U.S. DEPARTMENT OF ENERGY

JSA

USPAS June 2015

Rutgers

SURFACE & MATERIAL TECHNIQUES APPLIED TO SRF SURFACES

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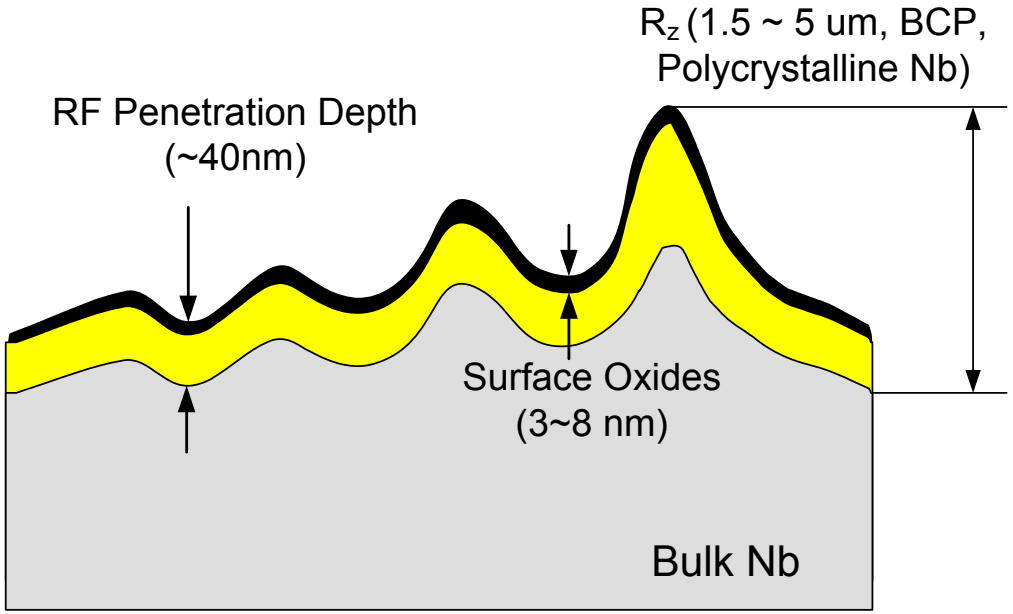
Performance of Nb SRF Cavity Strongly Impacted By Its Topmost Surface



Shallow RF penetration depth
(~ 36 nm @ 1.5 GHz)

Cavities' surface treatments
(BCP/EP removes mechanical damaged layer; low-T- improves Q-drop)

Undesirable surface effects including: magnetic field enhancement at a sharp transition, such as a grain boundary edge, the creation of anomalous "hot spots," and electron multipacting.

Surface Chemistry | **Surface Structure** | **Surface Topography**

H. Tian

Surface Science for SRF Surfaces

- Surface science is key to understand the RF performance and superconducting properties of SRF surfaces in both bulk and thin film technology.

- It is useful not only for R&D but also for process validation (chemistry, HPWR, heat treatment…) and for cavity production support, from Nb sheet characterization to detecting defect on the surface of ill-performing cavities.

Surface Science for SRF Surfaces

Morphology:

- Optical Inspection
- SEM/FIB
- Profilometry/AFM (UFM, MFM)
- Replicas
- Eddy Current scanning for Nb sheets

Structure:

- XRD
- EBSD/ECCI/TKD
- TEM/HR-TEM/STEM, EELS
- RHEED/STM

Chemical composition:

- XPS/HR-XPS
- SIMS
- EDS
- AES
- TDS
- APT

Surface Science for SRF Surfaces

Characterization of bulk Nb surfaces

Topography – **stylus profilometry, atomic force microscopy (AFM), optical profilometry, replicas**
Near surface (< 8 nm) chemistry – **X-ray photoelectron spectroscopy (XPS), Auger Electron Spectroscopy, SIMS**
Micro-contaminant defects – **Secondary ion mass spectrometry, with standards (SIMS)**
Structural cross-section – **Transmission electron microscopy associated with electron energy loss (TEM/EELS), Focused Ion Beam (FIB)**
10 nm-scale crystallographic texture within ~ 50 nm of surface – **Electron backscatter diffraction (EBSD)**
Visualization of defects on cavity surface – **Optical/interferometry inspection of cavities**
Nb sheet material for cavity production – **Eddy current scanning**

Surface Science for SRF Surfaces

Characterization of SRF thin film surfaces

In-situ crystallographic structure characterization – **(RHEED), Scanning Tunneling Microscopy (STM)**
Large area crystallographic structure – **X-ray diffraction (XRD)**
10 nm-scale crystallographic texture within ~ 50 nm of surface – **Electron backscatter diffraction (EBSD)**
Topography – **stylus profilometry, atomic force microscopy (AFM), optical profilometry**
Near surface (< 8 nm) chemistry – **X-ray photoelectron spectroscopy (XPS)**
Micro-contaminant defects – **Secondary ion mass spectrometry, with standards (SIMS)**
Structural cross-section of film – **Transmission electron microscopy associated with electron energy loss (TEM/EELS), Focused Ion Beam (FIB)**

SURFACE TOPOGRAPHY

- 3-D arrangement of physical attributes such as shape, height, depth

  R_a - Roughness Average

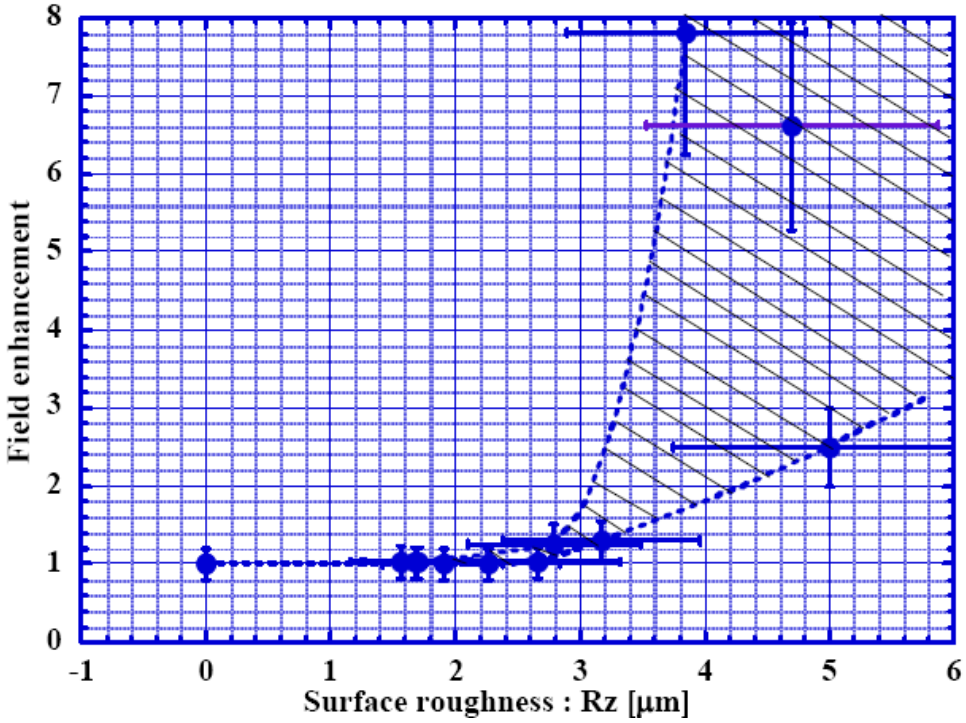
  RMS (R_q) – Root mean square

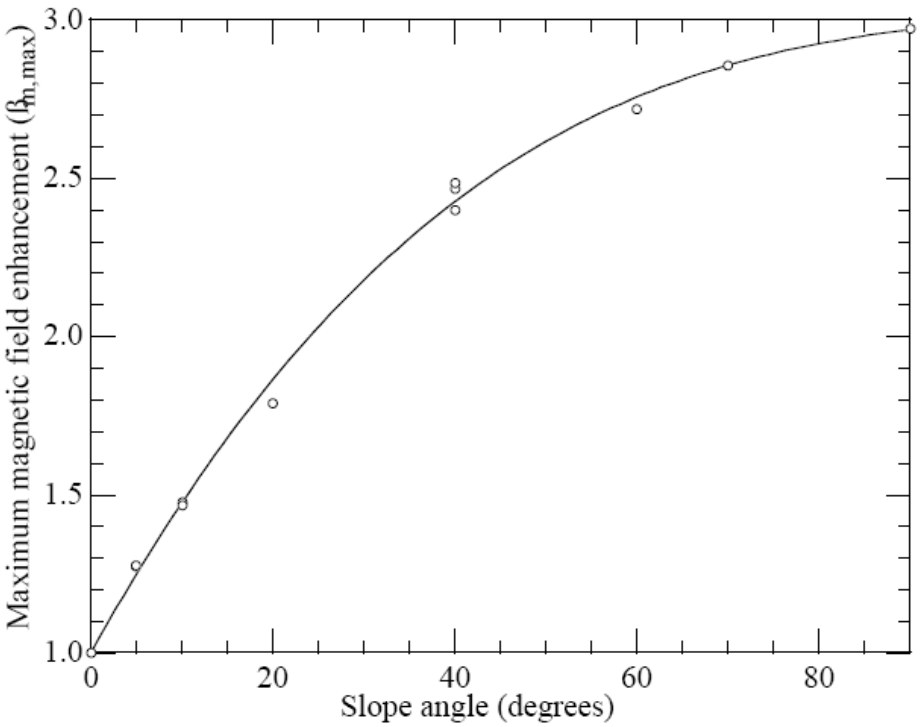
  R_z – Mean Peak-to-Valley Height

  R_{max} – Maximum Peak-to-Valley Height

- Importance for SRF
  - Roughness
  - Presence of step edges @ grain boundaries
  - Presence of defects

Surface Topography Is a Critical Factor For Nb SRF Cavities





Rz < 2 µm ➡ high gradient cavity (> 30 MV/m). ***K. Saito, the 9th SRF workshop in Santa Fe, NM.***

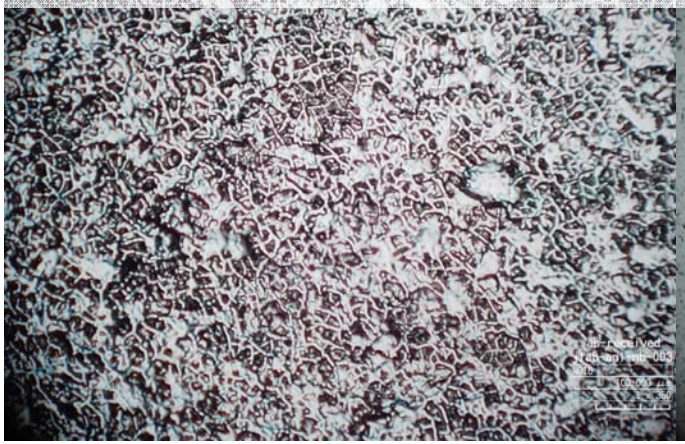
Magnetic field enhanced at the sharp protrusions. ***J. Knobloch et. al, the 9th SRF workshop in Santa Fe, NM.***

Optical Microscopy (OM)

Optical microscopy is used to determine the large scale morphology of samples. There are different types of OM available– HiRox and a metallographic microscope. The HiRox is a state of the art digital microscope that can take images up to 7000X. The metallographic microscope has digital image acquisition capabilities and numerous filters, lenses and attachments for staining and metal examination.

