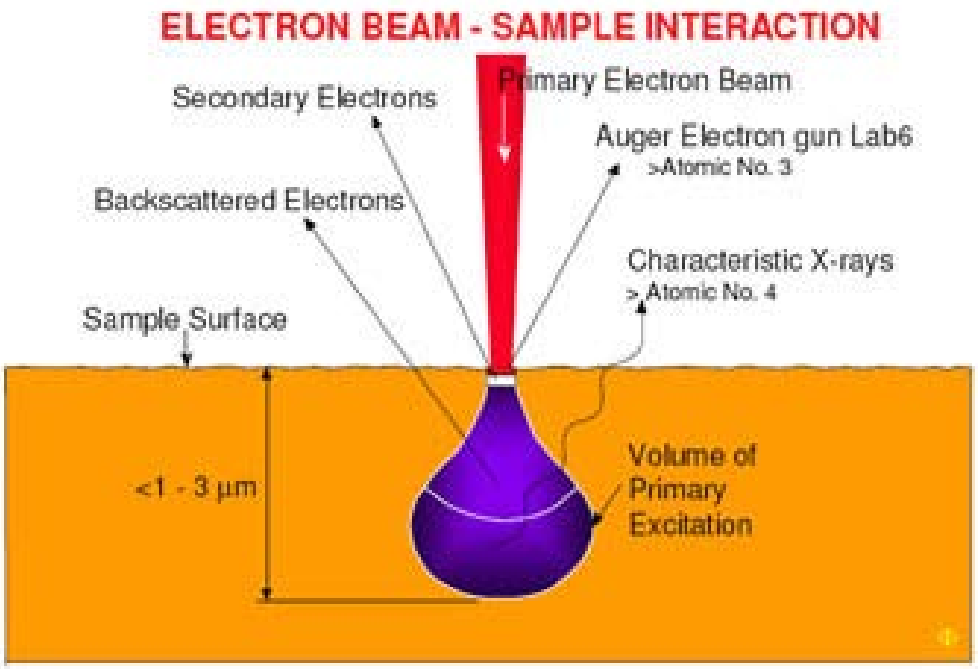


Elemental Analysis

- X-ray **E**nergy **D**ispersive **S**pectroscopy (EDX)
- **A**uger **E**lectron **S**pectroscopy (AES)
- **X**-ray **P**hotoemission **S**pectroscopy (XPS)
- **S**econdary **I**ons **M**ass **S**pectroscopy (SIMS)

Material Science of Thin Films, Tutorials at JLab, Xin Zhao

Scanning Electron Microscope (w/ EDX) vs. Scanning Auger Microscope/Spectroscope (SAMs)

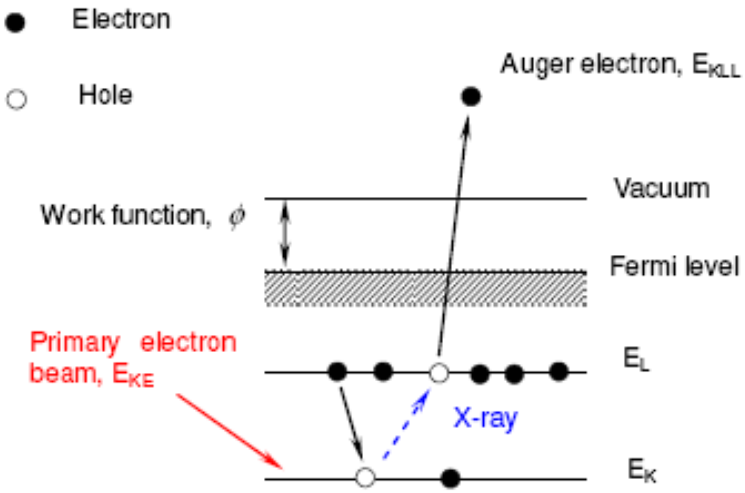


EDX vs. AES

	AMU Resolution	Sampling Depth
AES	~0.2%	**~4 atomic layers**
EDX	~ 1%	**~3000 atomic layers (1um)**

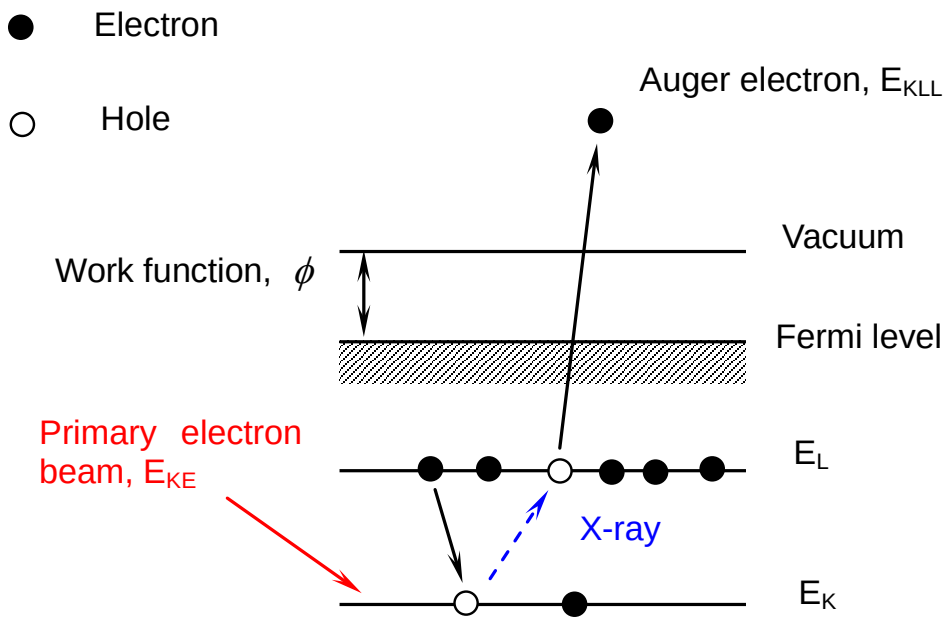
An emitted Auger electron will have a precise kinetic energy E_k

$$E_k = E_{\text{Core State}} - E_B - E_C'$$

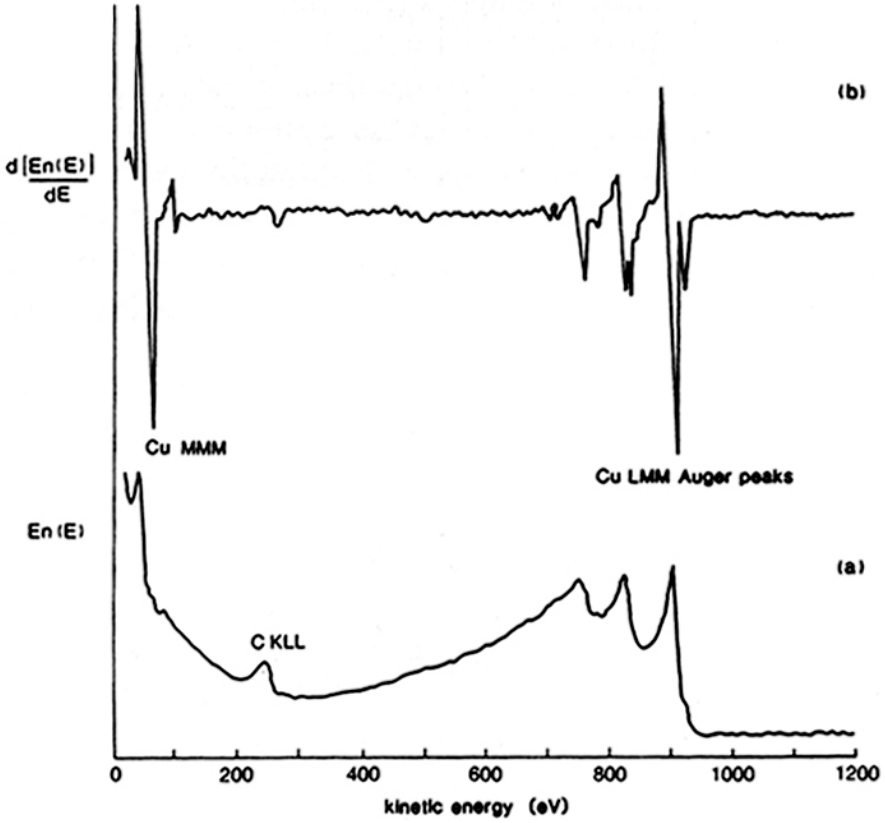


Schematic of Auger Effect

Auger Electron Spectroscopy



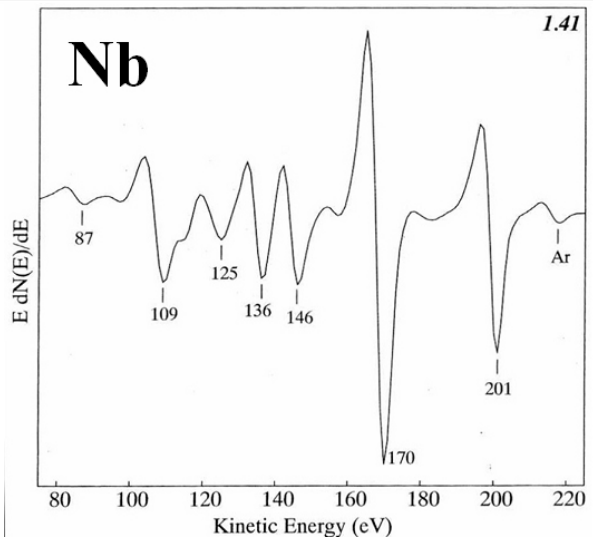
Schematic of the Auger process

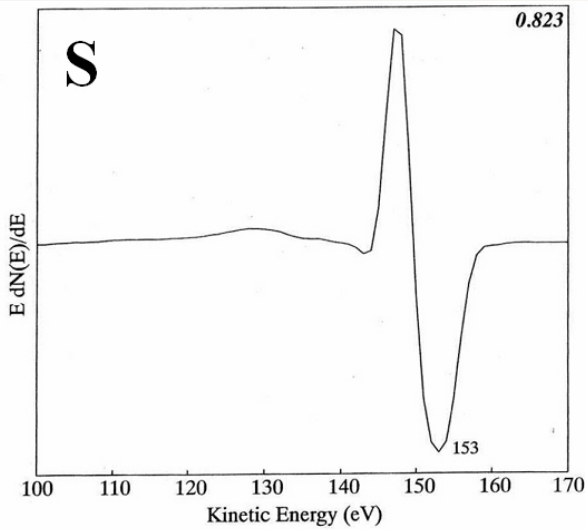


Because the Auger peaks are superimposed on a large continuously incremental background in direct Auger spectrum, the peak feature is not distinguished in the direct representation. The energy distribution spectrum N(E), is differentiated to enhance the peak features. Thus, the conventional Auger spectrum's representation is the function, dN(*E*)/d*E*.

Material Science of Thin Films, Tutorials at JLab, Xin Zhao

AES and EDX Spectrum





"Finger print" Auger spectrum of niobium and sulfur

	Nb	O	S	Fe	N	C
Characteristic X-ray photo energy (eV)	2164 (La1) 2254(La2) 172(Mz1)	515(Ka1)	2308(Ka1) 149(LI)	6402(Ka1) 705(La1)	384(Ka1)	266(Ka1)
Auger electron kinetic energy (eV)	87 109 125 136 146 170 201	510	153	589 645 700	375	272

Elements characteristic X-ray photo energy and Auger electron kinetic energy (eV)

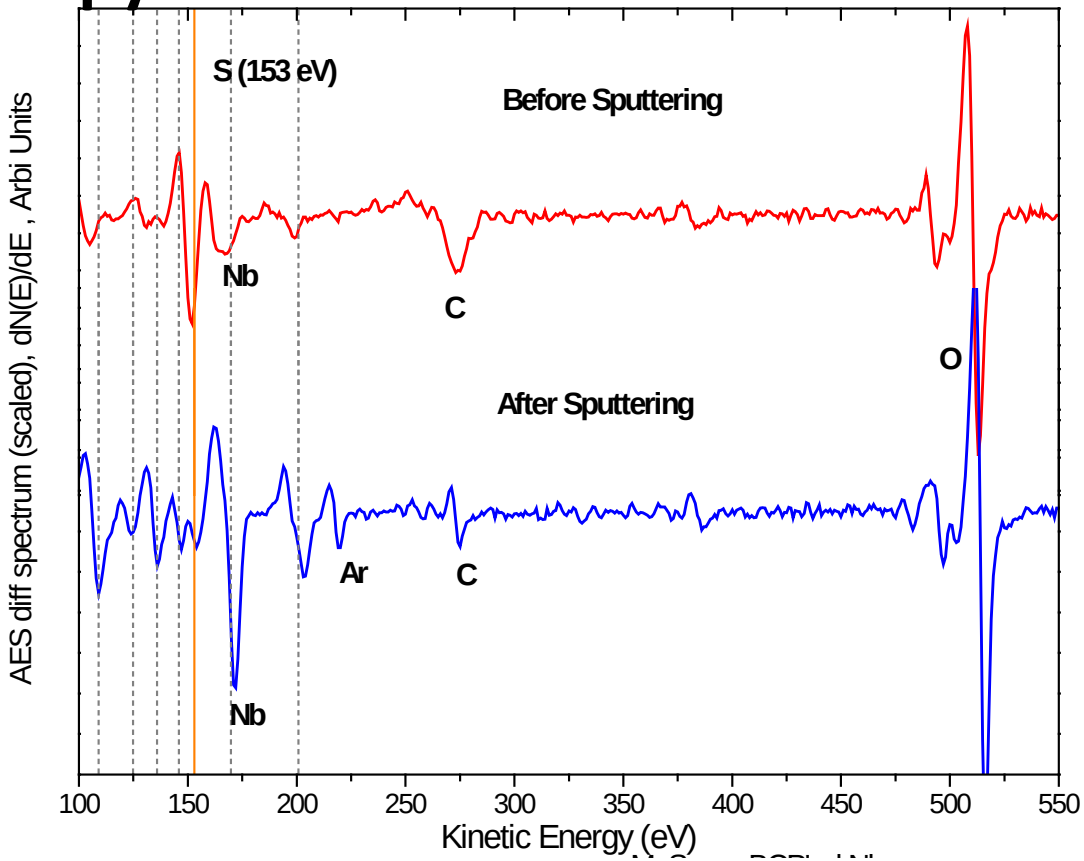
SRF Surfaces

Auger Emission Spectroscopy – AES

- Very surface sensitive: few monolayers
- Not commonly used
- Adsorbed gases are usually irrelevant to SRF performance

Trouble-shooting sulfur surface contamination following EP

X. Zhao, et al. PRST-AB **13**, 124702 (2010), http://link.aps.org/doi/10.1103/PhysRevSTAB.13.124702



AES spectra of a spot before and after a slight sputtering. **Fewer than 10 atomic layers** were removed by the Ar^+ beam. The sulfur peak was greatly reduced after sputtering, which indicated sulfur coverage is ultra-thin.