Niobium Surfaces

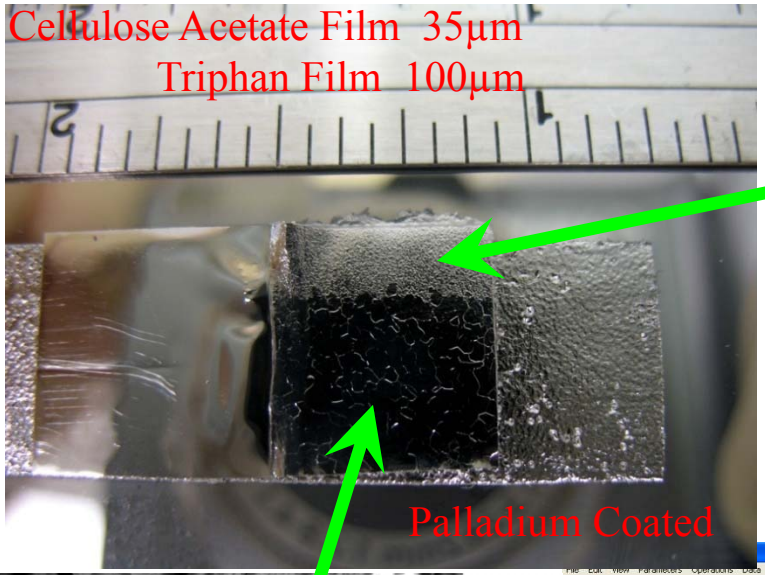
Single Crystal Nb – EP 10:1 H_2SO_4:HF

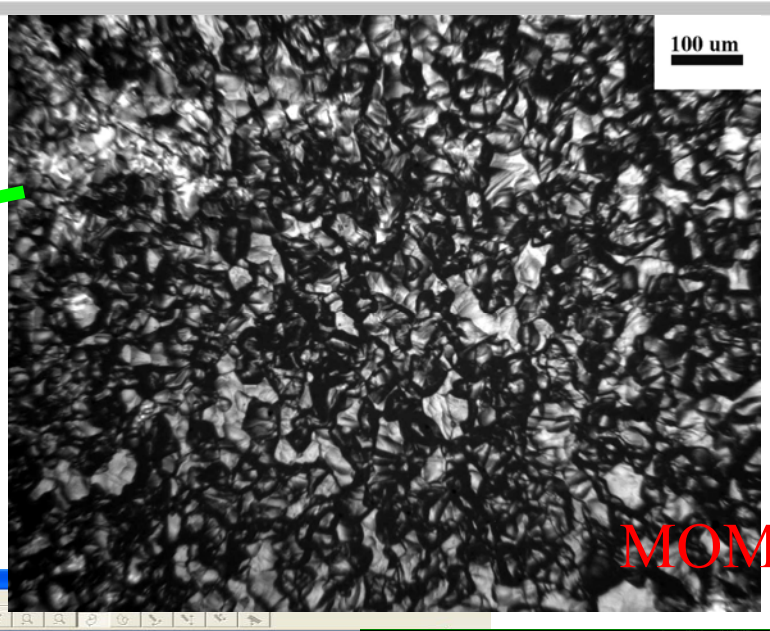


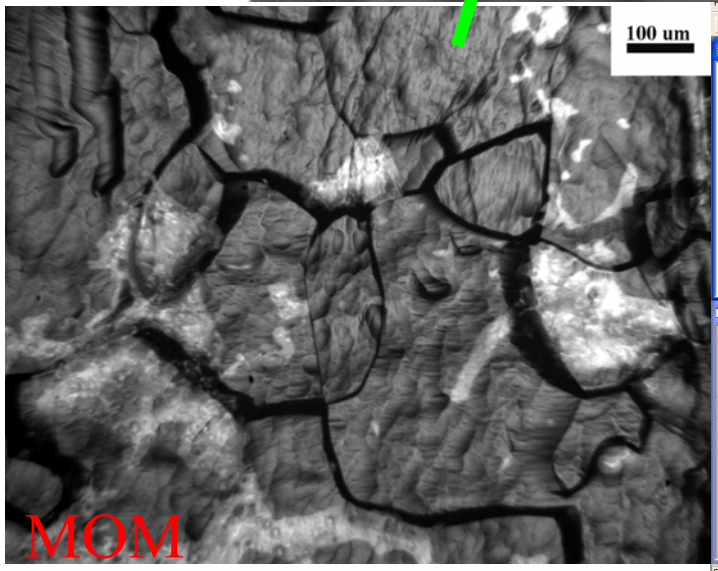
Fin Grain Nb – Mechanically Polished

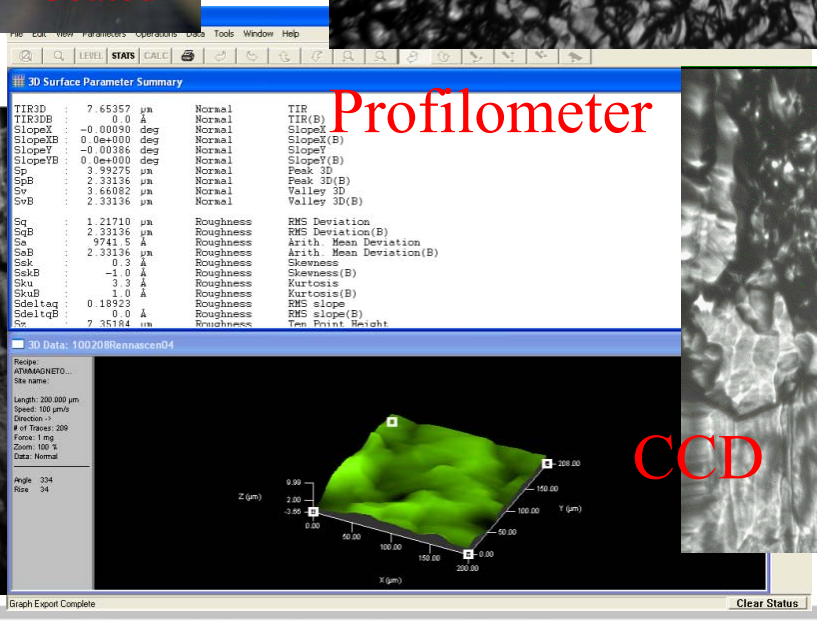
Fine Grain Nb – As-Received

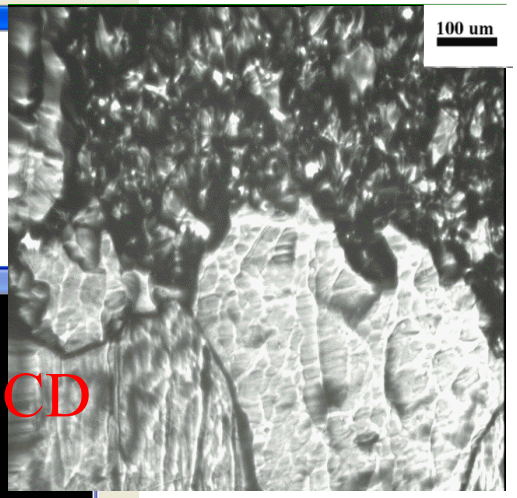
Surface topography of Nb Cavity: Replicas





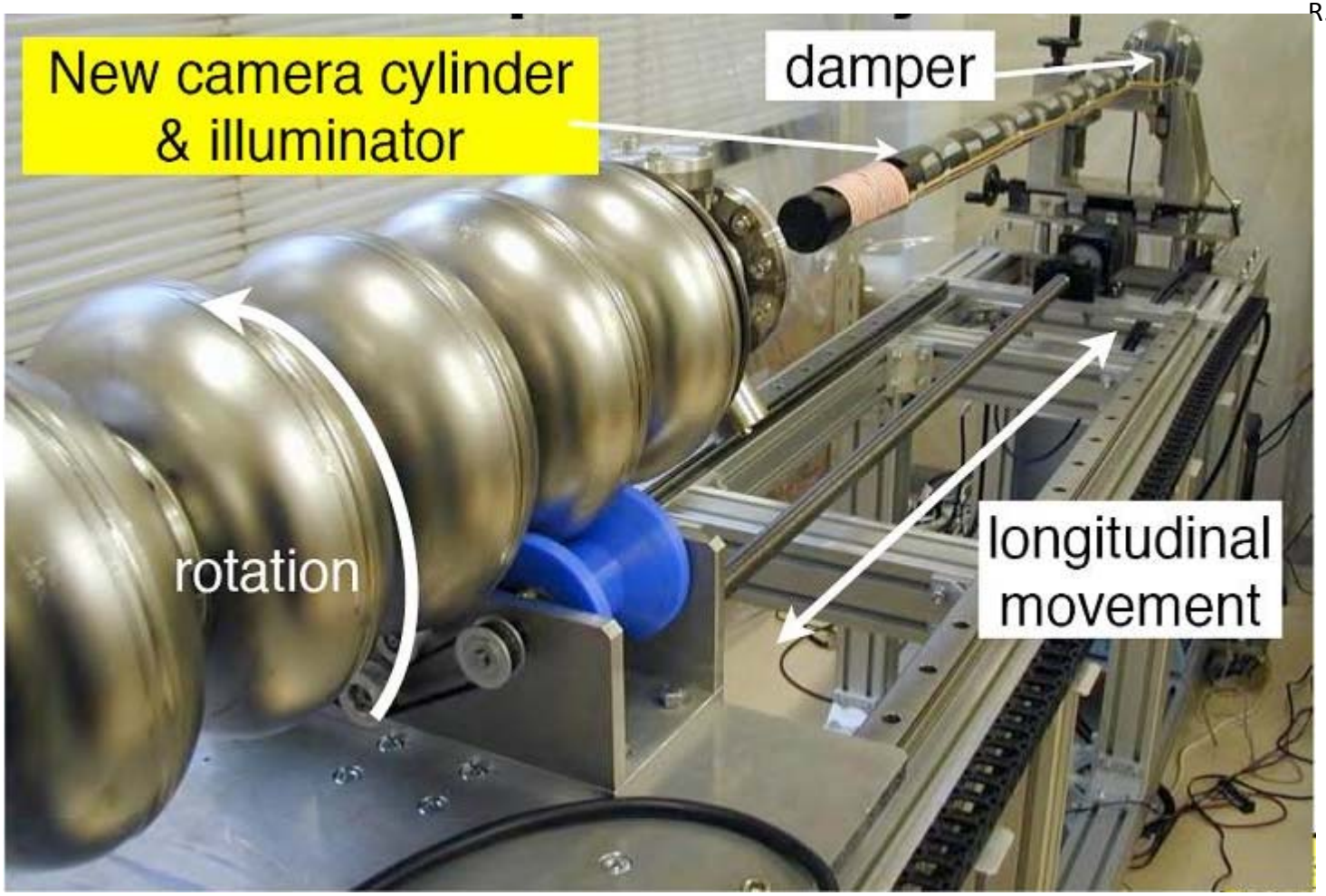




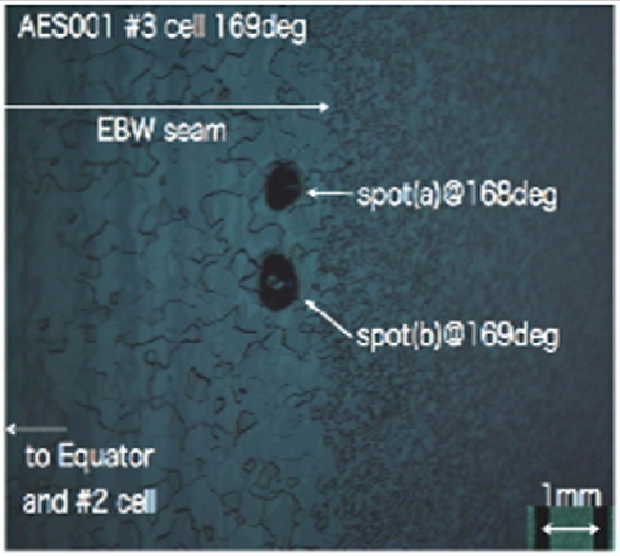


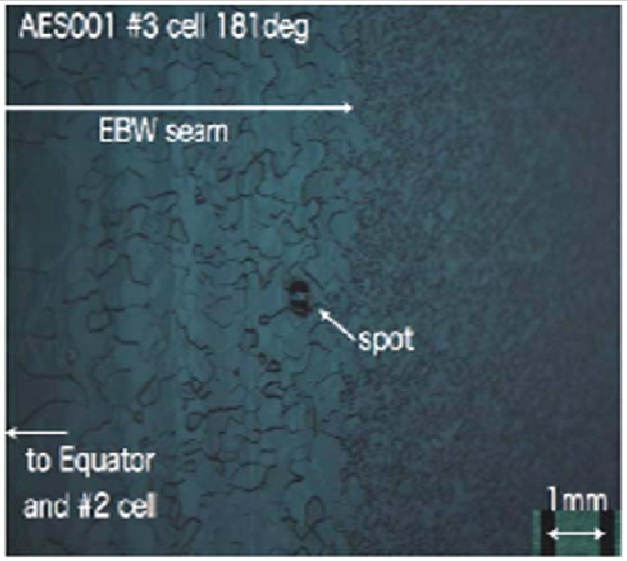
Cavity Inspection system

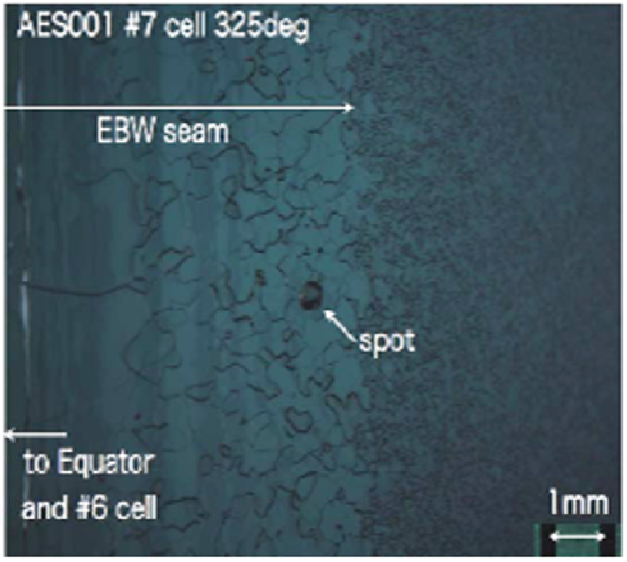
R. Geng, JLab



Cavity Inspection system





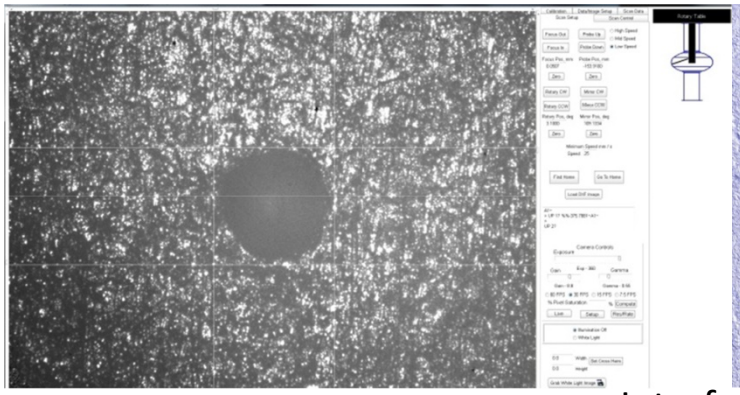


Y. Yamamoto, H. Hayano, E. Kako, S. Noguchi, M. Sato, T. Shishido, N. Toge, K. Umemori, K. Watanabe(KEK), H. Sakai(ISSP, Univ. of Tokyo) and T. X. Zhao(IHEP) TTC Otober 21,2008

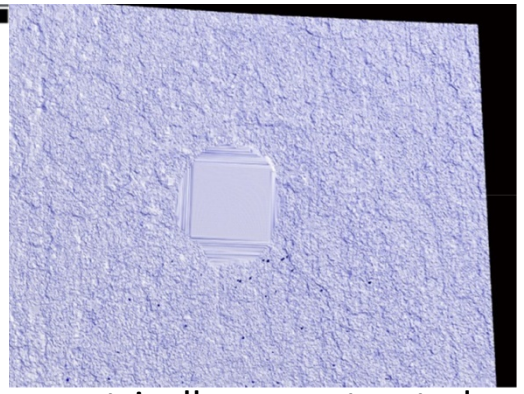
Y. Tajima 4

CYCLOPS - CavitY CaLibrated Optical Profilometry System

Detailed finish inspection and mapping of the inside surface of accelerator cavities



680 µm blind drilled hole



Interferometrically reconstructed surface profile

Non contacting optical prove travels vertically down the cylindrical axis. Probe = 2 concentric hollow cylinders, an outer probe (positions lower mirror, inner probe (moves vertically with rest of the optical system and the reference leg of the interferometer)

System optimized for a very narrow depth of field for interferometric measurements.
Reflections from cavity surface return to a CCD camera. Surface profile is derived by tracking the interference fringes from a blue LED via a series of digital optical images from an area ~2.6 x 2 mm.

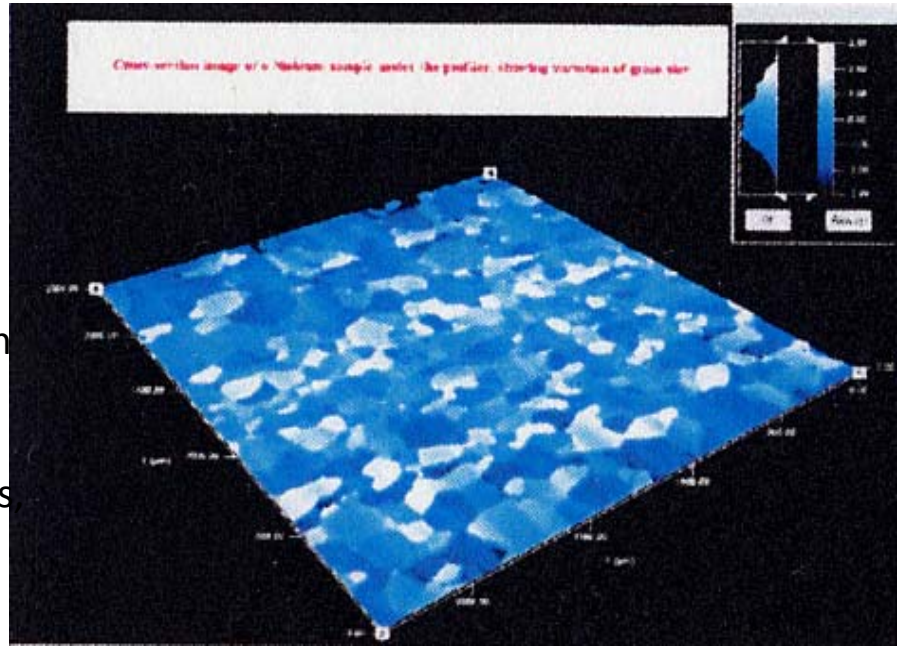
Measurement of interior surface roughness and identification of blemishes as small as 10 µm.
Precision optics and motion control allow mapping of the roughness with 75 nm precision

Profilometry

Measurement of the profile of a surface in order to quantify its roughness.

Contact profilometer

A diamond stylus scans laterally across the sample for a specified distance and (10 nm – 1 mm)
The height position of the diamond stylus generates an analog signal converted into a digital signal stored, analyzed and displayed. The radius of diamond stylus ranges from 20 nm to 50 µm, and the horizontal resolution is controlled by the scan speed and data signal sampling rate.
Surface Independence: insensitive to surface contaminants surface reflectance or color.
Lateral resolution: stylus tip radius ~20 nm
Vertical resolution: sub-nm.
Direct Technique: No modeling required



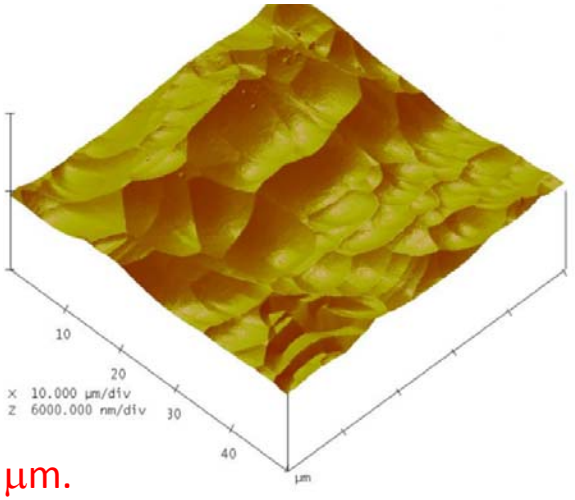
- Several profilometry techniques - The most common is a stylus based method for determining the texture of a surface.
- A stylus is dragged across a sample surface and the displacement is measured to create a topographic map of the surface.
- Used for large area scans and thickness measurements of deposited films or etched features.

Atomic Force Microscopy (AFM)

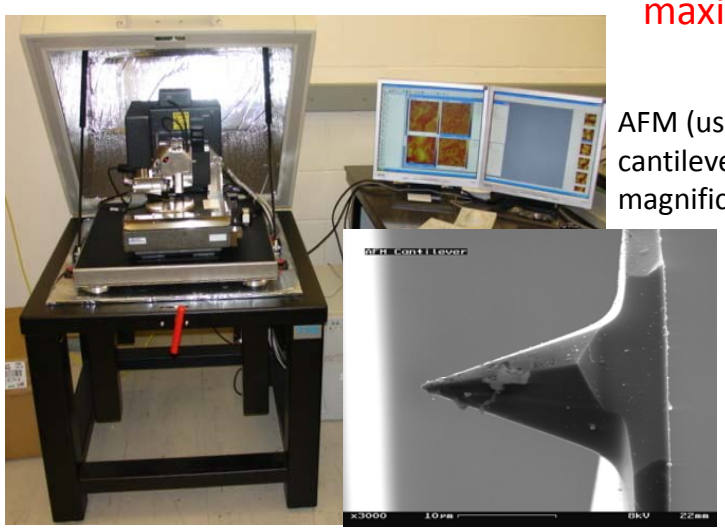
Atomic force microscopy (AFM) or scanning force microscopy (SFM) is a very high-resolution type of scanning probe microscopy, with demonstrated **resolution** on the order of **fractions of a nanometer**, more than 1000 x better than the optical diffraction limit.

AFM measurements provide high resolution images of surface. A tip is used like a spring board to map out the surface of materials with < 1 nm vertical resolution in the best cases.
Imaging modes: static (contact) mode, dynamic (non-contacting) mode

BCP Etched Niobium

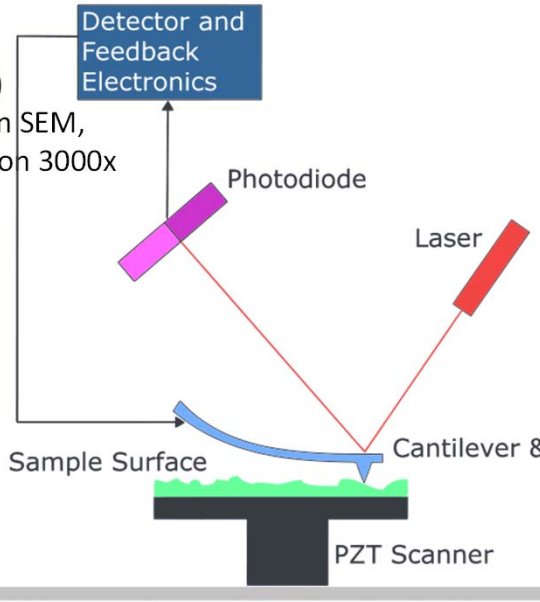


Maximum height imaged~10-20 µm
maximum scanning area ~150 µm ×150 µm.

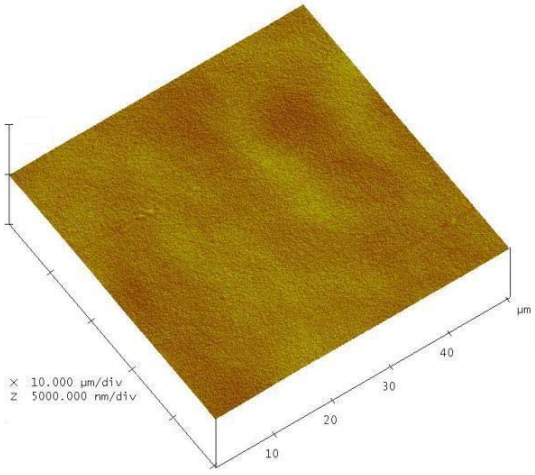


Atomic force microscope (AFM/MFM) on the left with controlling computer on the right

AFM (used) cantilever in SEM, magnification 3000x



Electropolished Niobium

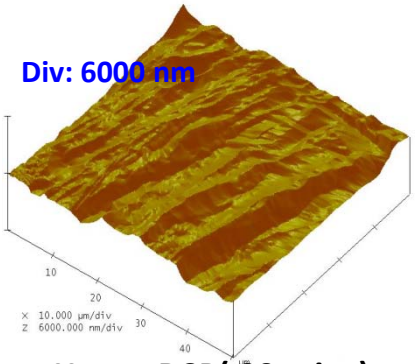


Surface Topography of Niobium Samples after BCP/EP Treatment

H. Tian

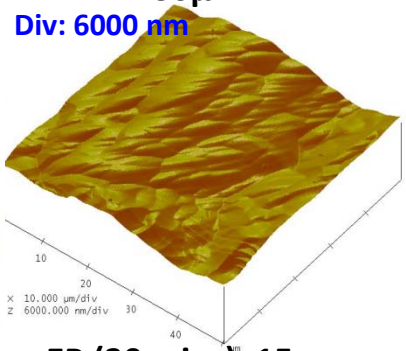
Ground

Div: 6000 nm



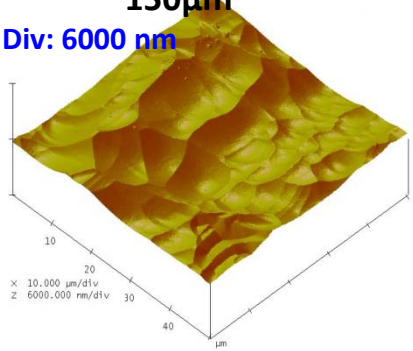
light BCP(20 mins) ~30µm

Div: 6000 nm



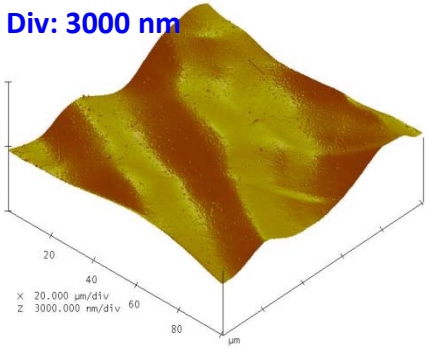
Heavy BCP(90 mins) ~150µm

Div: 6000 nm



EP (30 mins)~15µm

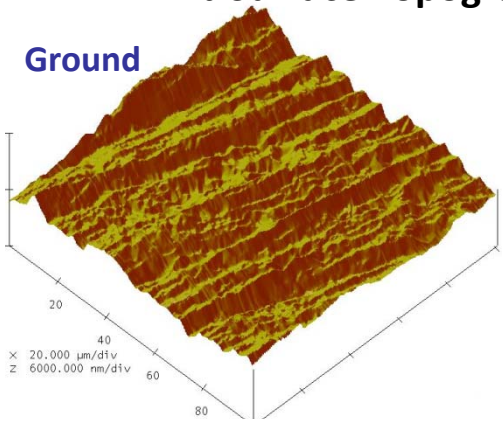
Div: 3000 nm



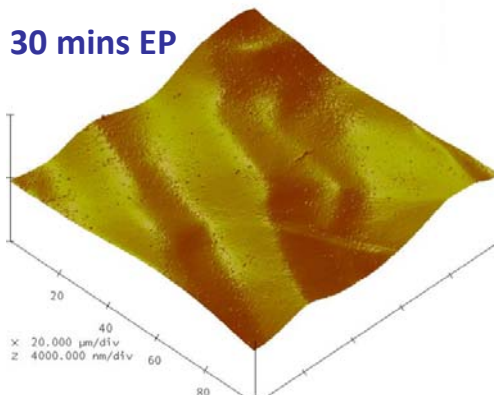
Heavy BCP removes all mechanical damage, but results in a rougher surface.

Nb Surface Topographic Variation Under EP

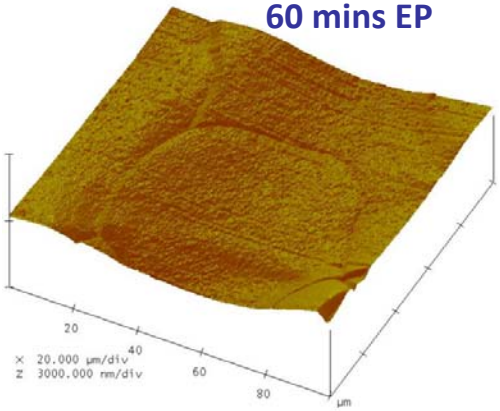
Ground



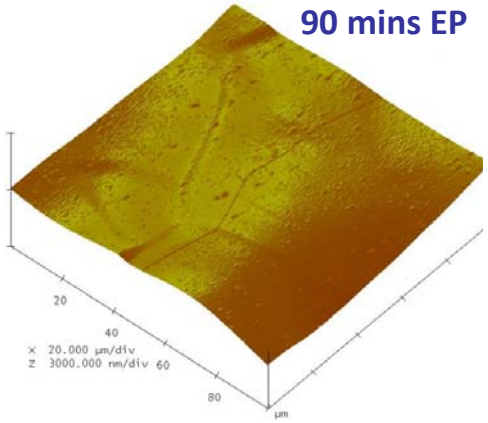
30 mins EP



60 mins EP



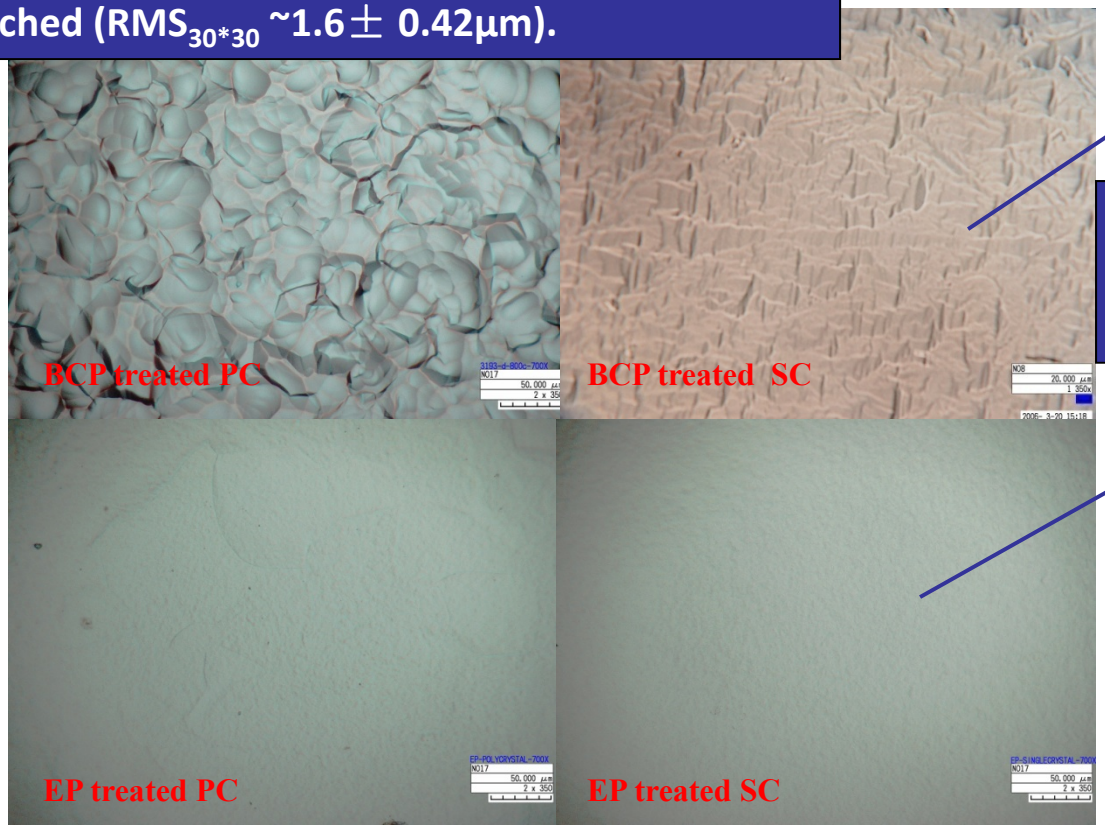
90 mins EP

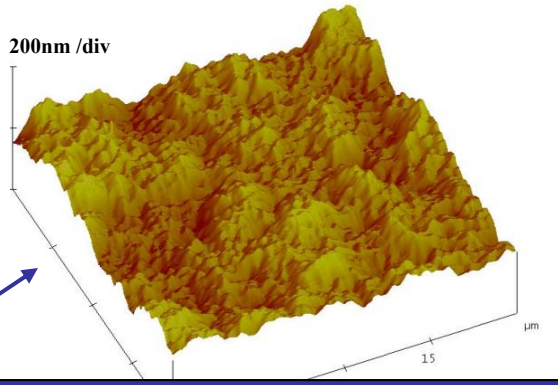


Surface protrusions caused by mechanical grinding were quickly leveled out by a short period of EP, the edges of grain boundaries and recessed parts of surface were continually smoothed out by EP