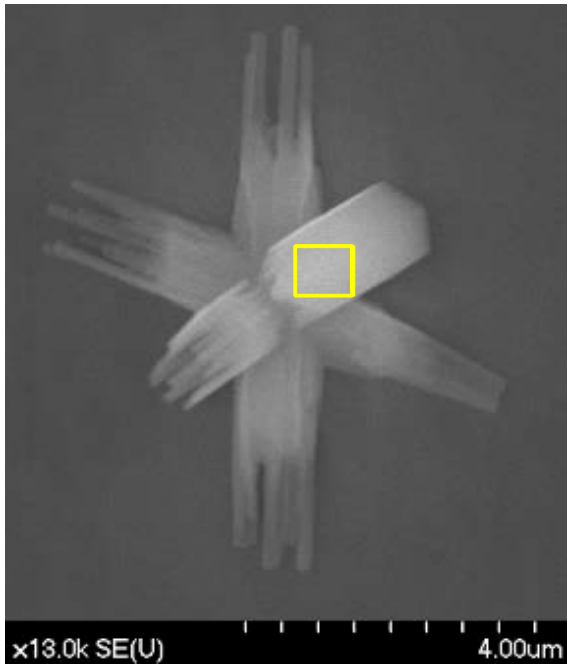
SRF Surfaces

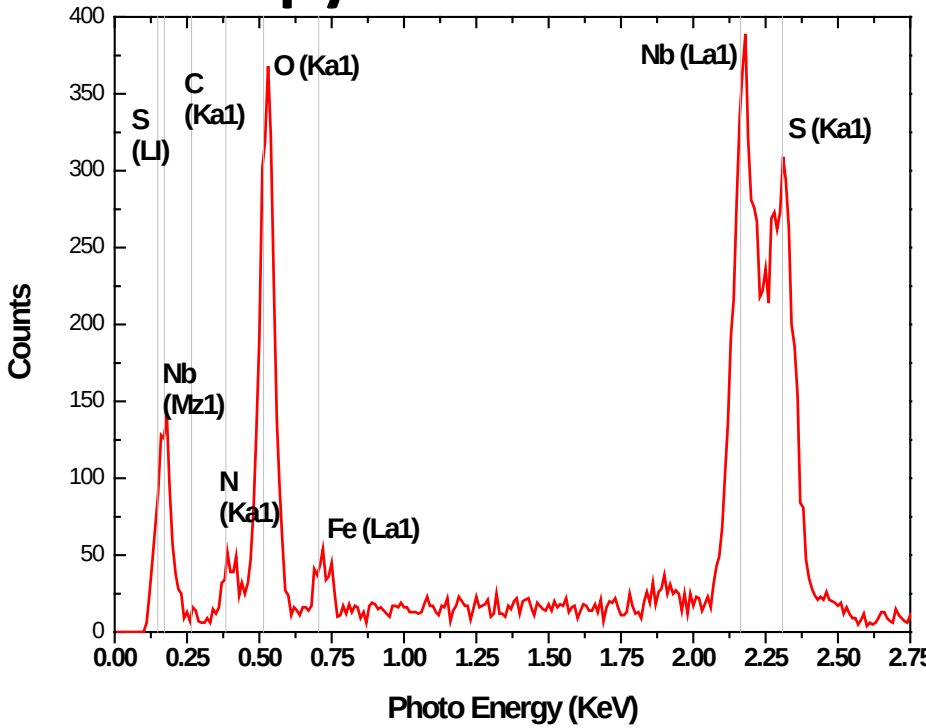
SEM/EDX – Scanning Electron Microscope with Energy Dispersive X-ray spectroscopy

Probing depth: ~1 µm

SEM micrograph of one crystallite-like particle on Nb surface after EP.

The yellow box labels an area surveyed by EDX.





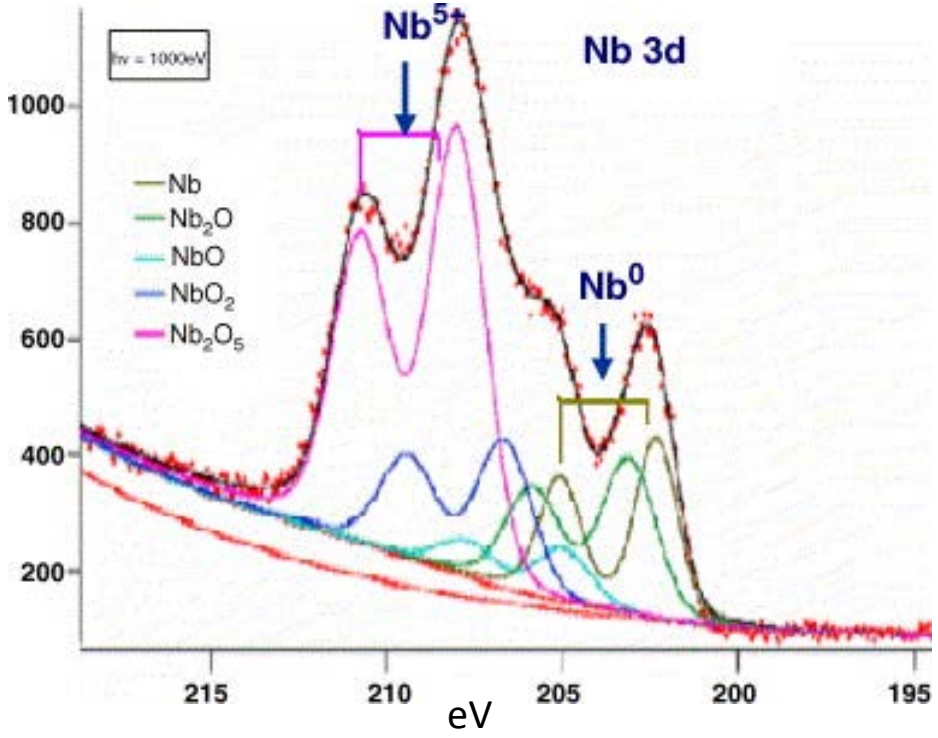
EDX spectrum surveyed from the yellow box area. It contains S, Fe, N element besides Nb and O. The origin of Fe and N are unknown. The elemental ratio of N, O, S, Fe and Nb is 19:72:5:3:1 after commercial EDAX software evaluation.

X. Zhao, et al. PRST-AB **13**, 124702(2010)
http://link.aps.org/doi/10.1103/PhysRevSTAB.13.124702

XPS

- X-ray photoemission spectroscopy
  - Measure the binding energy of electrons reveals their atomic and chemical origin
  - Surface sensitive probe of chemical composition

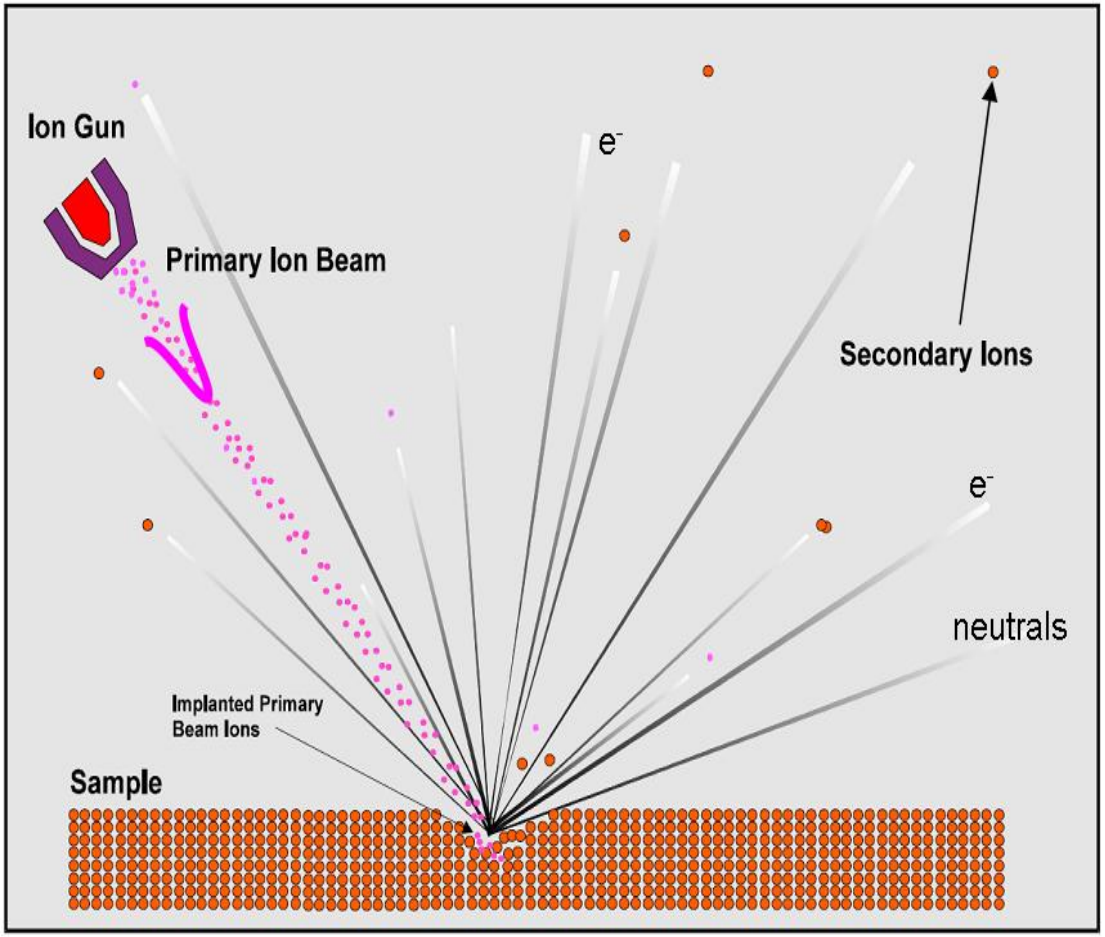
- For fixed photon energy hν, measuring the kinetic energy (KE) of the ejected electrons leads to an energy balance: hν = KE + BE, where BE is the binding energy.
- Measuring the KE of ejected electrons gives their BE, a description of the electron structure.



Example:

Near-Surface Composition of Electropolished Niobium by Variable Photon Energy XPS
H. Tian et al. SRF2003

Secondary Ion Mass Spectrometry (SIMS)



- Escape depth of sputtered species only few Angstroms
- All elements and isotopes measurable (including H)
- ppm to ppb detection limit
- **10-20 nm** depth resolution typical, **1-2nm** at low energies

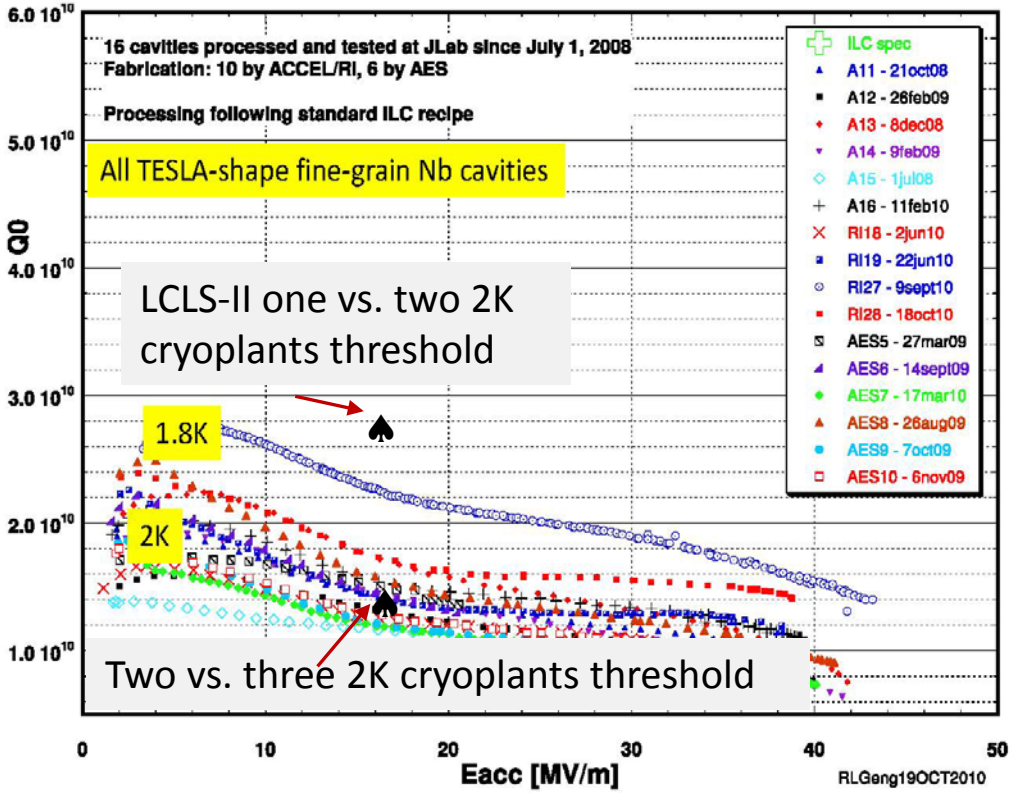
R. G. Wilson, F. A. Stevie, C. W. Magee: Secondary Ion Mass Spectrometry, Wiley-Interscience (1989)

Improving SRF with “Pollution”

- “Pollution” of near surface discovered to have beneficial effect
- “High-Q_0” by N-doping or Ti-doping

- **What is going on here?**

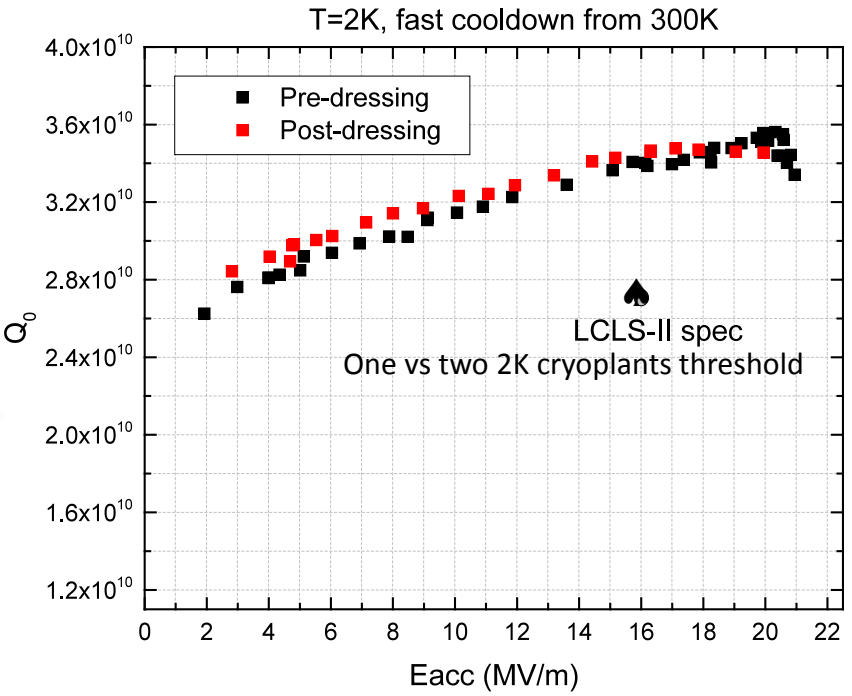
XFEL/ILC recipe vs. N doping



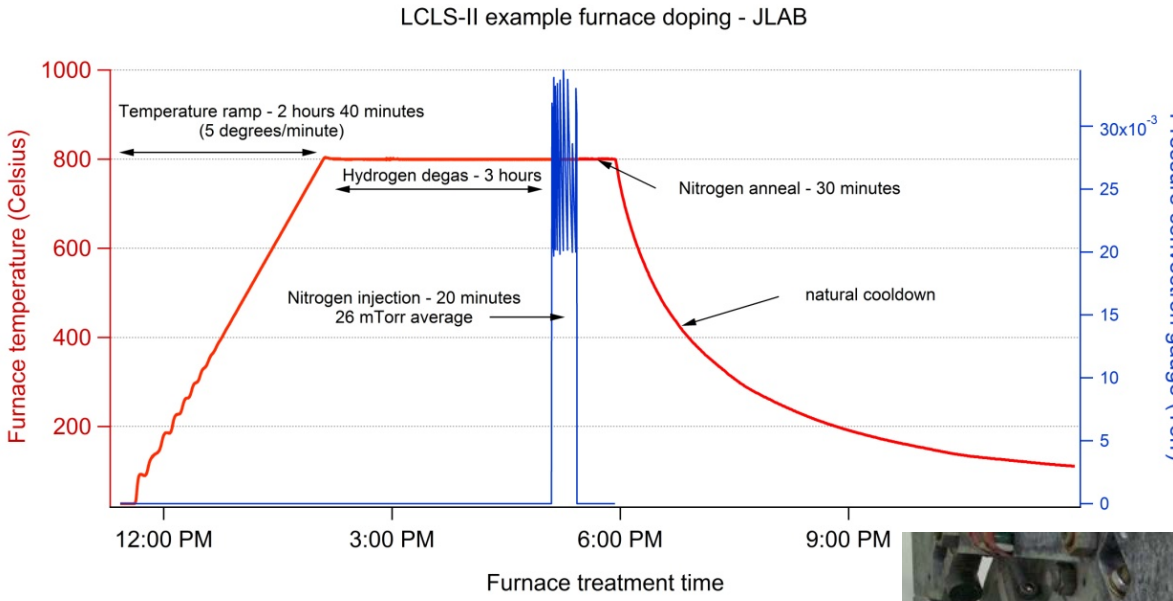
"The best cavities of 2010" (120C bake)
→ Could be marginal for 2 cryoplants (likely to require 3 with slow cooling)

The SRF world is changing

"The best dressed cavity of 2014"
(N doped)
TB9AES011



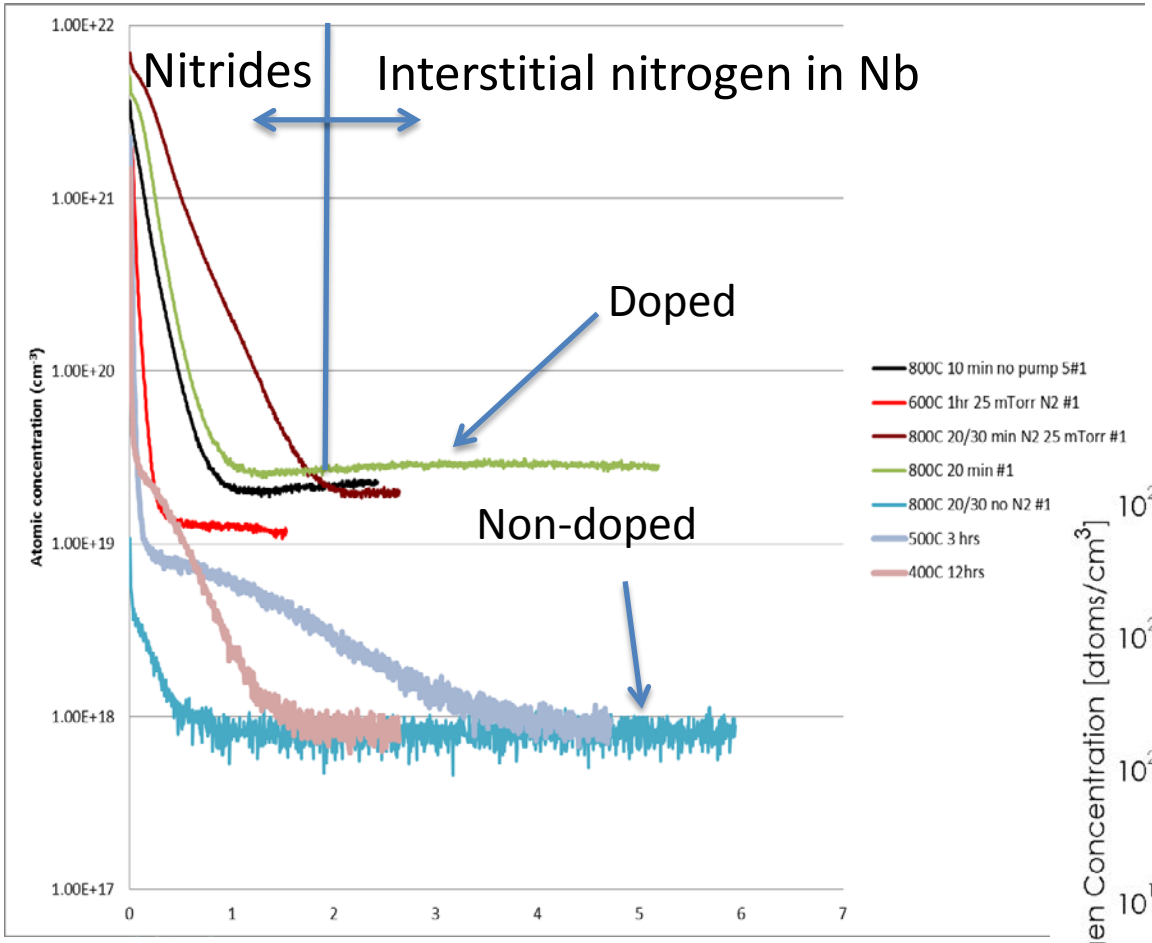
Nitrogen Doping Process



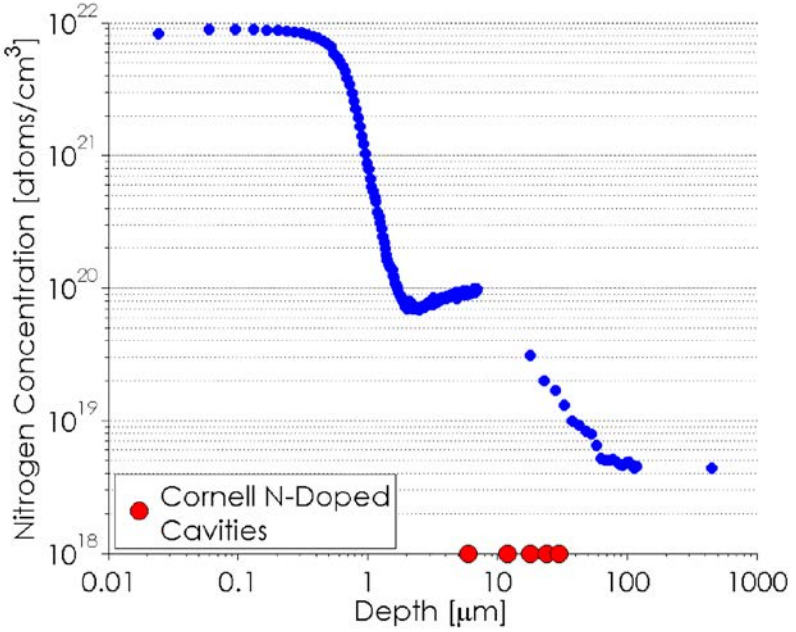
Palczewski

JLab HT-N treatment and triple single cell HEP configuration

What does N treatment do? N depth profiles by SIMS



See A. Romanenko, talk at LINAC 2014, Geneva
And D. Gonnella et al, LINAC 2014, Geneva



Crystallography Measurements

- X-ray Diffraction (XRD)
- Electron Backscattering Diffraction (EBSD)
- Transmission Electron Microscopy (TEM)

Diffraction measurements probe the atomic structural patterns in the surface material

SRF requires high-quality lattice structure

Material Science of Thin Films,
Tutorials at JLab, Xin Zhao

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.*

Misorientation Angles

- as one caliber of crystal quality

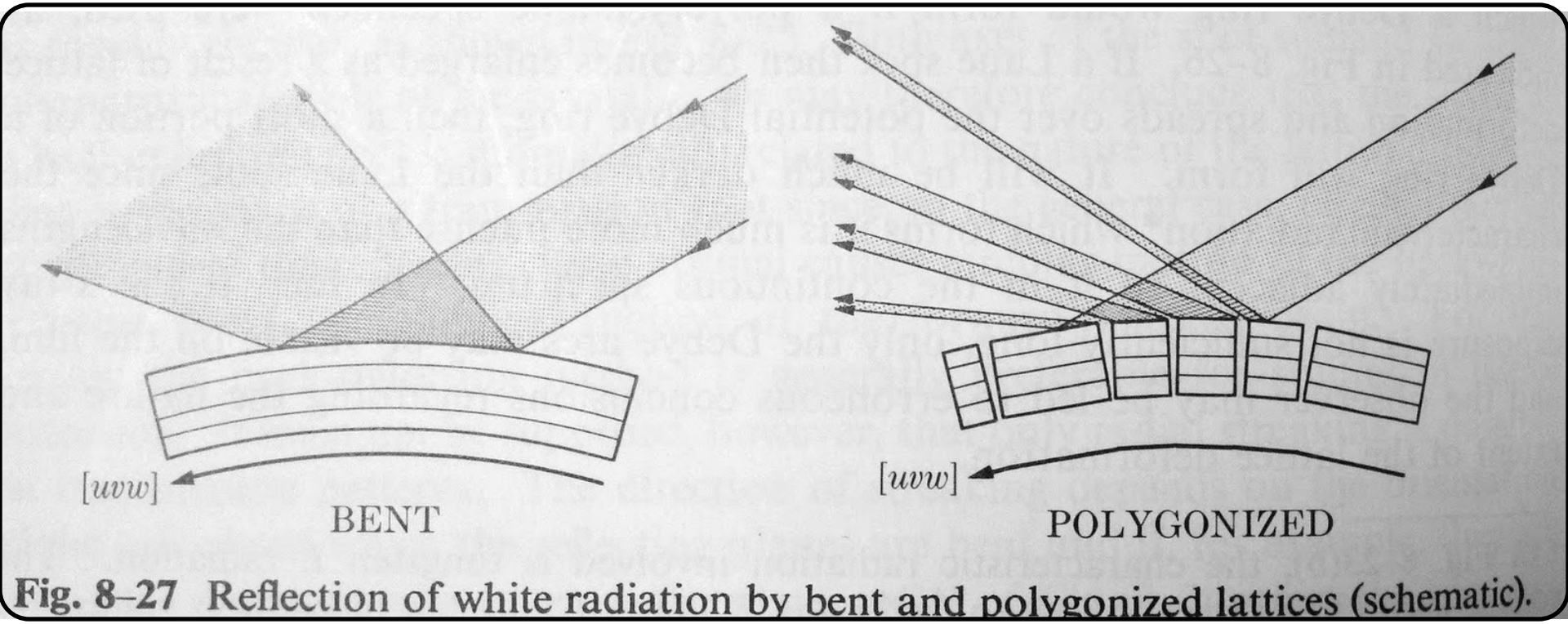


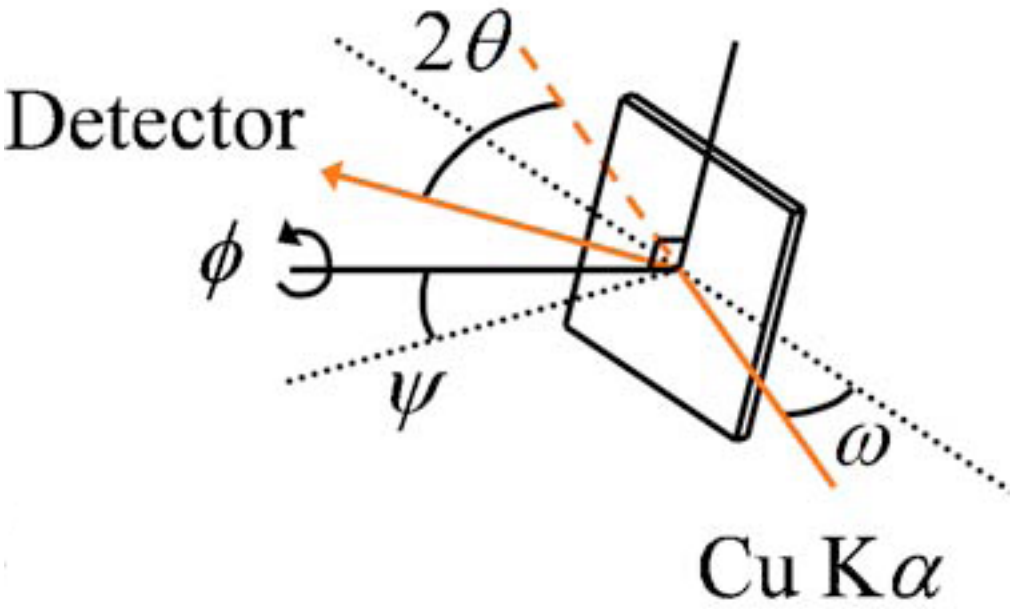
Fig. 8–27 Reflection of white radiation by bent and polygonized lattices (schematic).