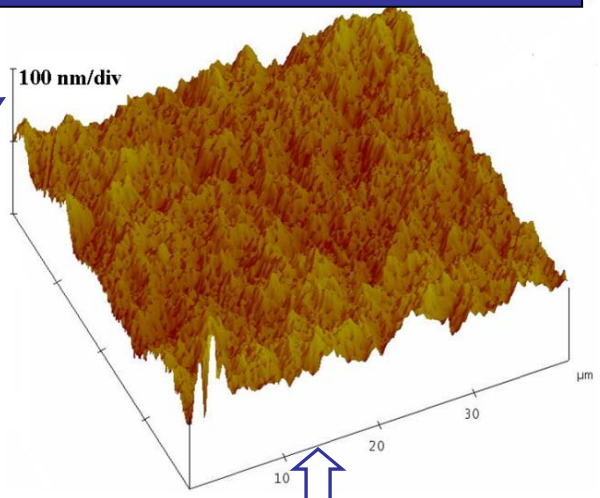
Surface Topography of BCP/EP Single Crystal and Polycrystalline Nb

Compared with EP treated poly-Nb (RMS_{30*30} ~0.34 ± 0.11µm), grain boundaries and other features of BCP treated poly-Nb are heavily etched (RMS_{30*30} ~1.6± 0.42µm).





Surface of single crystal BCP (RMS_{30*30} ~0.3µm) appears more undulating.



The above optical images were taken with HIROX KH-3000VD high resolution digital video microscopy system

Single crystal after EP. > 100 nm step height still remains.

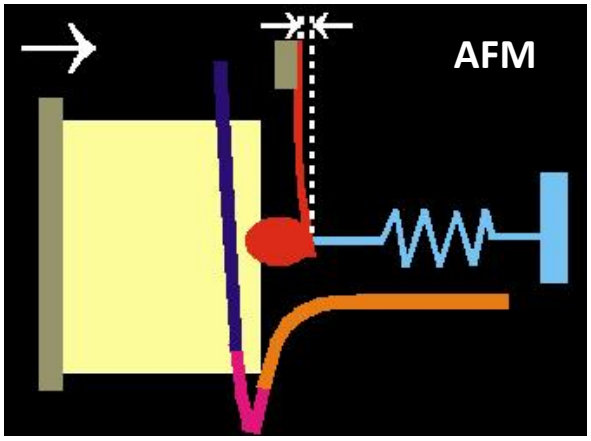
Ultrasound Force Microscopy (UFM)

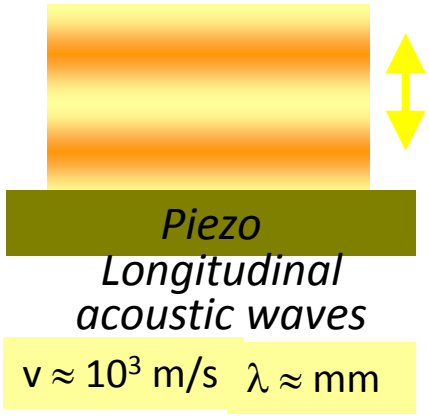
The combination of AFM-UFM allows a near field acoustic microscopic image to be generated. The AFM tip is used to detect the ultrasonic waves and overcomes the limitation of wavelength that occurs in acoustic microscopy. By using the elastic changes under the AFM tip, an image of much greater detail than the AFM topography can be generated.

Improved details & image contrast on "flat" areas of interest where AFM is limited in contrast.
Elastic properties and adhesion of the samples with nanoscale lateral resolution.
Measured magnitude: static cantilever displacement induced by the ultrasonic force.

➢ Information from sub-surface features in the image contrast

➢ Potential to provide information about dynamic surface adhesive properties, capillarity or entropic effects, etc.





APPLICATIONS

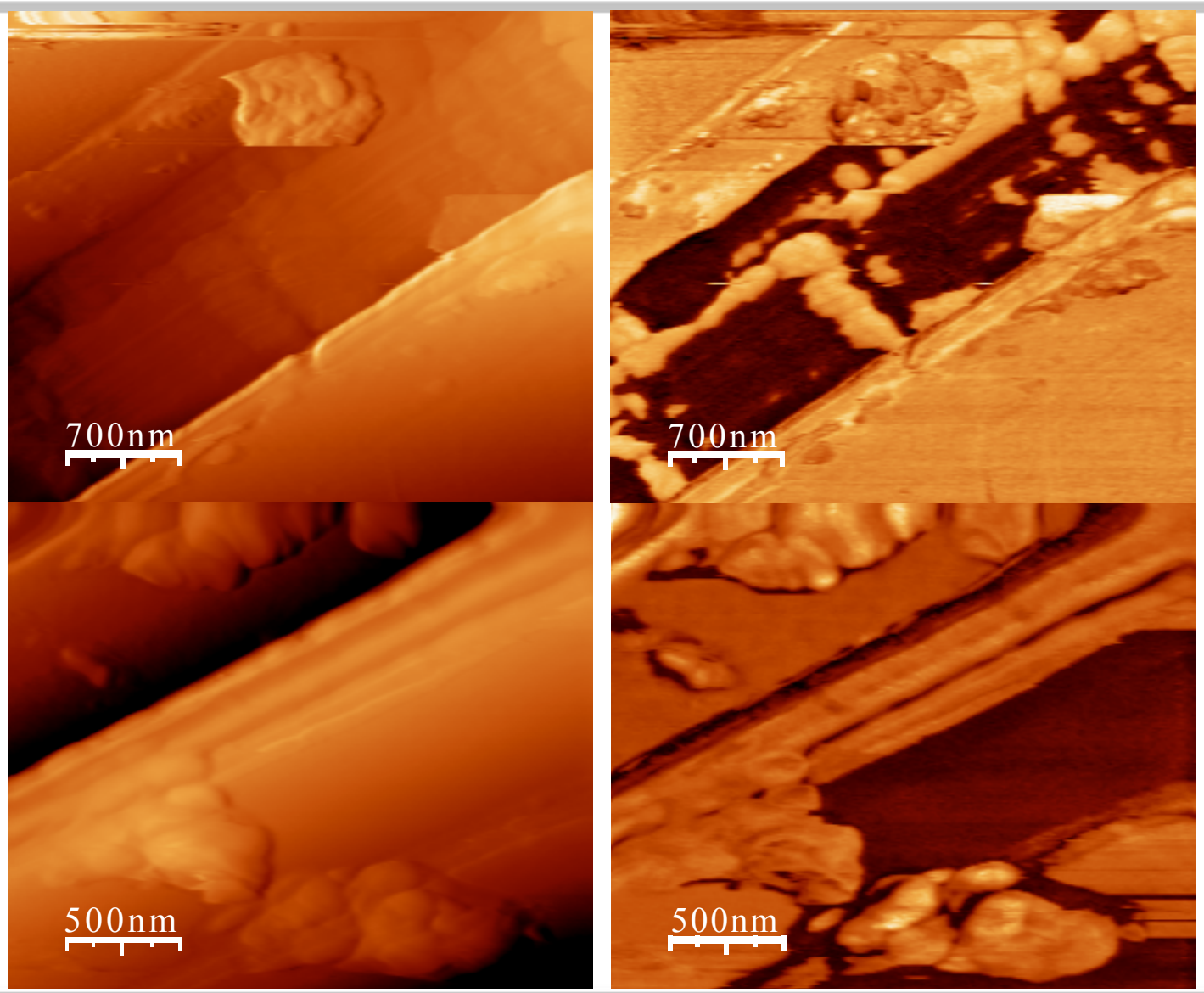
ω : from 20 kHz up to GHz

- Determination of elastic properties
- Non-destructive testing
- Sensor of materials internal structure
- Use in materials processing, metrology, etc.

Ultrasound Force Microscopy (UFM)

AFM

UFM



AFM

UFM

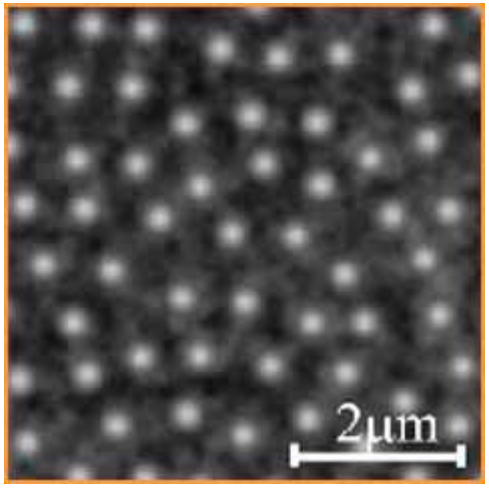
Magnetic Force Microscopy (MFM)

MFM images the spatial variation of magnetic forces on a sample surface. For MFM, the tip is coated with a ferromagnetic thin film. The system operates in non-contact mode, detecting changes in the resonant frequency of the cantilever induced by the magnetic field's dependence on tip-to-sample separation.

The tip-sample magnetic interactions are used to reconstruct the magnetic structure of the sample surface. Many kinds of magnetic interactions are measured by MFM, including magnetic dipole–dipole interaction. MFM scanning often uses non-contact AFM (NC-AFM) mode.

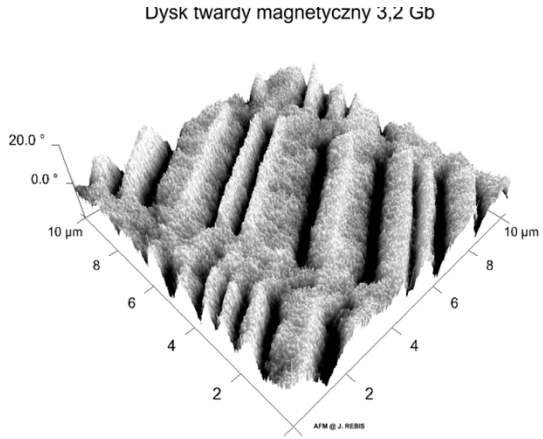
Typical resolution of 30 nm can be achieved, although resolutions as low as 10 to 20 nm are attainable.

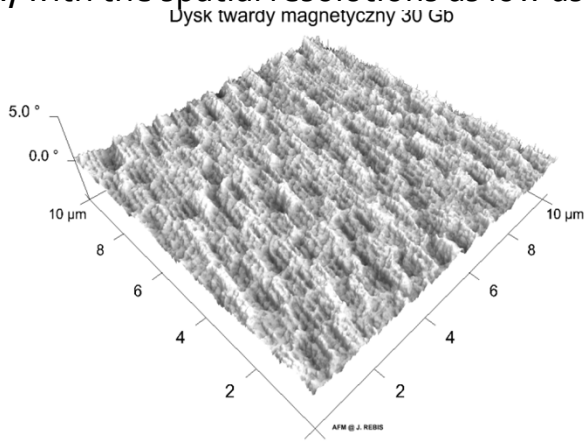
Magnetic-force microscopy of Vortex Lattice in Nb film, 40G, 4.3K



A. Volodin et al., Europhys. Lett. 58, 582 (2002)

- Measurement @RT, in UHV, in liquid environment, and at different temperatures.
- Non-destructive to the crystal lattice or structure.
- Long-range magnetic interactions are not sensitive to surface contamination.
- Detectable magnetic field intensity, **H**, is in the range of 10 A/m
- Detectable magnetic field, **B**, is in the range of 0.1 G (10 μT).
- Typical measured forces are as low as 10^{-14} N, with the spatial resolutions as low as 20 nm.

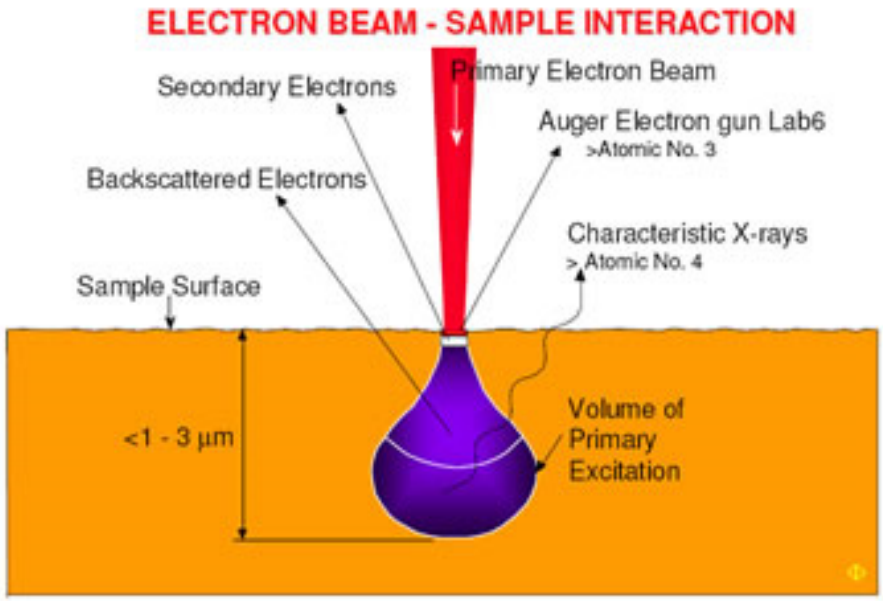




Scanning Electron Microscopy (SEM)

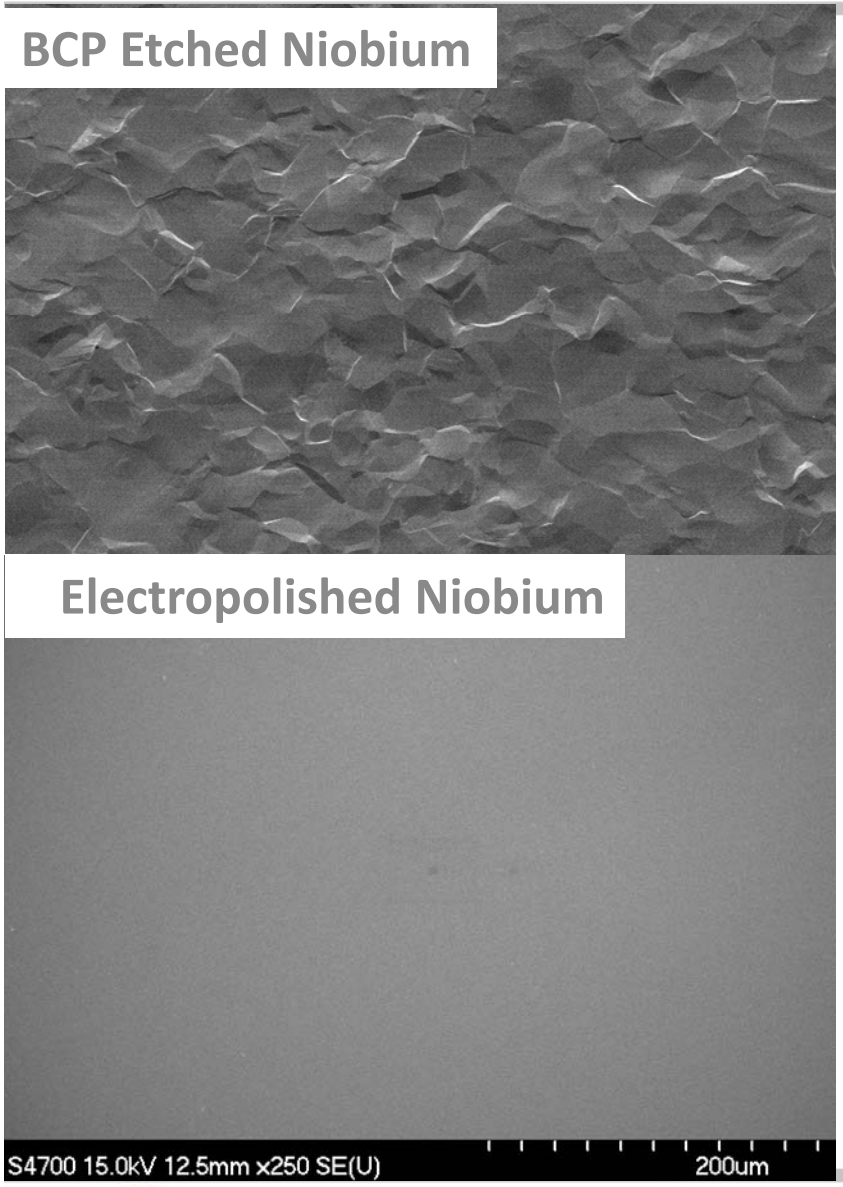
Standard inspection tool which provides a direct image of the topographical nature of the surface from all emitted secondary electrons. Scanning electron microscopy (SEM) is one of the most commonly used technique in material science and engineering researches due to the combination of the high magnification, great resolution and easy sample preparation.

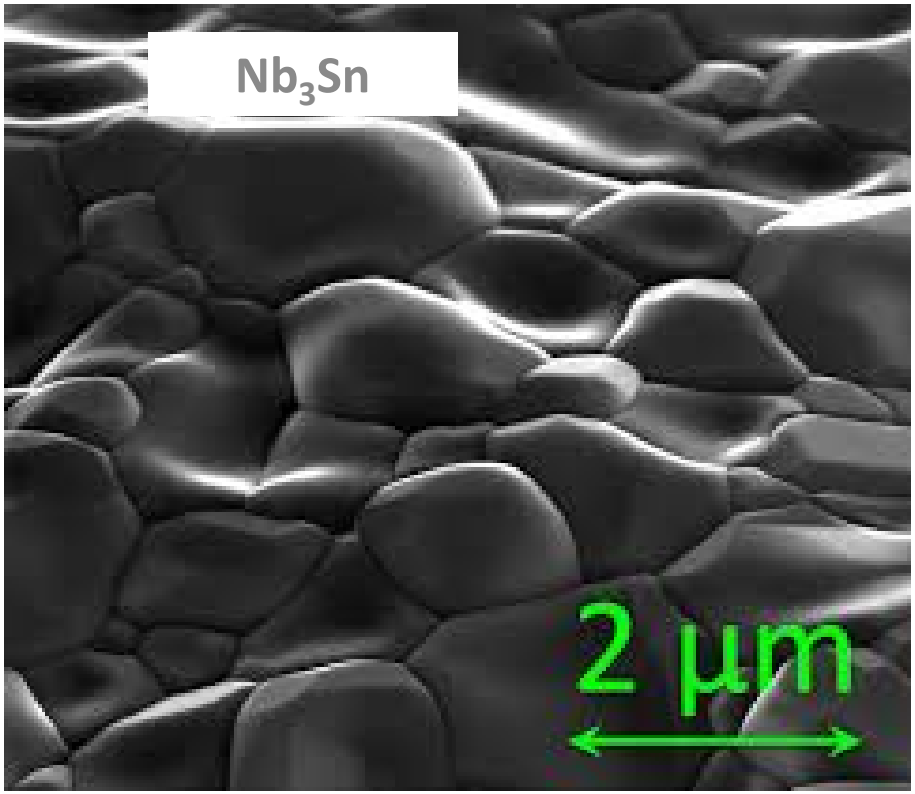
A high energy beam of electrons is accelerated into a conductive sample and the emitted and reflected electrons are captured to create an image. Elastically reflected electrons form the backscattered component of the image and the inelastically scattered electrons form the secondary image. The backscattered and secondary images are used separately or in combination to create a micrograph of the sample.



The electrons scattered from the sample can be used to collect other types of data and constitute different surface characterization techniques as Auger Electron Spectroscopy (AES), Electron Backscattered Diffraction (EBSD), and Energy-Dispersive X-ray Spectroscopy (EDX).

Scanning Electron Microscopy (SEM)

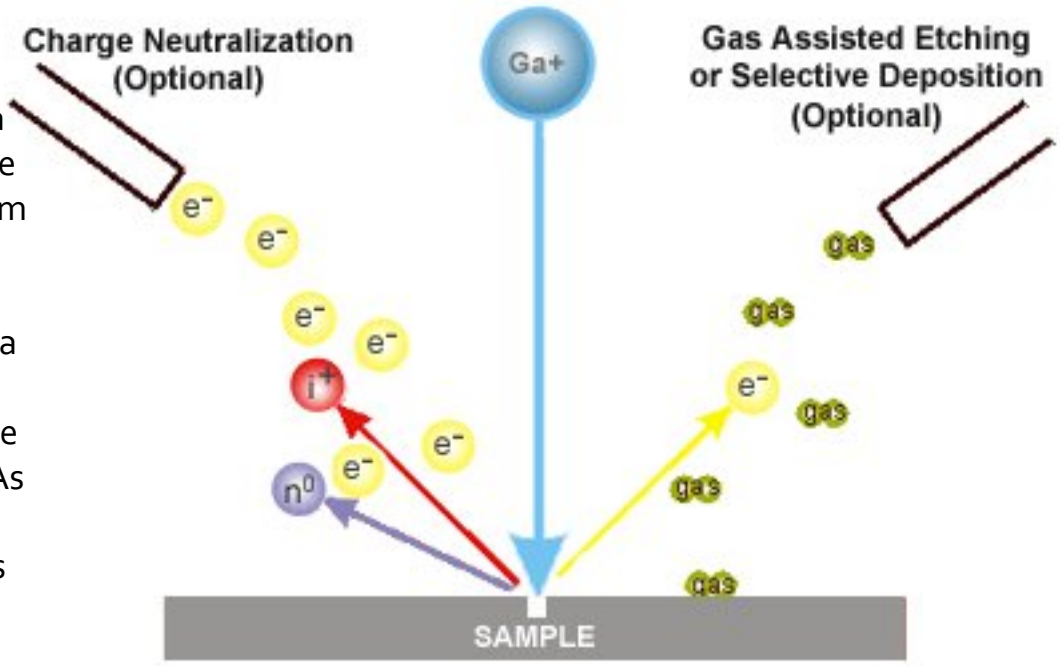




Focused Ion Beam - FIB

Technique used for site-specific analysis, deposition, and ablation of materials.

FIB systems operate in a similar fashion to a scanning electron microscope (SEM) except, rather than a beam of electrons and as the name implies, FIB systems use a finely focused beam of ions (usually gallium) that can be operated at low beam currents for imaging or high beam currents for site specific sputtering or milling.
As the diagram on the right shows, the gallium (Ga+) primary ion beam hits the sample surface and sputters a small amount of material, which leaves the surface as either secondary ions (i+ or i-) or neutral atoms (no). The primary beam also produces secondary electrons (e-). As the primary beam rasters on the sample surface, the signal from the sputtered ions or secondary electrons is collected to form an image.



TEM sample preparation

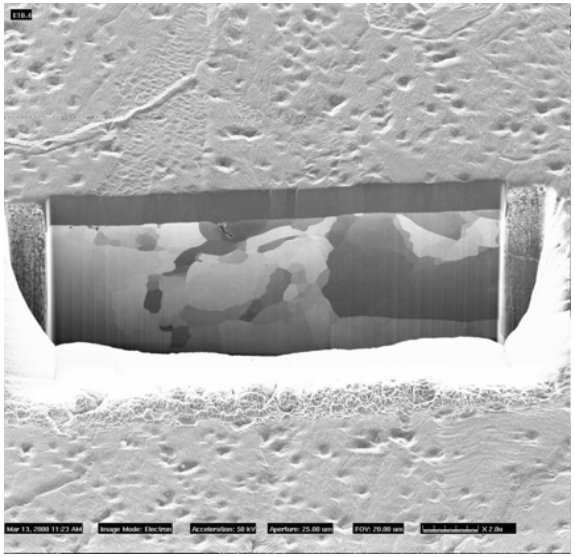
FIB imaging

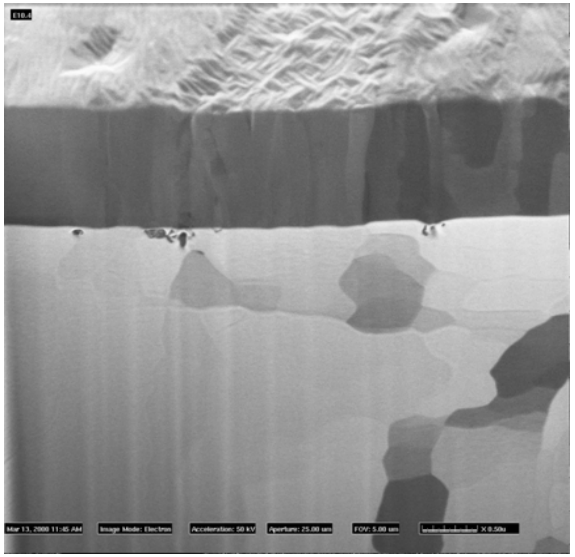
At lower beam currents, FIB imaging resolution begins to rival the more familiar scanning electron microscope (SEM) in terms of imaging topography, however the FIB's two imaging modes, using secondary electrons and secondary ions, both produced by the primary ion beam, offer many advantages over SEM.
FIB secondary electron images show intense grain orientation contrast. As a result, grain morphology can be readily imaged without resorting to chemical etching. Grain boundary contrast can also be enhanced through careful selection of imaging parameters.

Focused Ion Beam - FIB

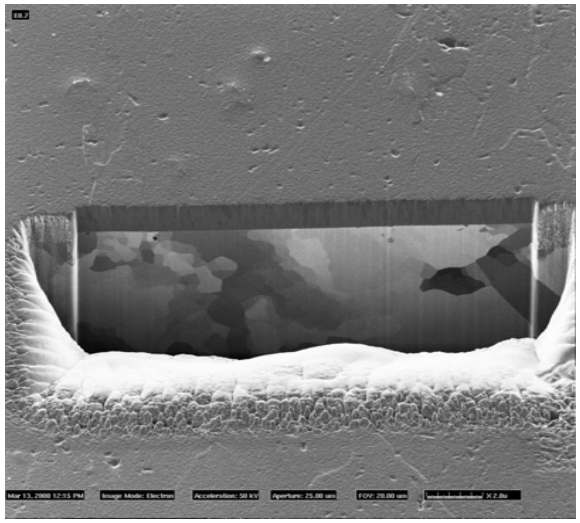
CERN

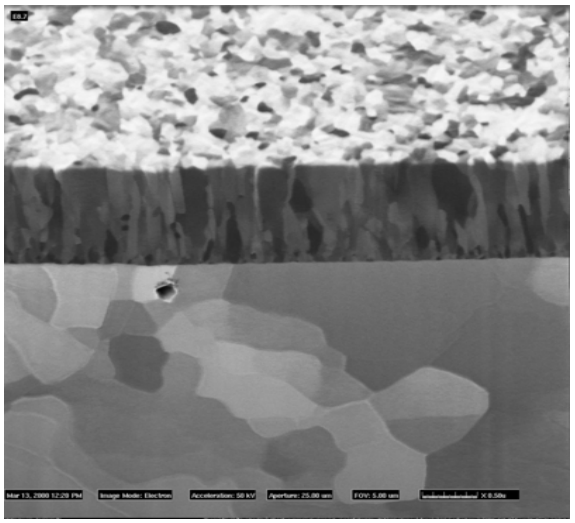
Nb/Cu film





Nb/Cu
Oxide film

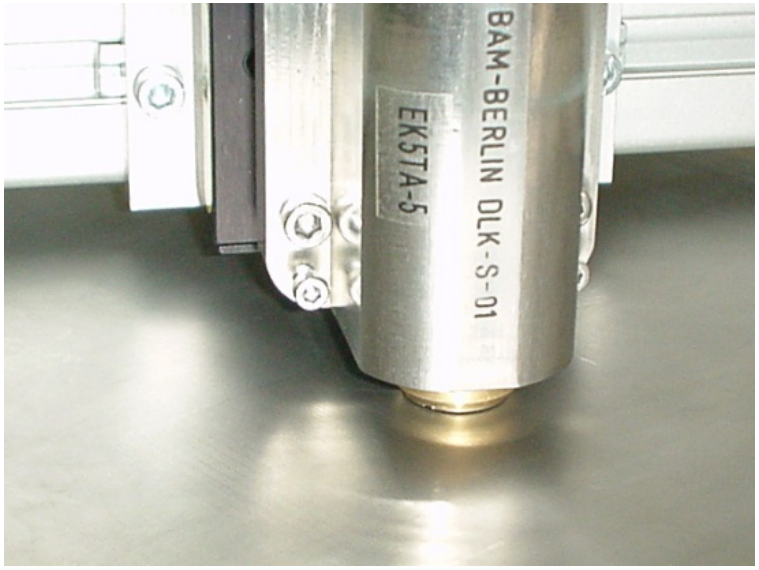




Eddy Current Scanning

Eddy-current scanning uses electromagnetic induction to detect flaws in conductive materials. limitations: only conductive materials can be tested, the surface of the material must be accessible, the finish of the material may cause bad readings, the depth of penetration into the material is limited, and flaws that lie parallel to the probe may be undetectable.