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

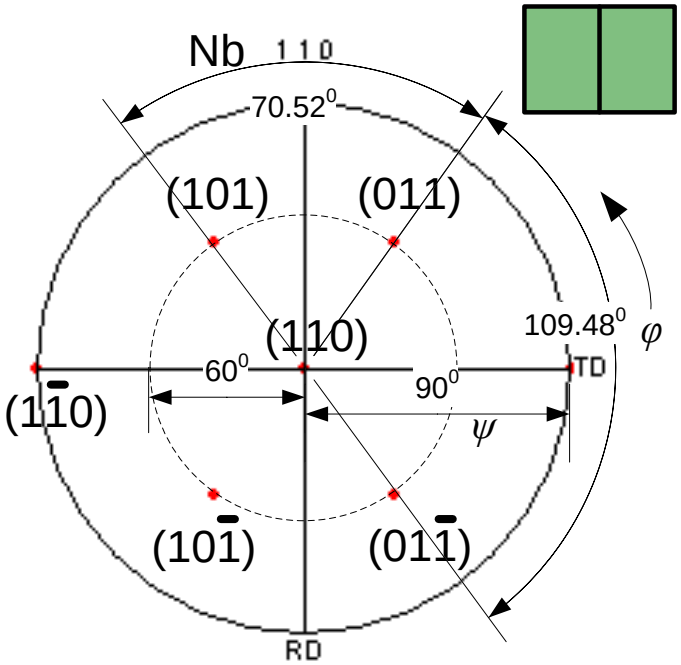
XRD vs. EBSD

	XRD	EBSD
Probing Area (Diffraction Area)	10*17 mm (selectable by X-ray aperture)	30*30 nm • By rastering e-beam, can scan a large area • Scanning area is limited by SEM magnification
Probing Depth (Diffraction depth)	1 - 2 µm	< 50 nm
Pole Figures	Yes	Yes
Grain size sensitivity	any	Must > 50 nm

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 $2d_{\{hkl\}}*sin(\vartheta)=\lambda$)
- Rotated around Normal Direction (Azimuthal φ, from 0-360^0)
- Titled off-angle from Normal Direction (ψ, 0-90^0)

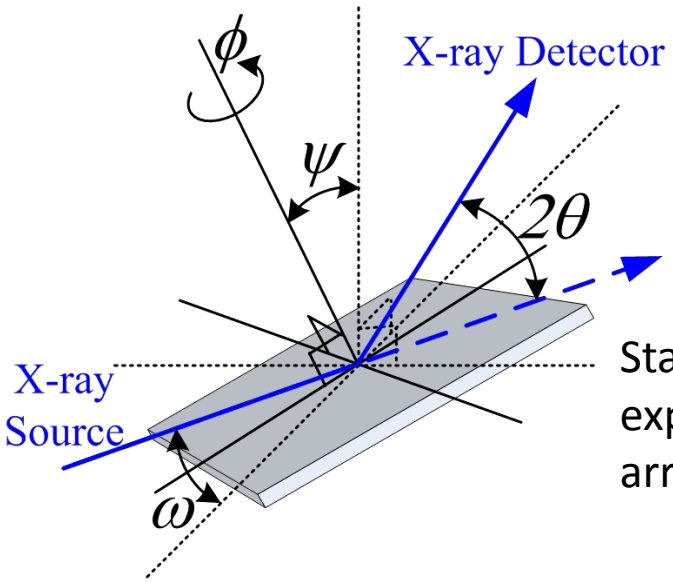
P.F. is to visualize **Reciprocal Lattice Space**

One **Crystal Plane stacks** in real lattice space is a **Pole** in reciprocal space

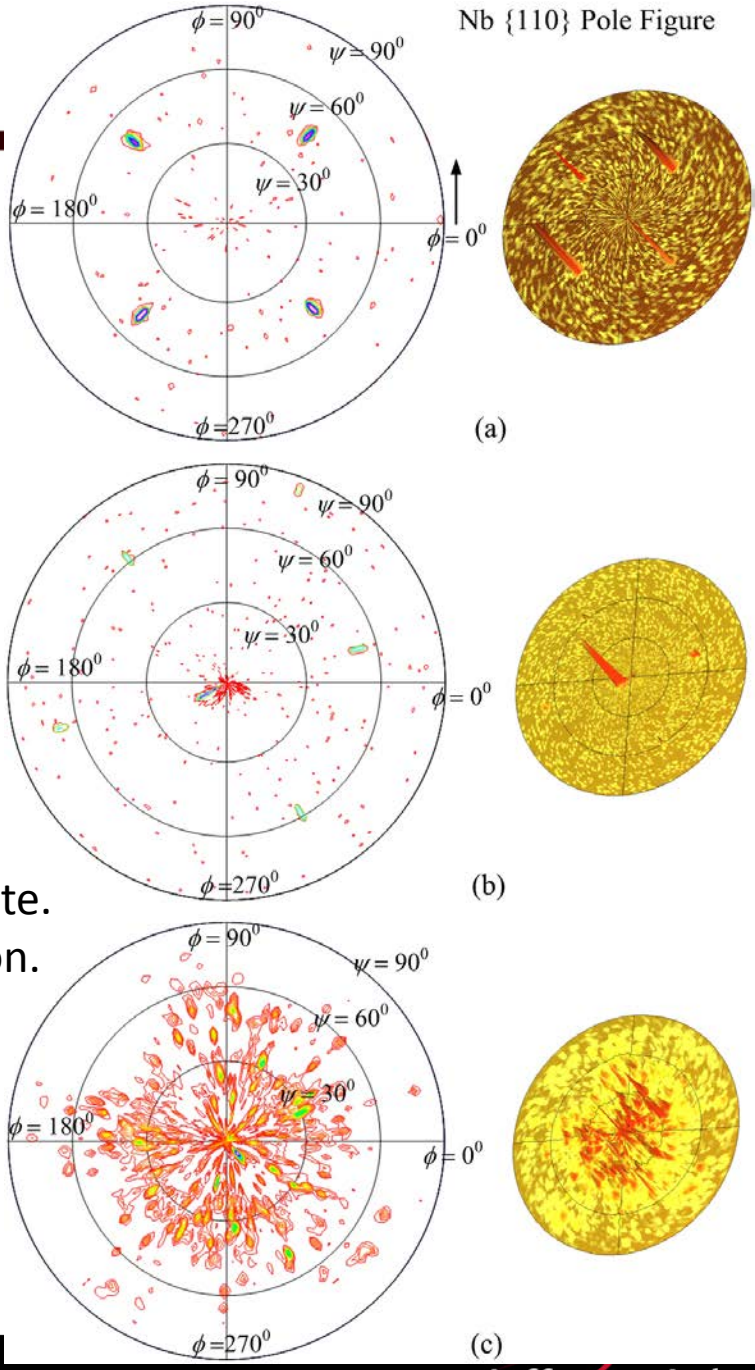
X.Zhao et al, Talk on 5th SRF Thin Film Workshop, JLab. 2012

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

XRD Characterization of Nb



Standard XRD experimental arrangement.



Experimental Nb {110} pole figures

(a) Sample CED-034: a Nb(100) film on Mgo (100) substrate.

(b) Sample Nb-SC-01: a single crystal bulk Nb (110) coupon.

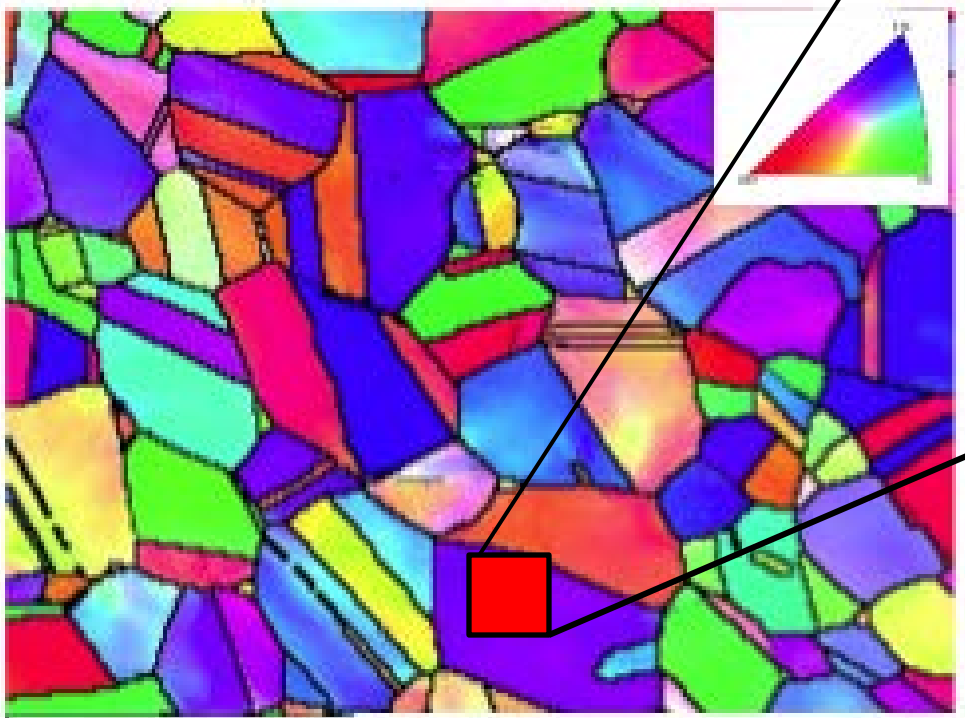
(c) Sample Nb-PC-01: a polycrystalline bulk Nb coupon.

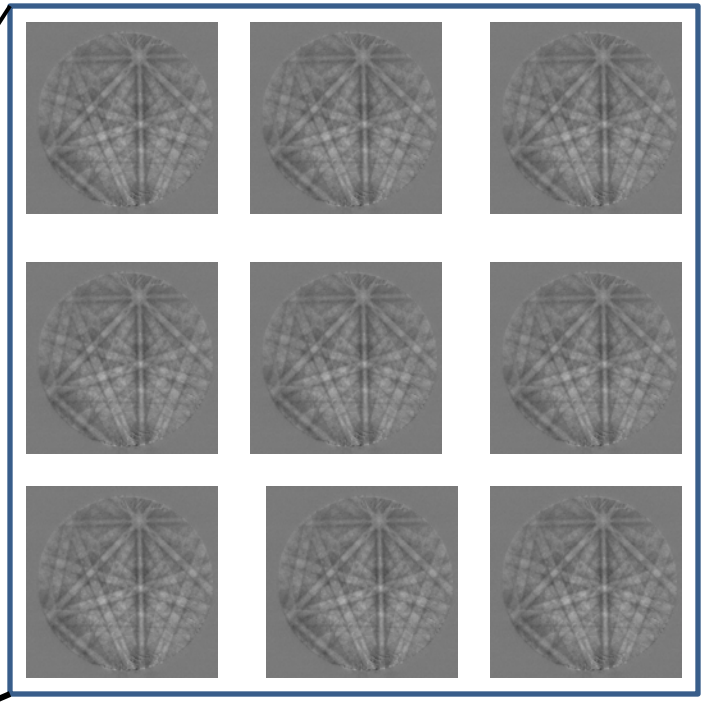
The right column shows a 3D view of the pole figures.

Phys. Rev. ST AB **17**, 013501

Grains Orientation Mapping by EBSD

- Electron Beam Spot is small (**few nanometers**)
- By rastering electron beam on a sample to map grain orientations



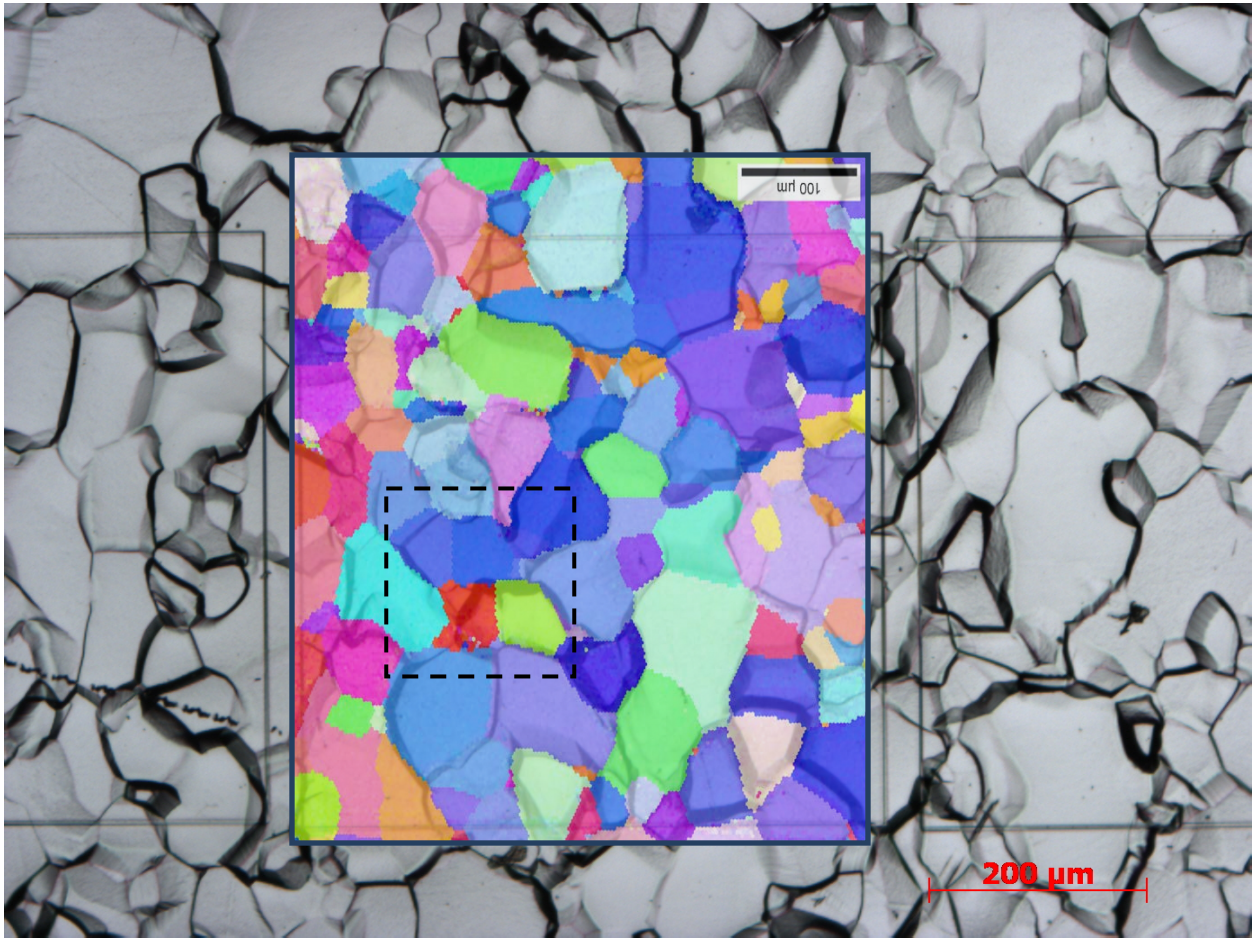


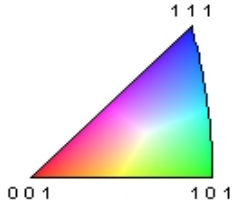
- Pattern matching and decomposition
- Computationally intensive
- But implementations are now quite fast

EBSD – BCP on fine grain, nano-polished niobium

Technique used to examine surface evolution during processing

6 minutes BCP at room temperature





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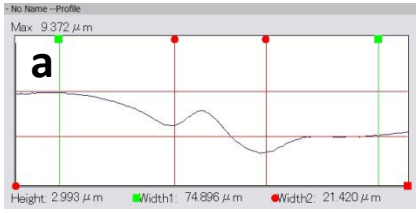
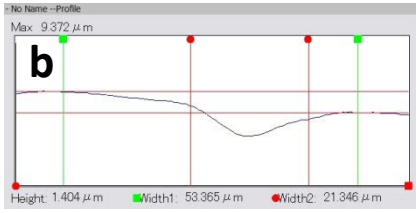
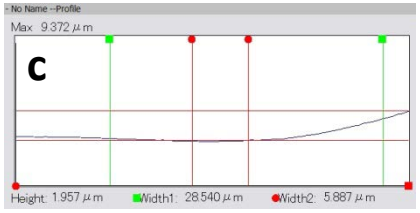
EBSD – BCP on fine grain, nano-polished niobium

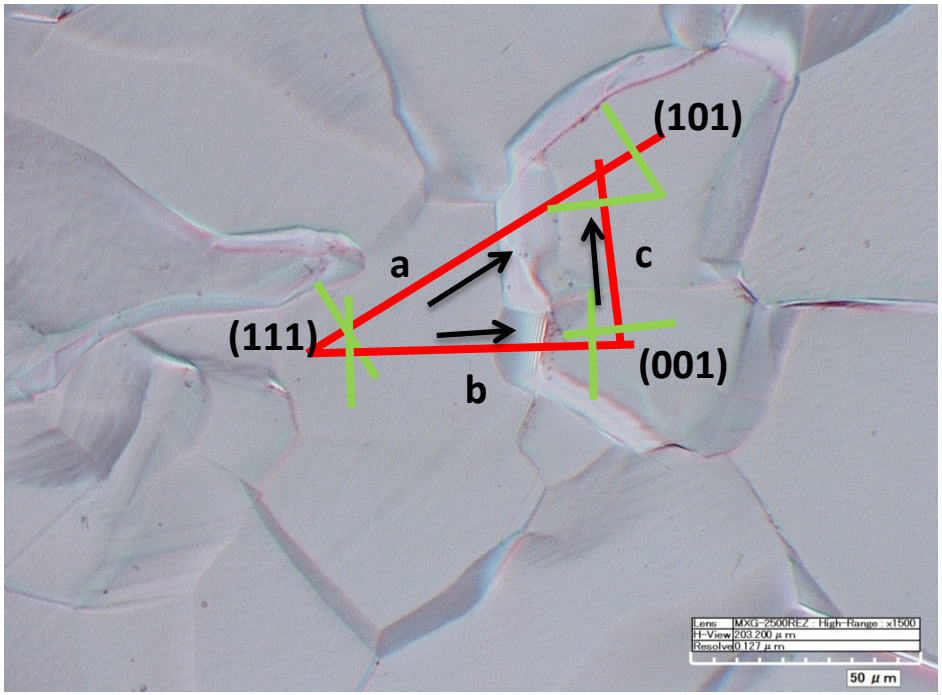
6 minutes BCP at room temperature

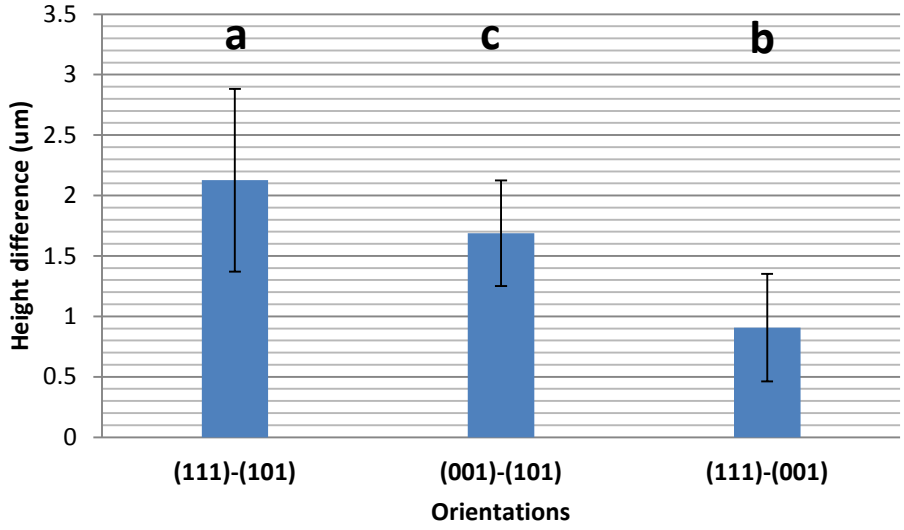


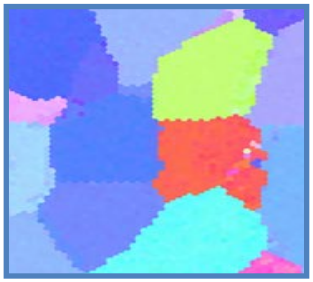


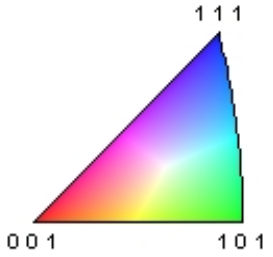


Polishing rate:
(110)>(100)>(111)



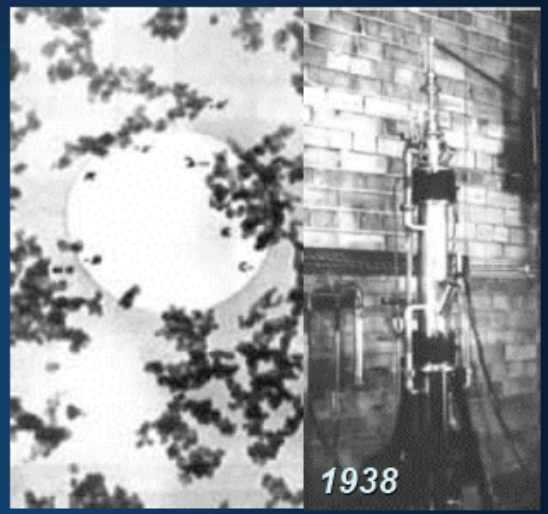




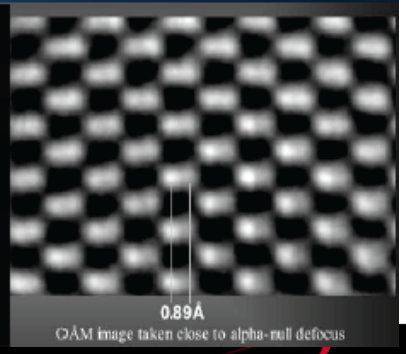


L. Zhao

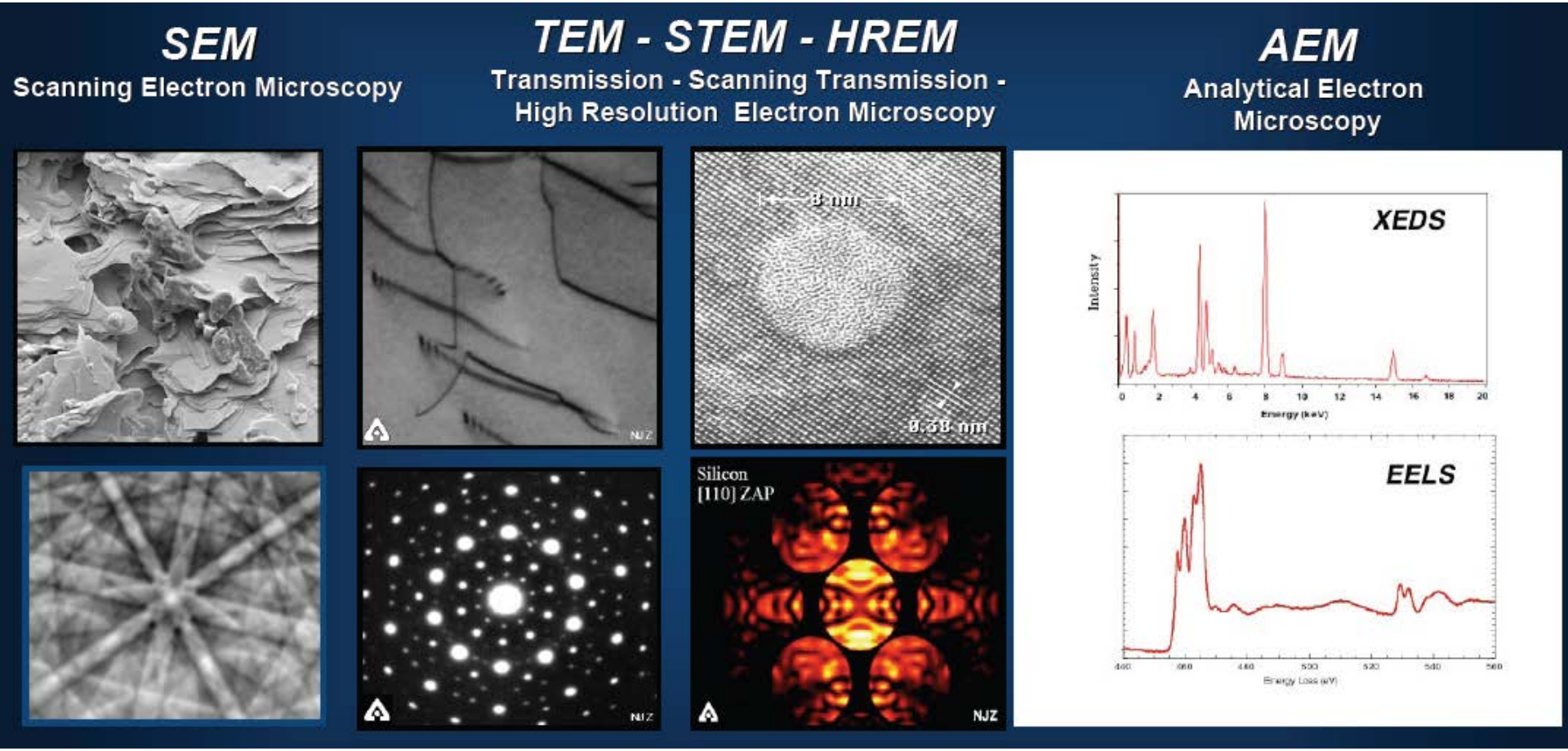
A Historical Time Line in Electron Optical Instrumentation



1897 JJ Thompson - Discovery of the Electron
1926 H. Bush Magnetic/Electric Fields as Lenses
1929 E. Ruska PhD Thesis Magnetic lenses
1931 Knoll and Ruska 1st EM built
1932 Davisson and Calbrick - Electrostatic Lenses
1934 Driest & Muller - EM surpases LM
1939 von Borries & Ruska - 1st Commerical EM
~ 10 nm resolution
1945 ~ 1.0 nm resolution (Multiple Organizations)
1965 ~ 0.2 nm resolution (Multiple Organizations)
1968 A. Crewe - U.of Chicago - Scanning Transmission Electron Microscope
~ 0.3 nm resolution probe - practical Field Emission Gun
1986 Ruska etal - Nobel Prize
1999 < 0.1 nm resolution achieved (OÅM)
2009 0.05 nm (TEAM)