In a standard eddy current testing a circular coil carrying current is placed in proximity to the test specimen (electrically conductive).The alternating current in the coil generates changing magnetic field which interacts with test specimen and generates eddy current. Variations in the phase and magnitude of these eddy currents can be monitored using a second 'search' coil, or by measuring changes to the current flowing in the primary 'excitation' coil. Variations in the electrical conductivity or magnetic permeability of the test object, or the presence of any flaws, will cause a change in eddy current flow and a corresponding change in the phase and amplitude of the measured current.

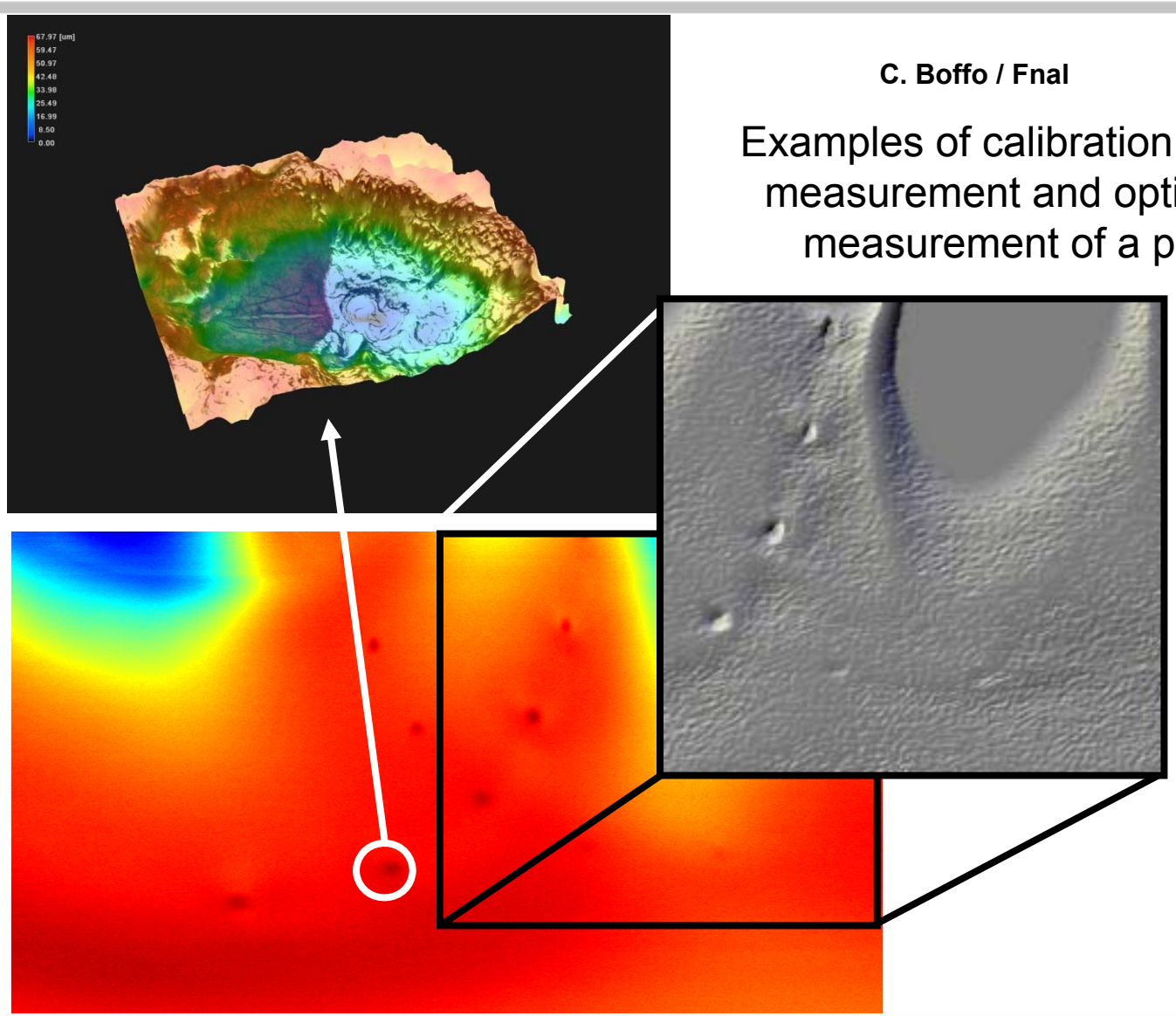


Eddy Current Scanning:

mostly detects in or near surface imperfections (pits, scratches, height / thickness variations)

electrical conductivity and coating thickness measurements.

Eddy Current Scanning (FNAL, DESY)



C. Boffo / Fnal

Examples of calibration disc measurement and optical measurement of a pit

STRUCTURE

- Crystallography
- Structural defects: stacking faults, dislocations
- Grain boundary type
- Grain size
- Strain, stress

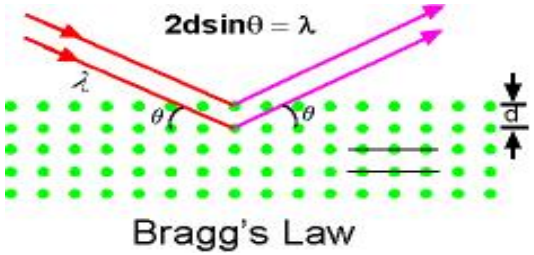
Mainly diffraction techniques

Importance for SRF

The microstructure can strongly influence the physical properties such as superconductivity, RF response for both bulk and film Nb.

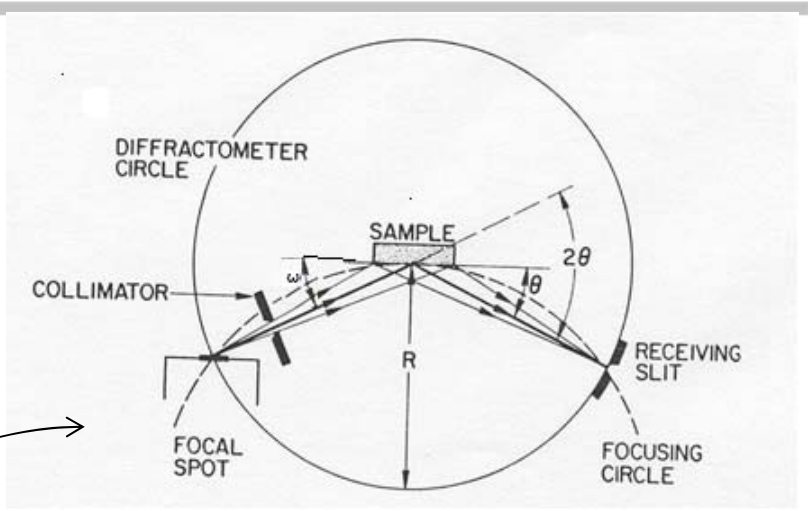
X-Ray Diffraction (XRD)

The scattering of x-rays by crystal atoms, produces a diffraction pattern that yields information about the structure of the crystal.

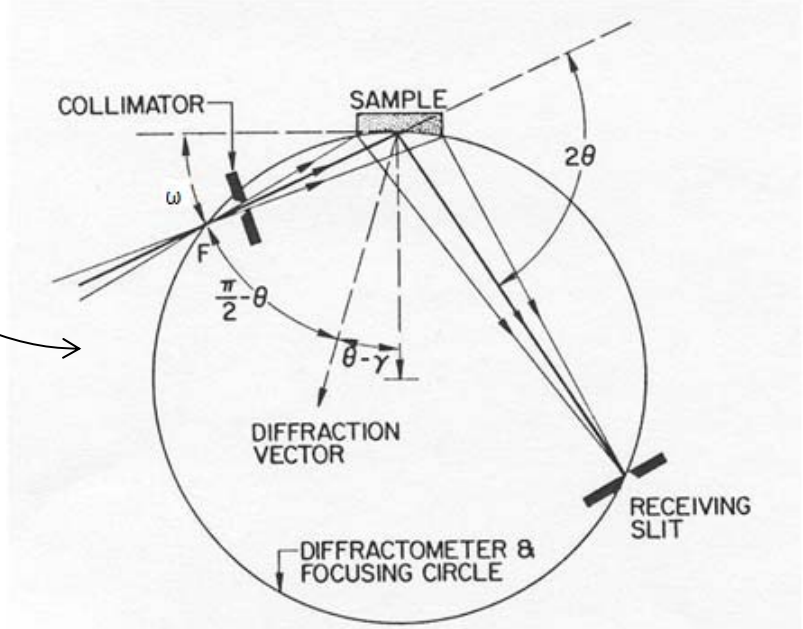


Bragg's Law

Bragg's Law $\lambda = 2d\sin(\theta_B)$

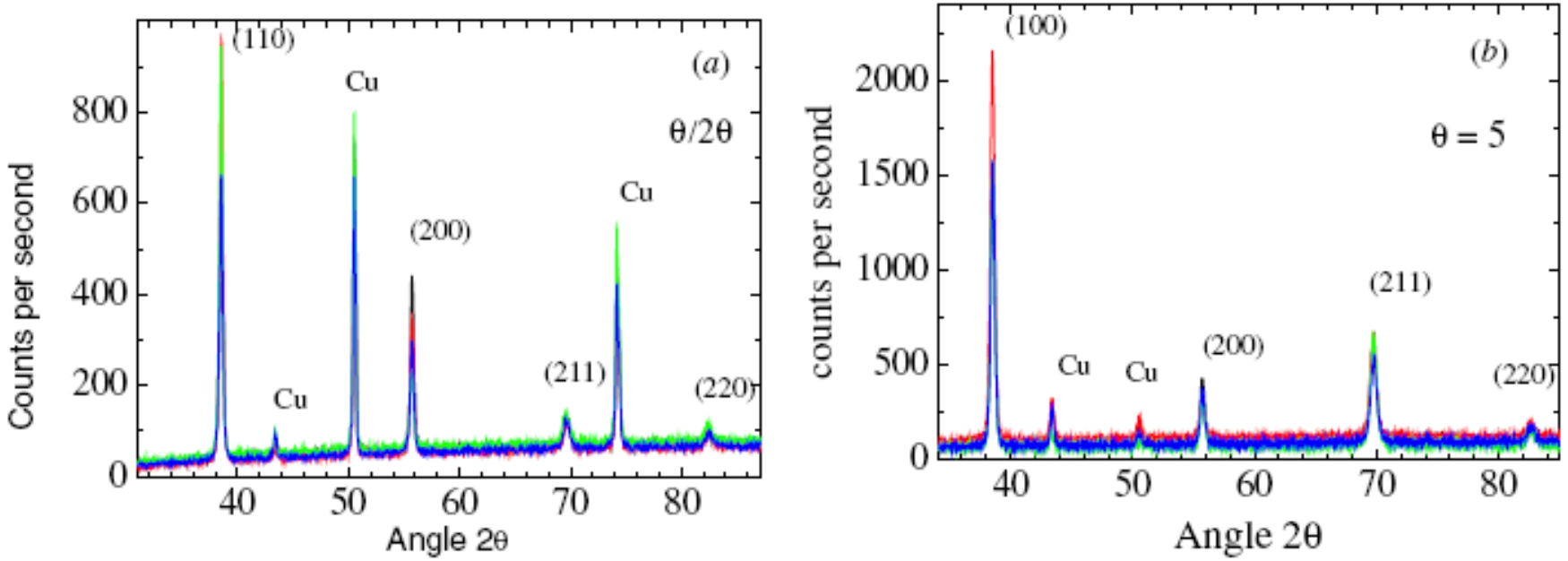


- *Bragg-Brentano* (B.B.) Configuration
- *Seemann-Bohlin* (S.B.) Configuration
- Glazing Incident Angle
- Rocking Curve Space Mapping
- Large Probing Area (X-ray Source Slit **17*20 mm**)



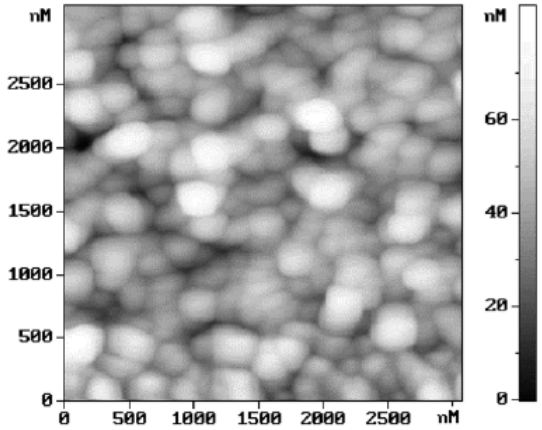
- Texture, preferred crystallographic orientation
- Thickness (films)
- Grain size
- Strain/stress

R. Russo, Meas. Sci. Technol. **18 (2007) 2299–2313**

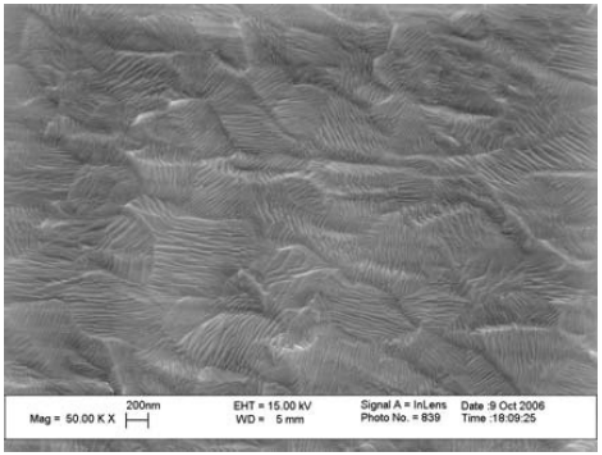


X-ray spectra of Nb films deposited by UHVCA in (*a) the Bragg–Brentano and (b) the Seemann-Bohlin configuration. The* Bragg–Brentano configuration shows the absence of a clear texture in the Nb film and the presence of a large signal from the copper substrate. In the Seemann-Bohlin configuration with a 5◦ incidence angle (*b) the signal originating from the copper substrate is much* reduced, indicating that the penetration depth on the x-ray is comparable to the film thickness

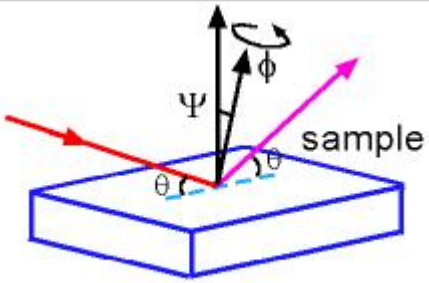
AFM image of a film deposited on sapphire by UHVCA. The grains have a round shape and the grain size can be estimated to be about 200 nm.