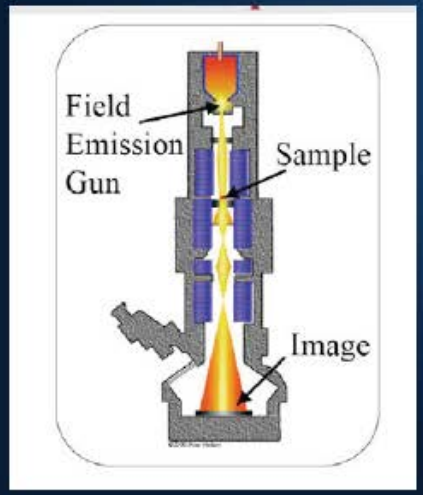
Service of Traditional Electron Microscope

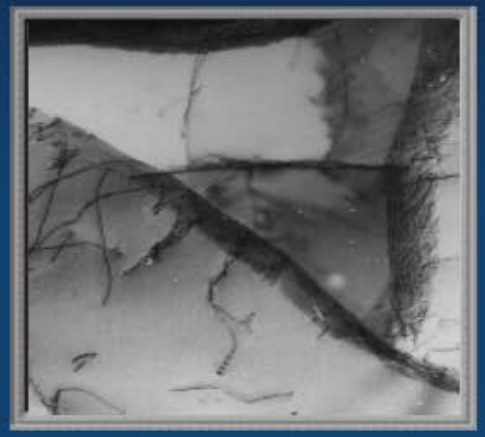


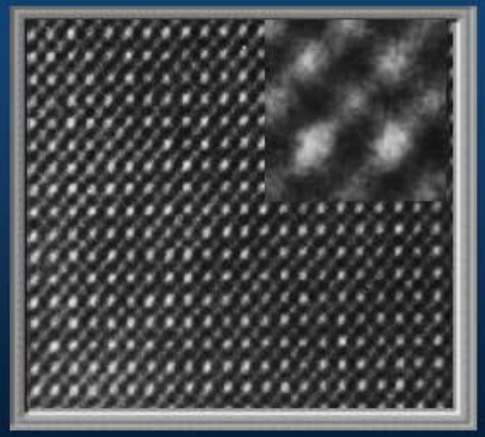
Morphology, Crystallography, Elemental, Chemical, Electronic Structure

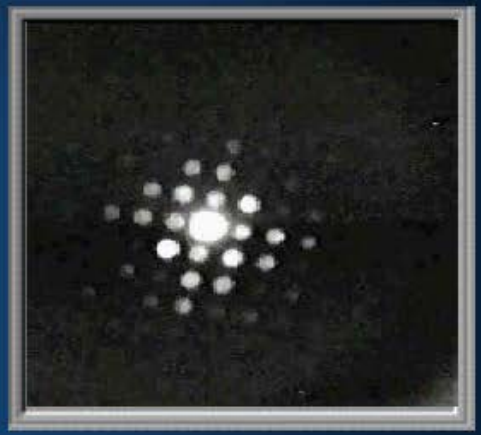
Material Science of Thin Films, Tutorials at JLab, Xin Zhao

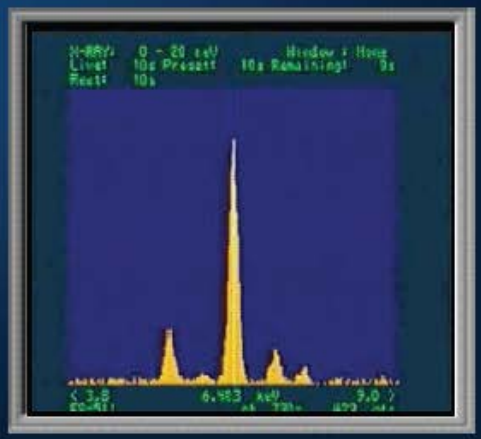
Transmission Electron Microscopy











Traditional TEM Specimen Preparation

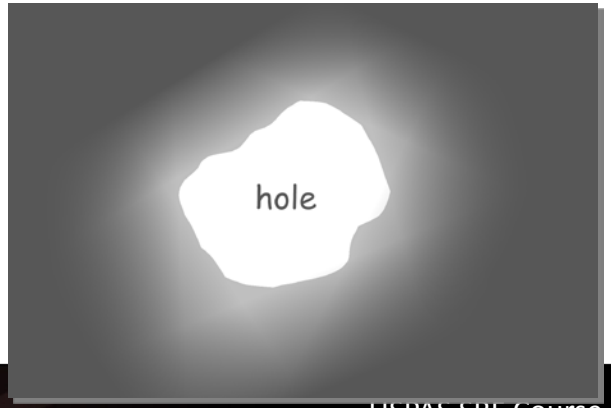
Foils

3 mm diam. disk

very thin (<0.1 - 1 micron - depends on material, voltage)

- **mechanical thinning (grind)**
- **chemical thinning (etch)**
- **ion milling (sputter)**

examine region around perforation



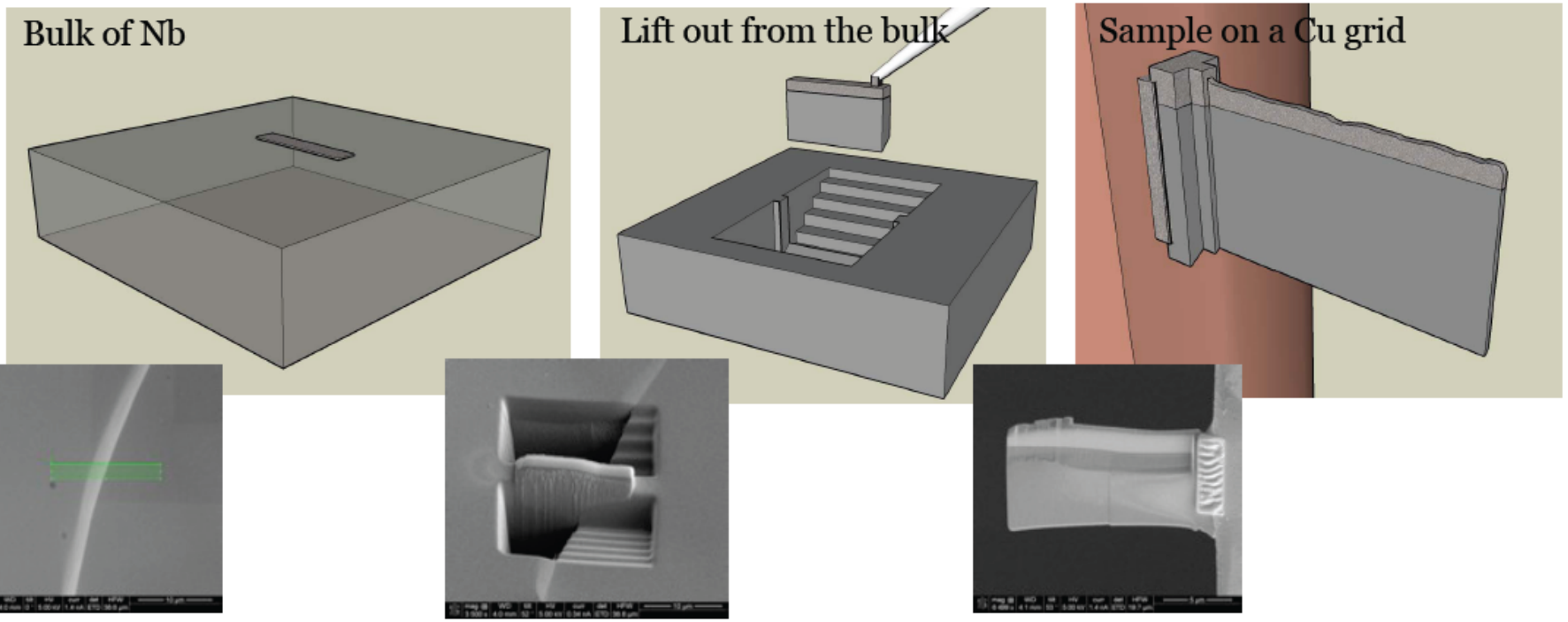
Sample Prep for TEM/STEM studies

TEM: high spatial resolution but sample has to be thin *for HRTEM thickness < 50nm*

Focused Ion Beam:

vertical SEM column + Ga ion column + micromanipulator
+ gas injection system + detectors

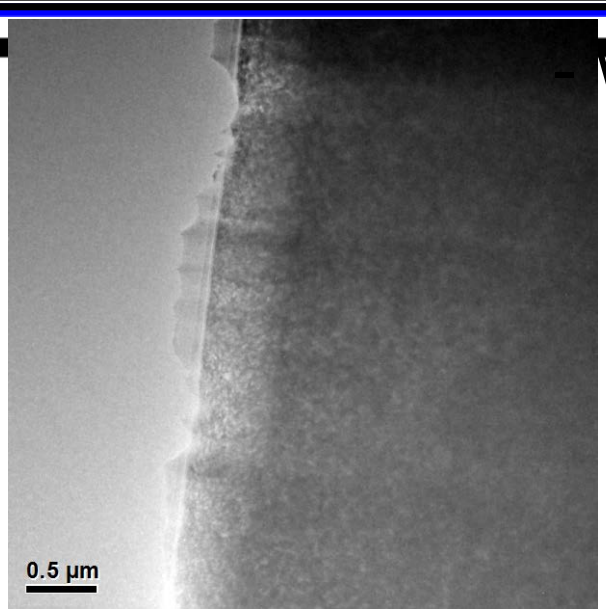
Schematic of the method [B.Myers]

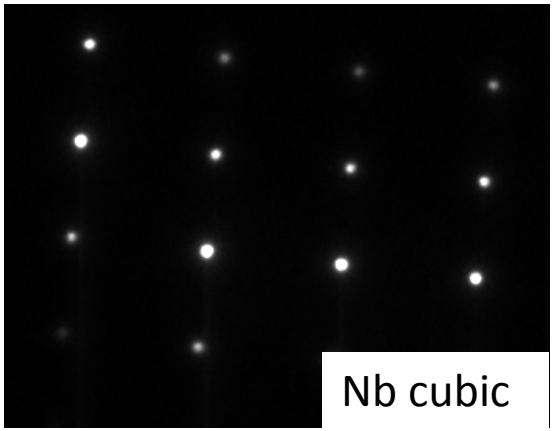


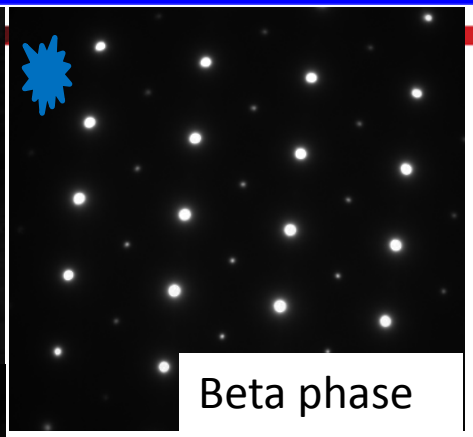
Result: cross-sectional cut from the bulk