SEM image of different UHCA deposited Nb samples deposited on sapphire substrate

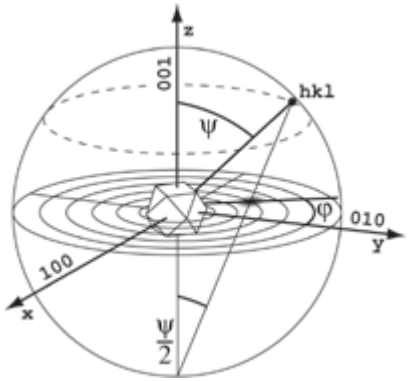


Texture Measurement (Pole figures)

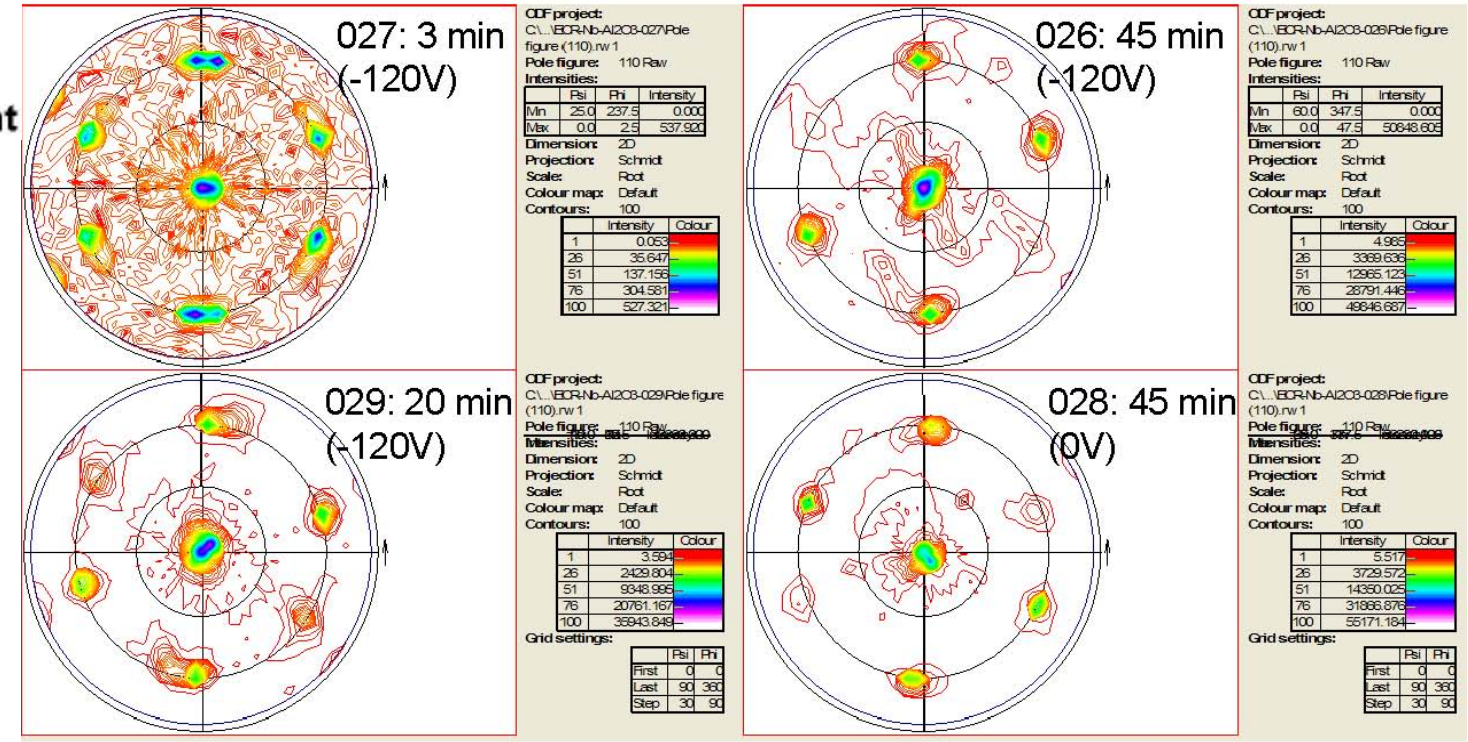


Pole Figure Measurement

stereographic projections to represent the orientation distribution of crystallographic lattice planes.



Orientation distribution of crystalline grains in a polycrystalline sample



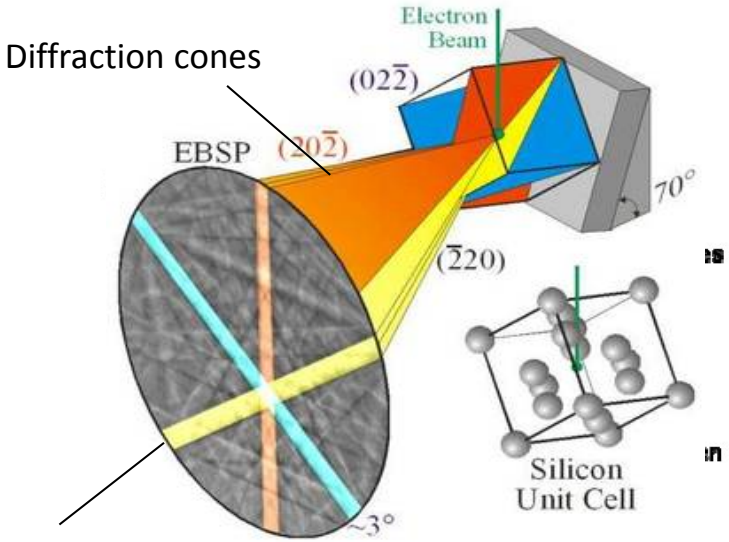
XRD Pole Figures of Nb/Al2O3 (11-20) ECR films of increasing thickness for continuous growth at 164 eV and compared to a film grown at 64 eV.

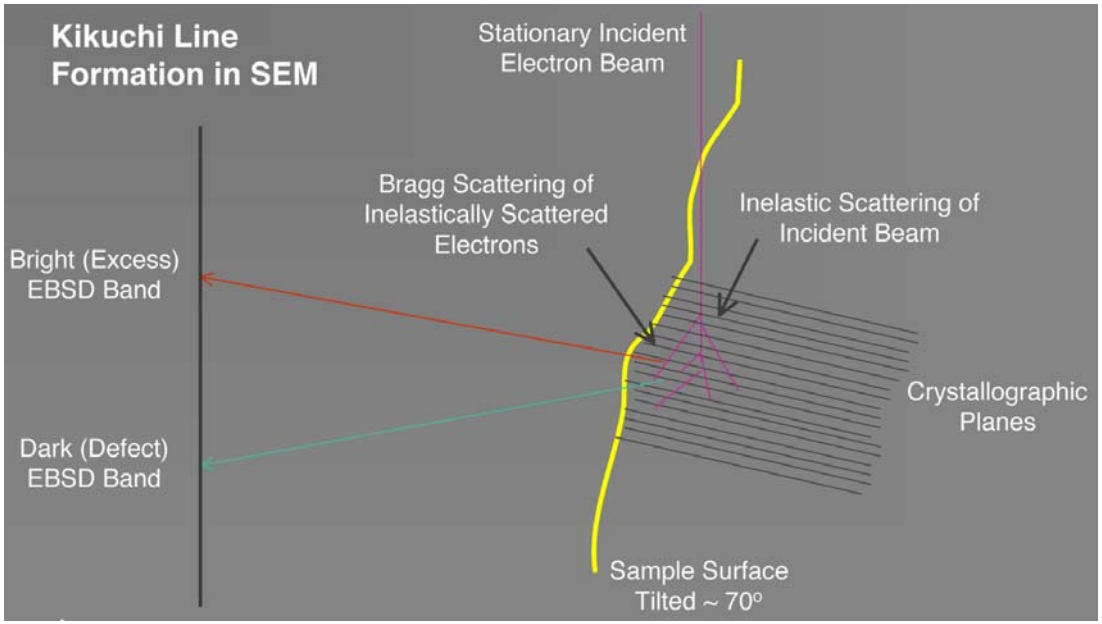
Electron Backscattered Diffraction (EBSD)

EBSD uses the backscattered electrons in ann SEM electron beam to create a Kikuchi pattern of the sample's lattice. Software uses algorithms to distinguish the crystallographic orientation of the material.

EBSD provides:

crystal orientation, misorientation mapping, defect studies, phase identification, grain boundary and morphology studies, regional heterogeneity investigations, material discrimination, microstrain mapping, grain orientation maps, grain boundary maps, image quality maps, grain size charts, misorientation charts and texture plots



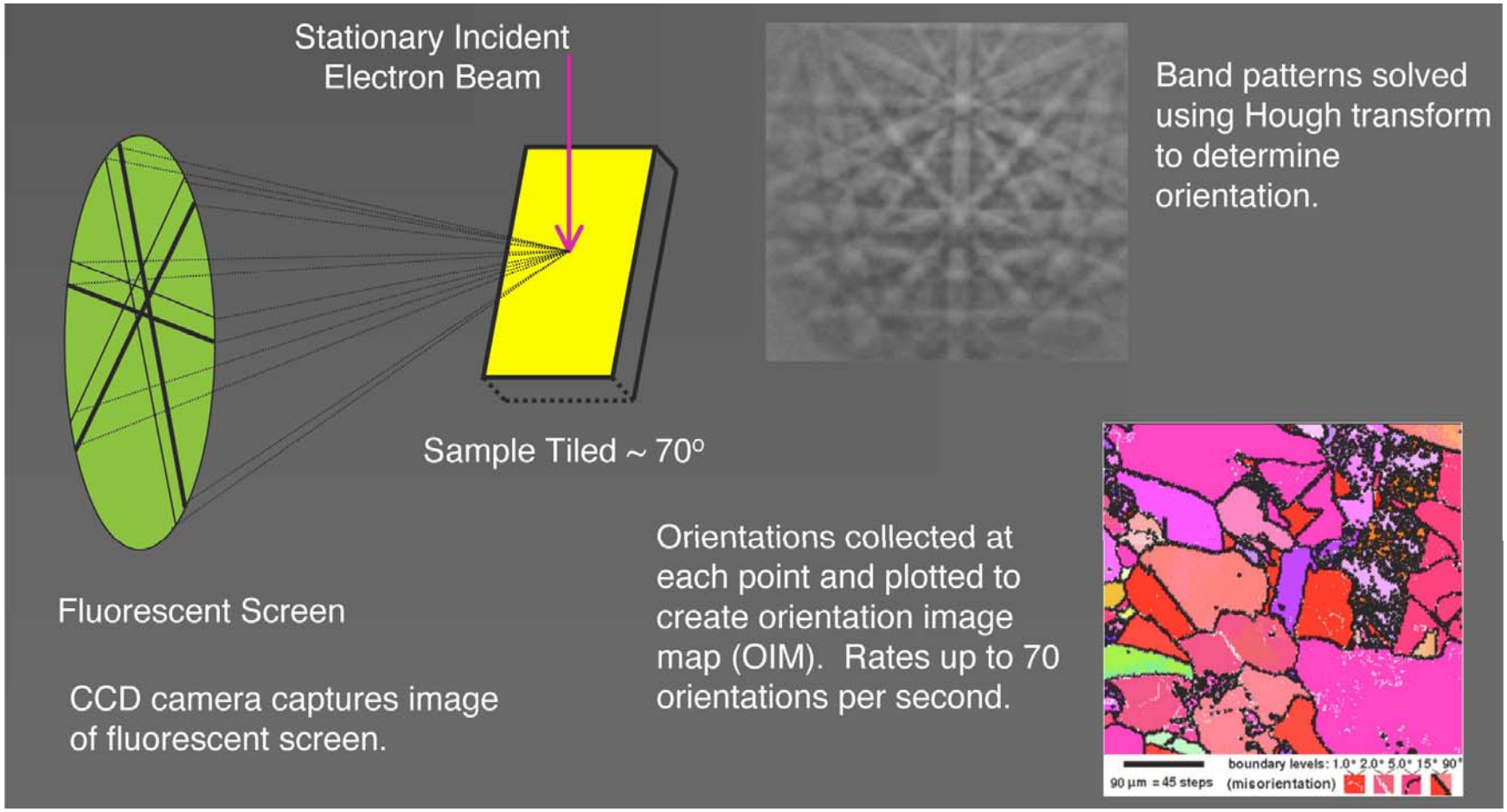


Typical scattering area is ~10nm x 10nm & probing depth is ~ 20-100 nm.