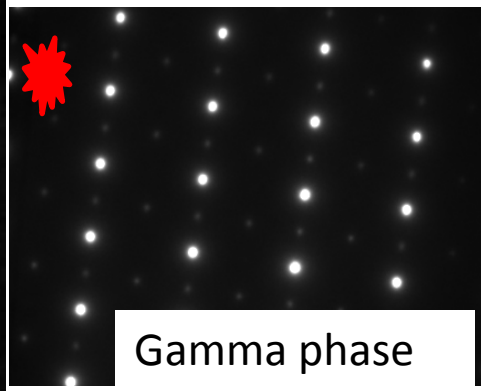
Nb-H Superlattice at 94 K,

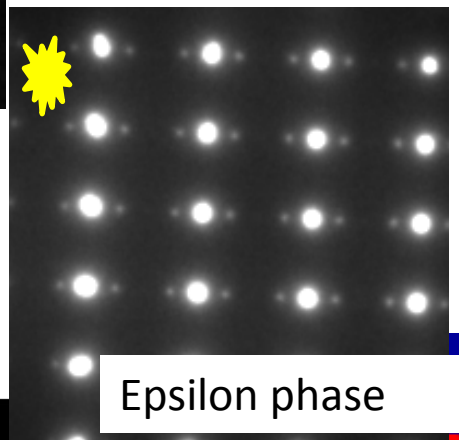
- work by Tao *et al*



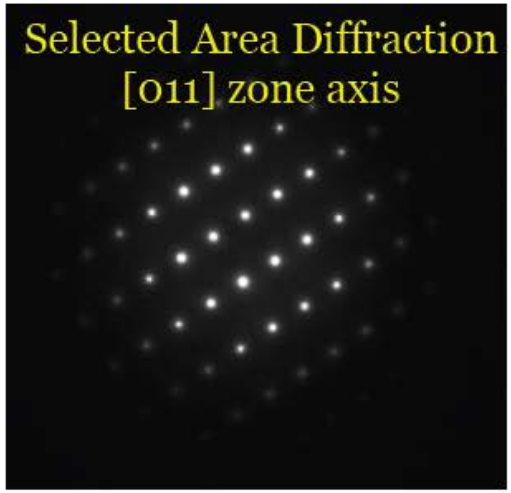


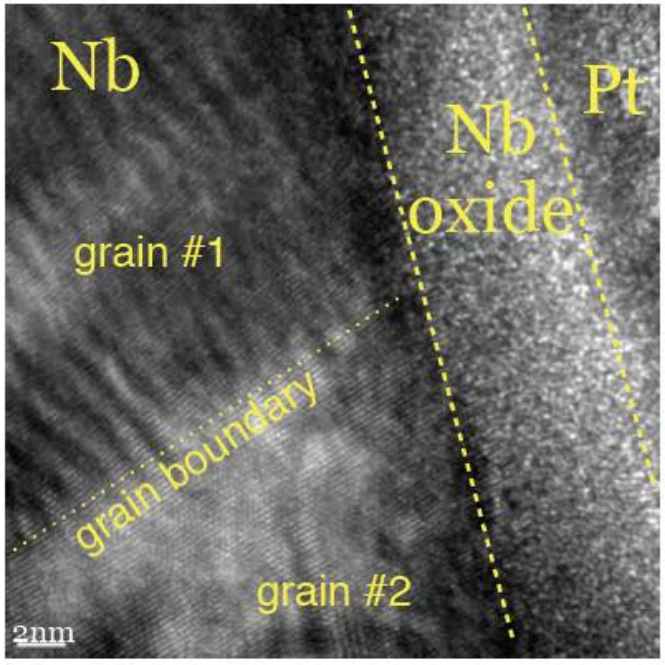




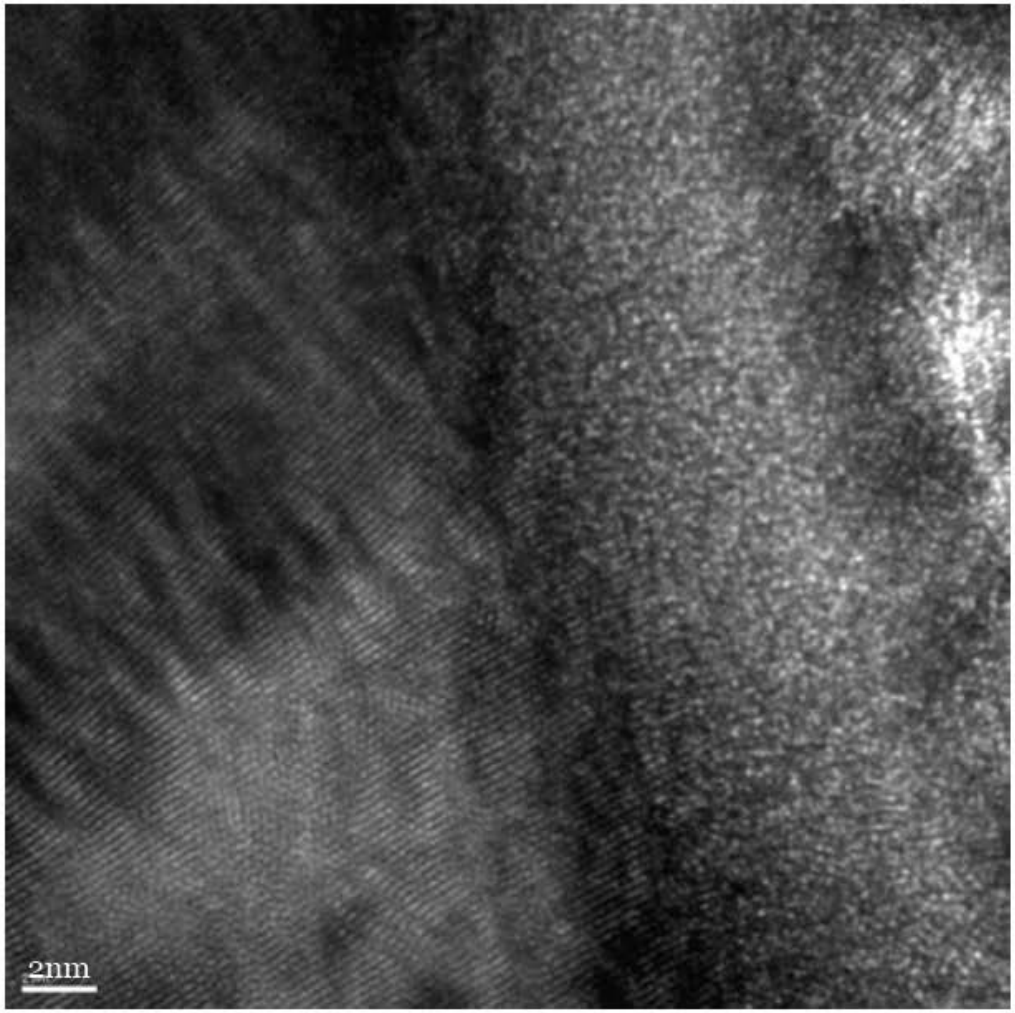


HRTEM imaging of Cold Spot at Room T continue



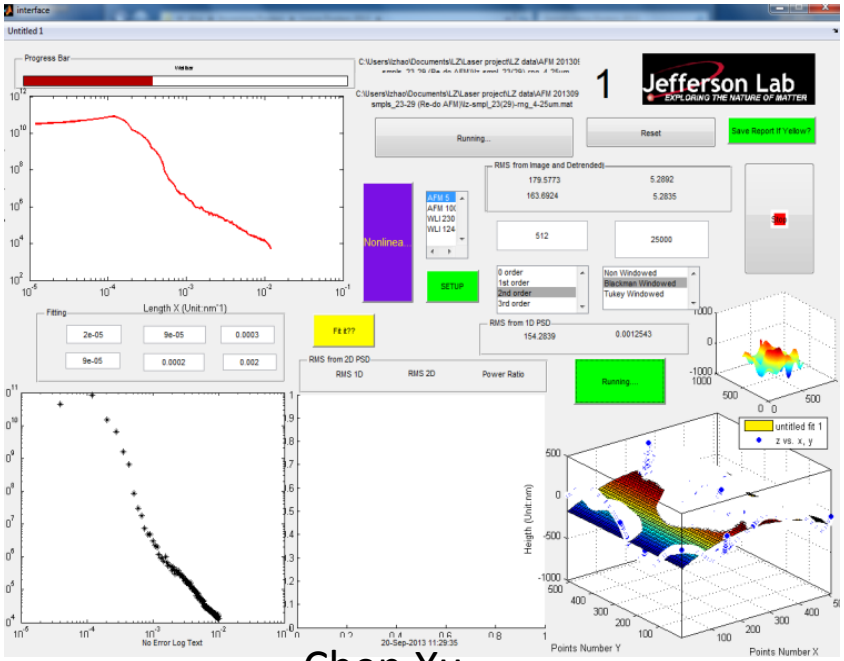


Phase Contrast of the Grain Boundary



No significant oxidation along Grain Boundary in contradiction to J.Halbritter (2001)

Topography characterization

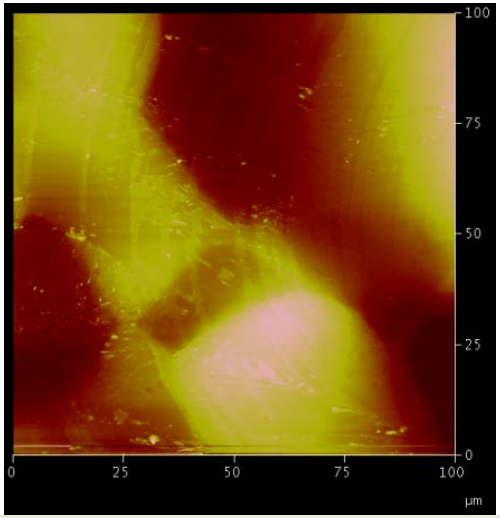


Chen Xu

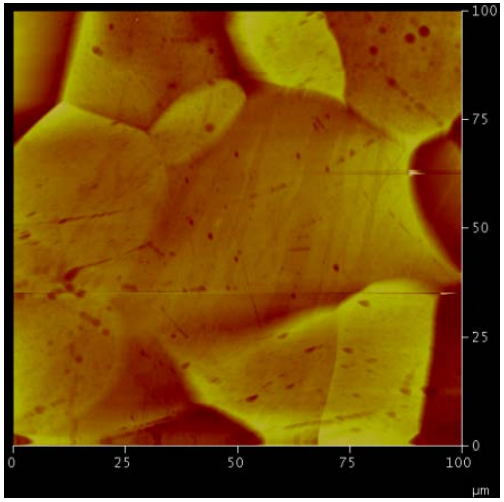
- Hirox optical microscope, Phenom SEM
- Atomic force microscopy (AFM)
  - Tapping mode
  - RMS roughness (R_q), height variation of peaks/valleys
- Power spectral density (PSD) of surface height
  - Customized program
  - 2nd order detrending
  - Blackman window
  - Width variation of peaks/valleys
  - Quantitatively describe sharp features

Case 3:BCP on Mechanical Polishing

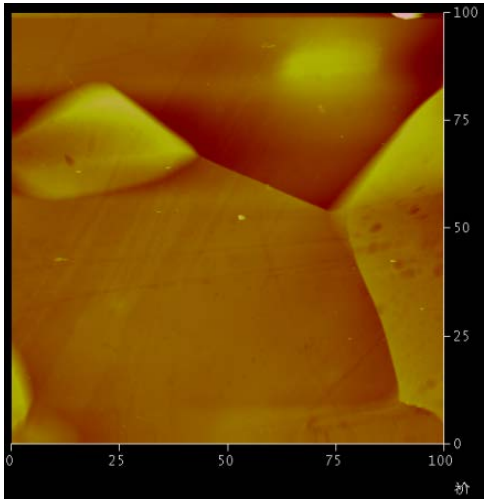
As Received

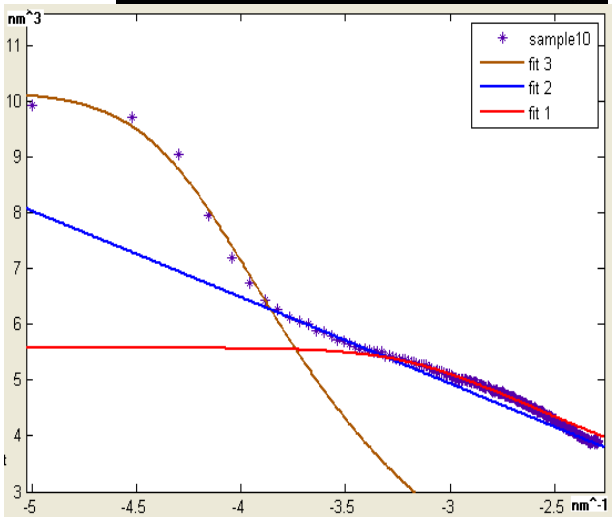


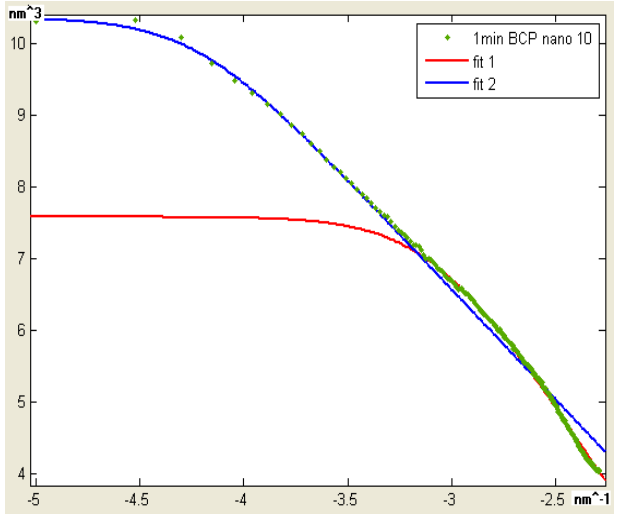
1 min

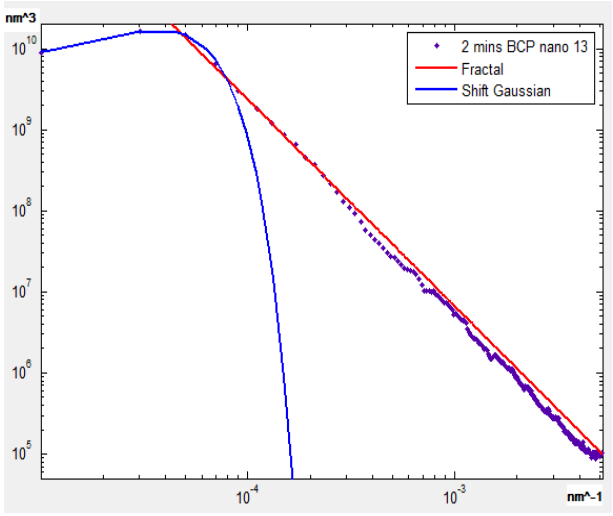


2 min





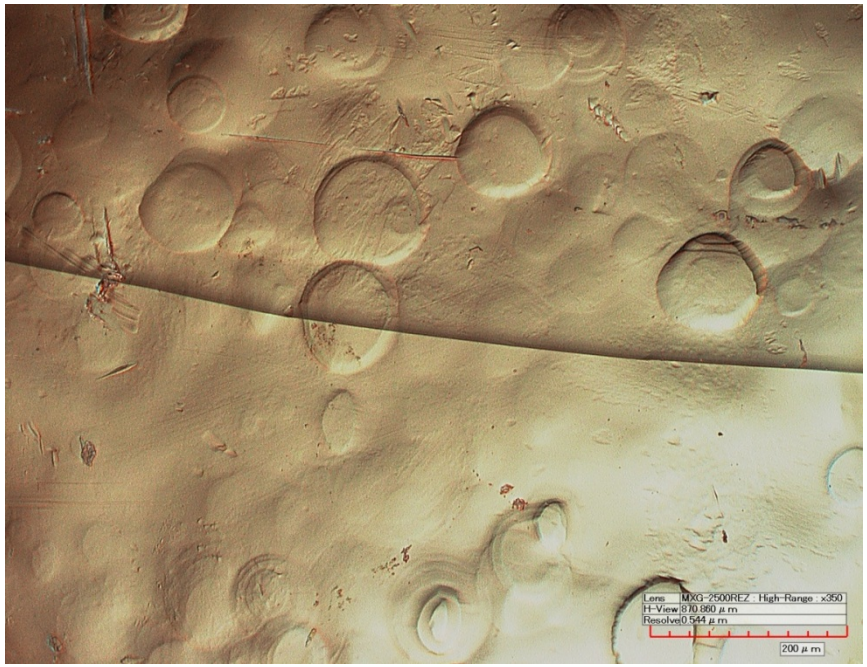




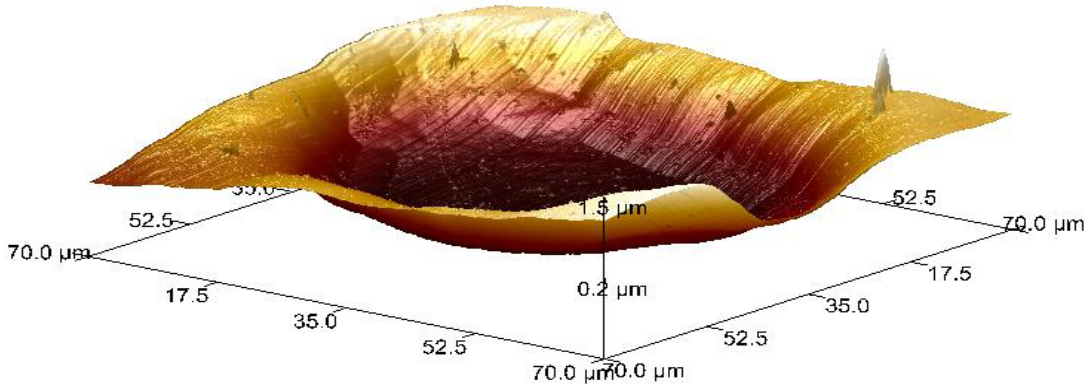
Typical surface finishes AFM scan 100µmby 100µm

PSD Structure changes! Why?

Optical, SEM, AFM - Bubble prints, BCP on bi-crystal niobium



BCP 20°C, 12 minutes
Print radius ~ 50 µm
Print depth ~ 1 µm

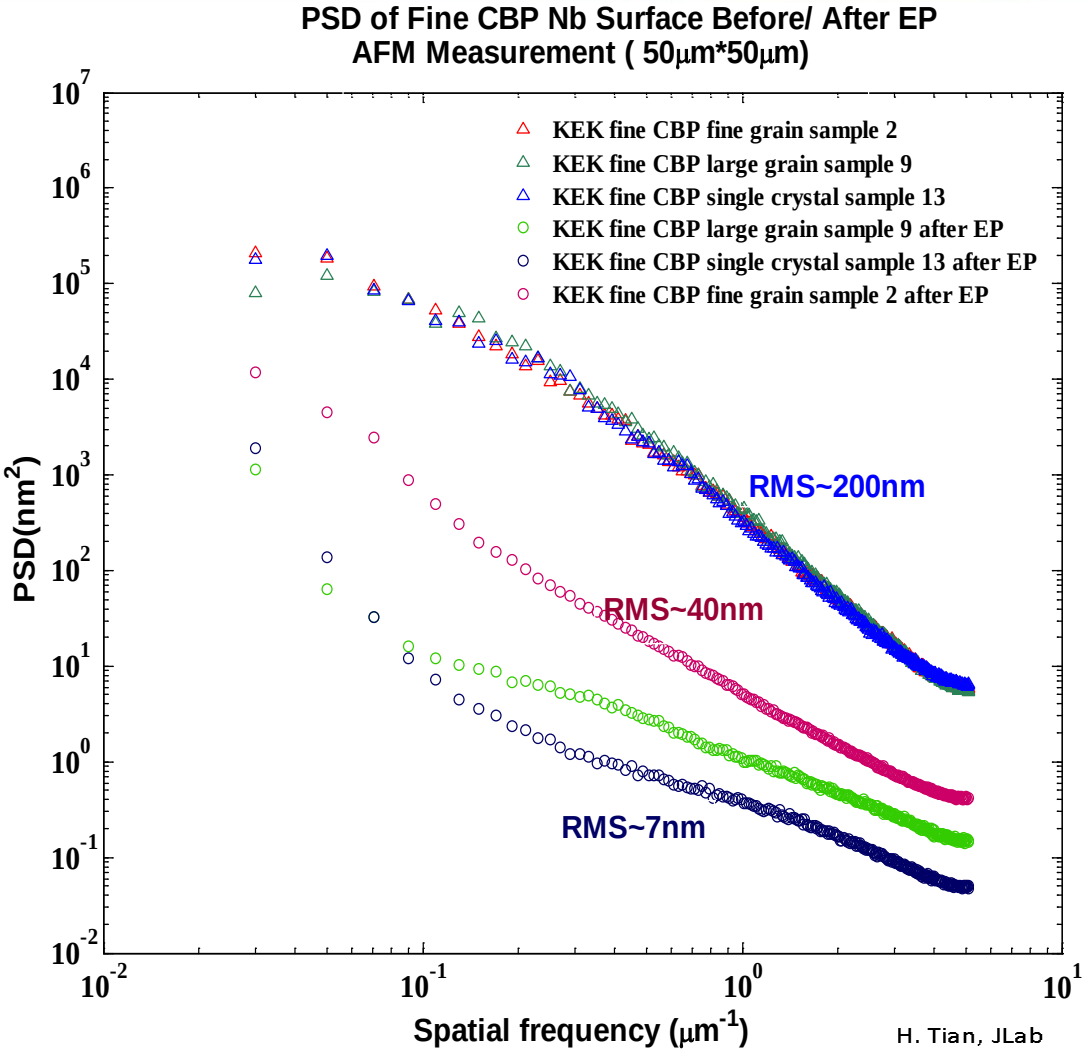


Not all Nb "EPs" the same

With "standard"1:10 HF/H_2SO_4 Electrolyte at 30°C Nb crystallography affects the polishing effectiveness.

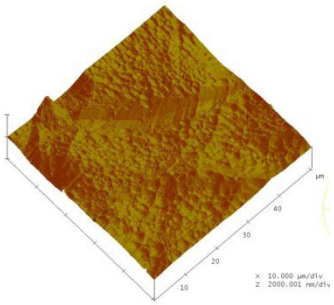
With identical starting topography from CBP, given identical 100 min "EP" at 30°C, single-crystal material was significantly smoother.

Evidence for a significant etching activity at 30°C

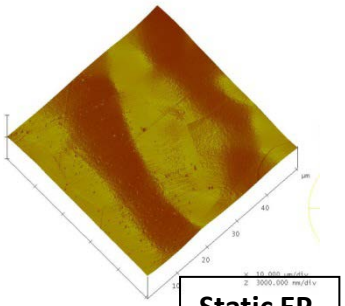


AFM, PSD - EP topography vs. surface flow rate

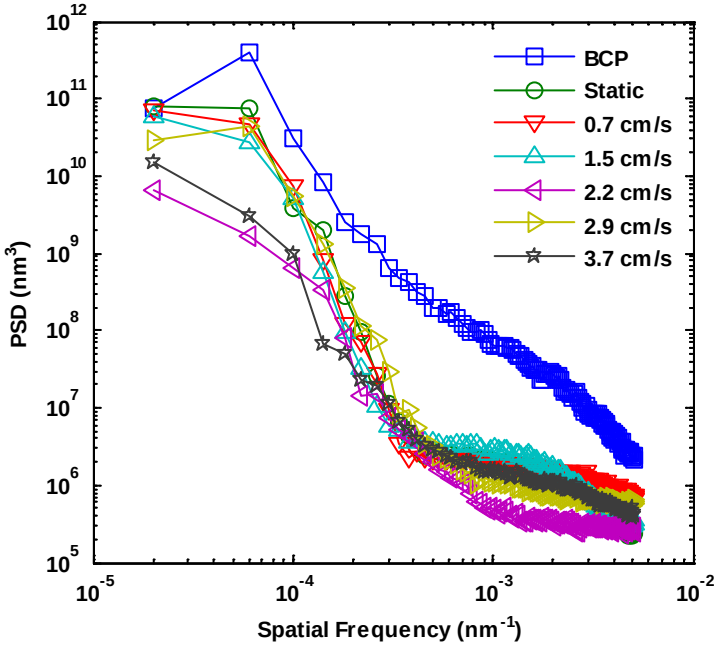
14 V, 20-22 °C, 90 minutes, ~40 µm removed

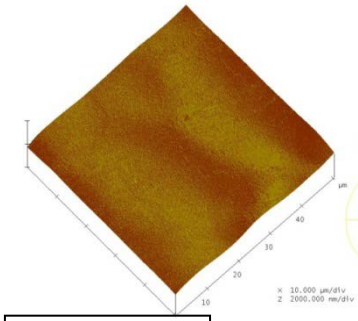


BCP

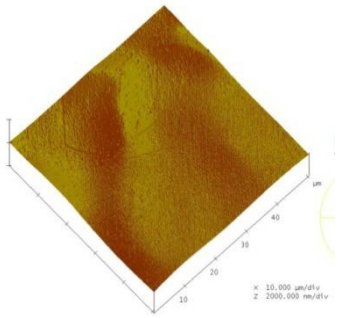


Static EP



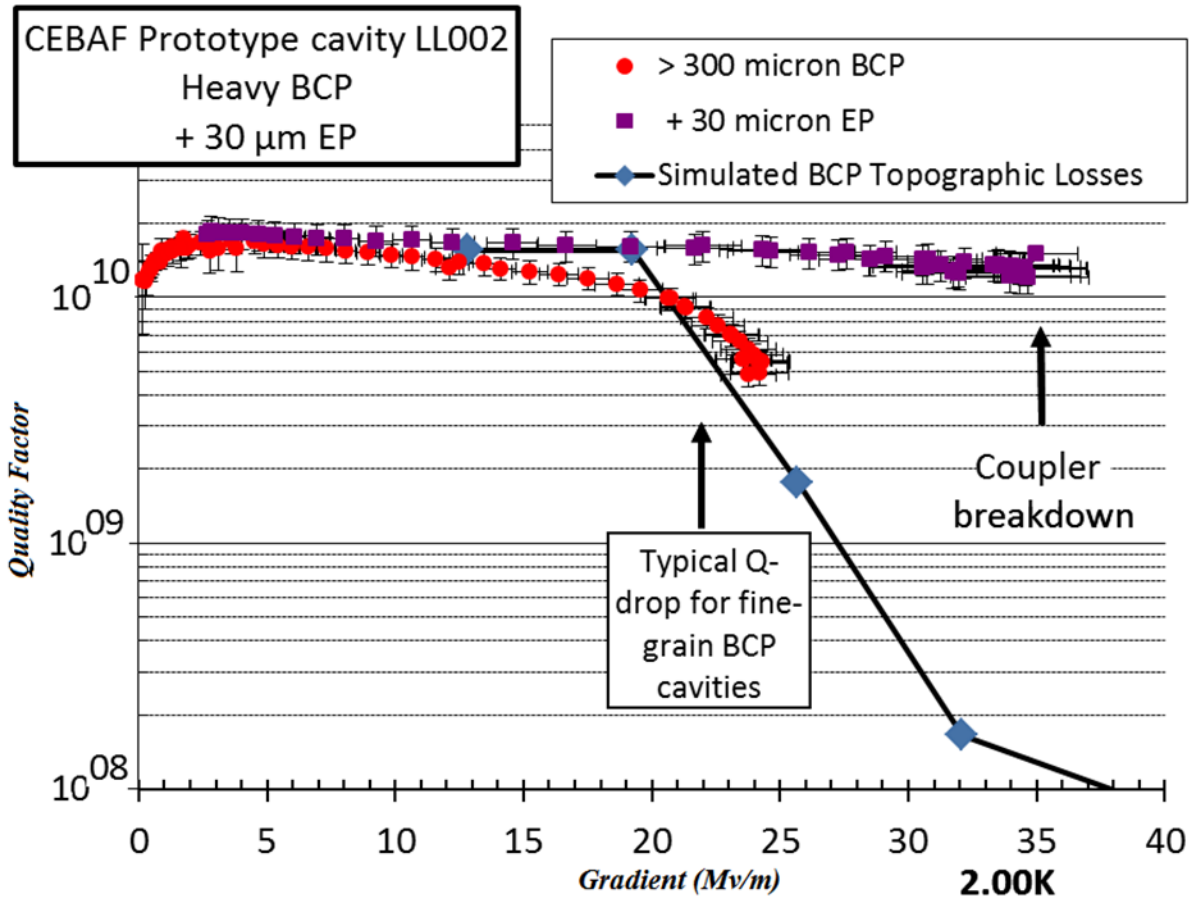


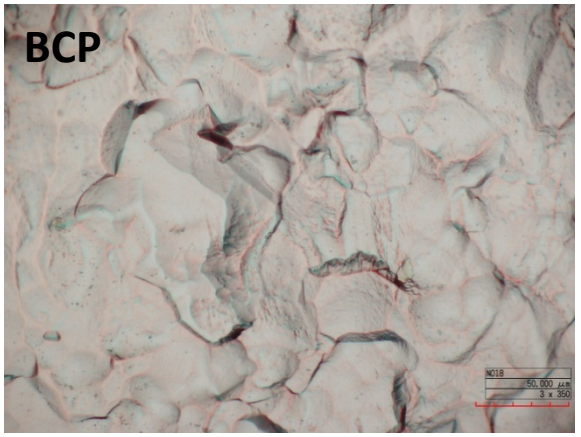
0.7 cm/s EP

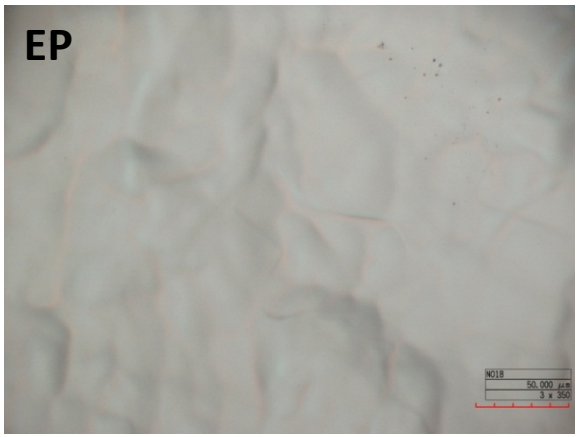


3.7 cm/s EP

Importance of topography







C. Xu, C. E. Reece and M. J. Kelley, "Simulation of non-linear SRF losses derived from characteristic Nb topography: comparison of etched and electropolished surfaces," *http://arxiv.org/abs/1406.7276,* 2014.

EP cavities often have higher field gradients
Difference between BCP and EP: topography

SRF is all about Surfaces

- Alphabet soup of analytical techniques available (short list)
  - Elemental analysis
    - EDX (bulk), AES, XPS, SIMS (surface sensitive)
  - Structural analysis
    - XRD (1-2 μm), EBSD (50 nm), TEM (~1 nm)
  - Topographical analysis
    - Profilometer, AFM
- RF measurements are always averages over large surface areas – often ambiguous interpretations