Limited by the pattern source volume to resolutions in the order of 25- 100nm

x1

Electron Back Scattering Diffraction (EBSD)

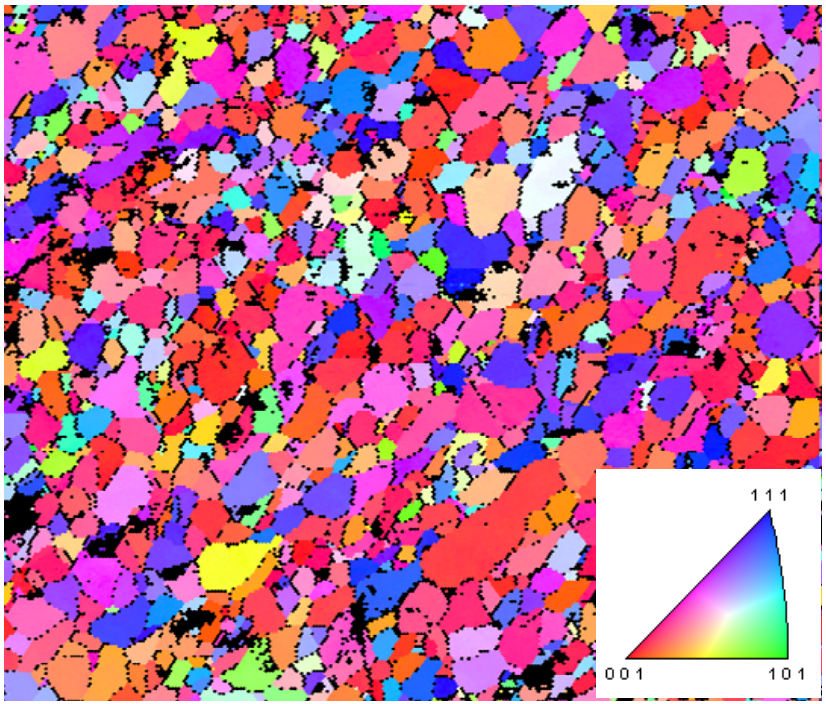


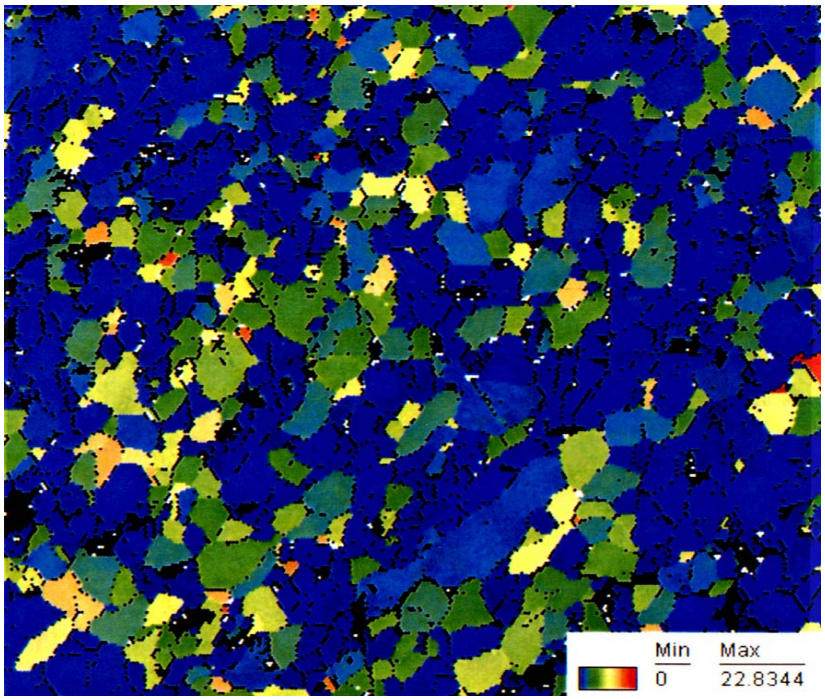
- Spatial resol. **10x30x30 nm** (Limits: thickness, roughness, short range order)
- Kikuchi Pattern
- Auto Indexing - Hough Transformation, Voting, **C.I.**, Calibration
- Microstructure analysis via OIM Analysis software

Slide 32

x1 xinzhao, 7/21/2008

Electron Backscattering Diffraction
Bulk Nb after BCP

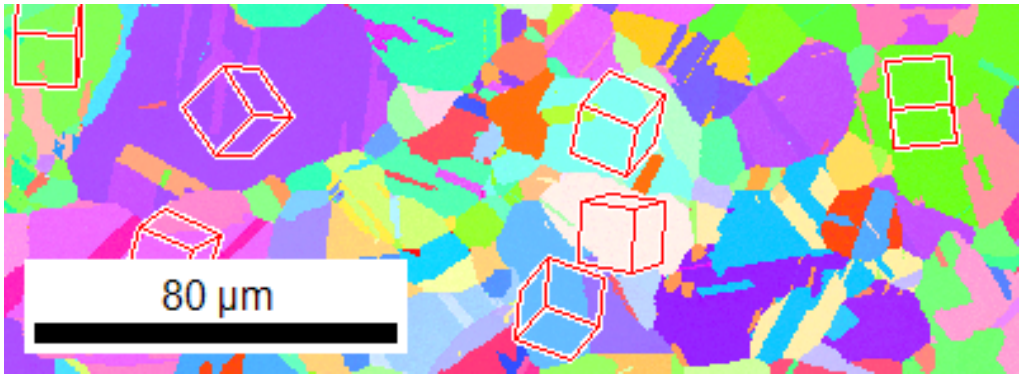




Grain orientation & misorientation deviation map(1.5 mm * 1.5 mm)

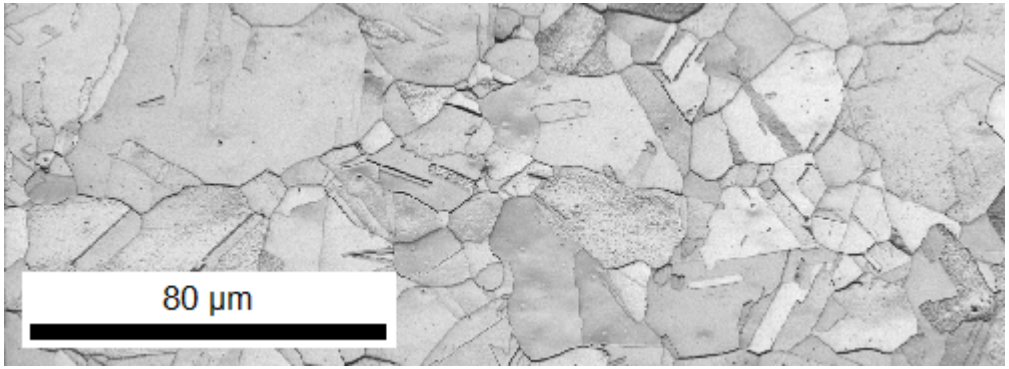
The EBSD reveals the orientation of individual grains in the niobium surface; The information depth is about the same as the *RF* penetration depth, EBSD selectively views the material that matters.

Electropolished Polycrystalline Cu Substrate Before Nb Thin Film Deposition



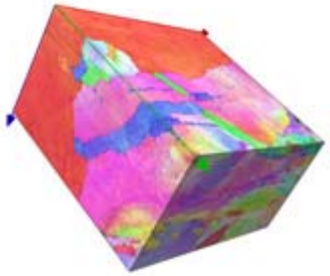
EP Copper Substrate EBSD -IPF View

EBSD Inverse Polar Figure (I.P.F.) indicates grain orientation of bare Cu



EP Copper Substrate EBSD -IQ View

SEM and Imaging Quality (I.Q.) view revealed grain boundaries

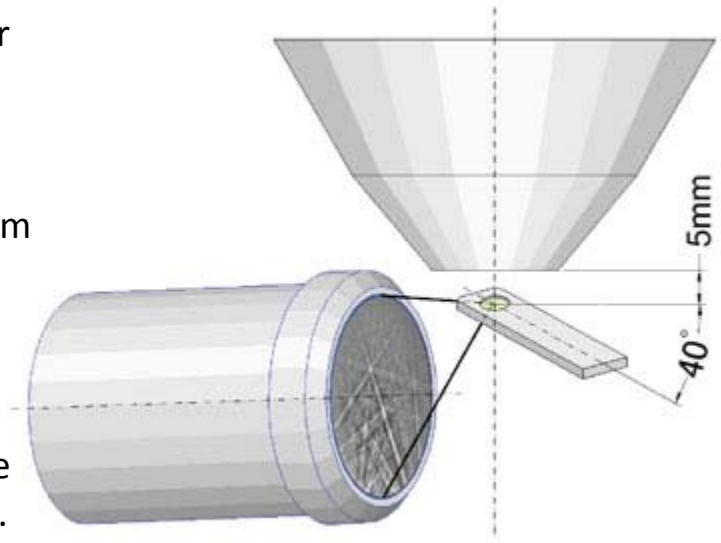


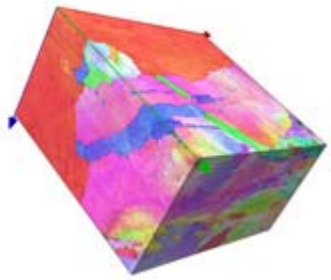
Transmission EBSD (KTD)

Transmission EBSD (t-EBSD: Keller and Geiss, 2012) or SEM transmission Kikuchi diffraction (TKD: Trimby, 2012) has been proven to enable spatial resolutions better than 10nm, and is ideal for routine EBSD characterization of both nanostructured and highly deformed samples.

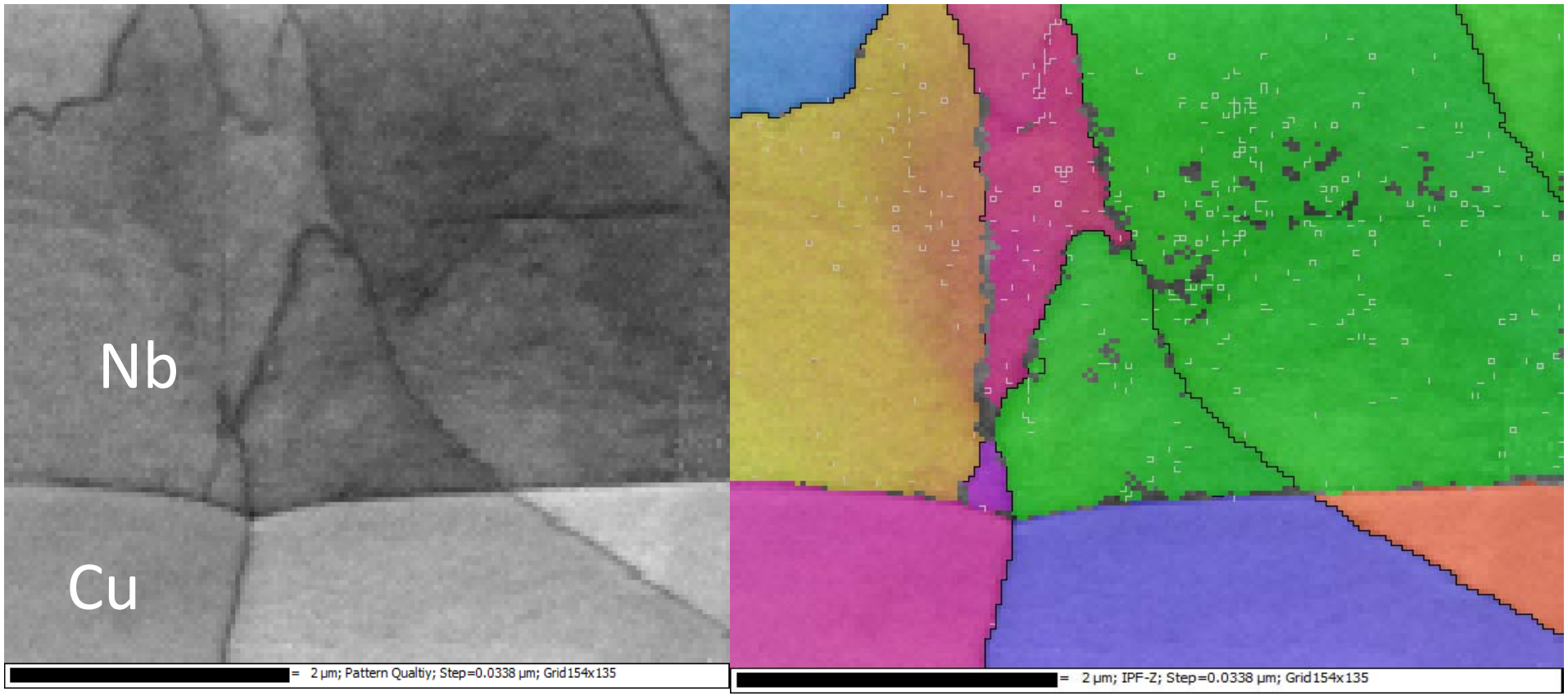
Sample Preparation: standard as for TEM. (electropolishing, ion beam milling or FIB).
Sample thickness critical: best results with relatively thin samples (50nm -150nm).

The electron beam is focused onto the electron transparent sample and the diffraction pattern is projected from the lower surface onto the phosphor screen. The majority of the pattern signal originates from the lowermost part of the sample, allowing successful analyses of samples in which the grain size is smaller than the sample thickness. Typically the maximum acceleration voltage of the SEM is used (normally 30kV), with a large beam current (i.e. 1nA to 20nA) and with the beam optimised to give the best depth of field. Orientation mapping is carried out in the same way as for conventional EBSD, although no tilt correction or dynamic focus is required, and step sizes can be as small as 2nm.
Forescatter detectors, positioned below the phosphor screen, can also be used to give orientation contrast images of electron transparent samples.



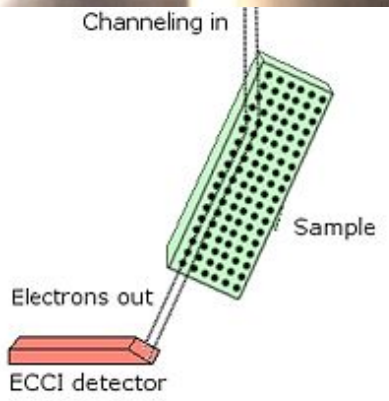


Transmission EBSD (KTD)



Electron Channeling Contrast Imaging (ECCI)

Electron channeling contrast imaging (ECCI) offers an alternative and non-destructive approach to TEM for imaging and characterization of crystalline defects such as dislocations, subgrains and microtwins, without being limited by difficult sample preparation, thin foil artifacts, relatively small viewable areas, and constraints on carrying out in situ studies.



ECCI images are produced from electrons which channel down the crystal planes. Tilt, strain and the presence of defects which distort the crystal planes (e.g. changes in crystallographic orientation or in lattice constant) will produce changes in grey scale in the ECC image.
Backscattered electrons (BSE) provide information about composition (Z contrast), topography and crystallography (via channeling). Tilting the sample increases BSE yield, reduces multiple scattering and energy loss processes and enhances channeling.

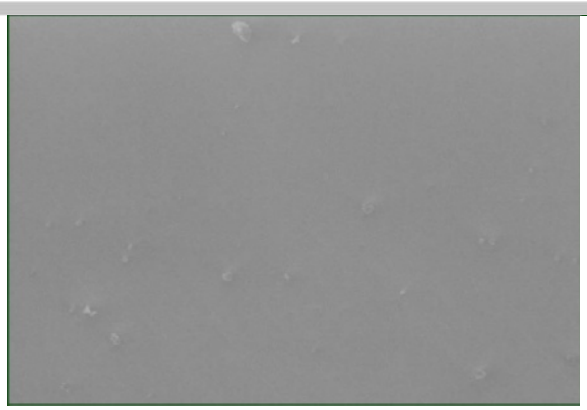
Implemented on a properly equipped SEM.

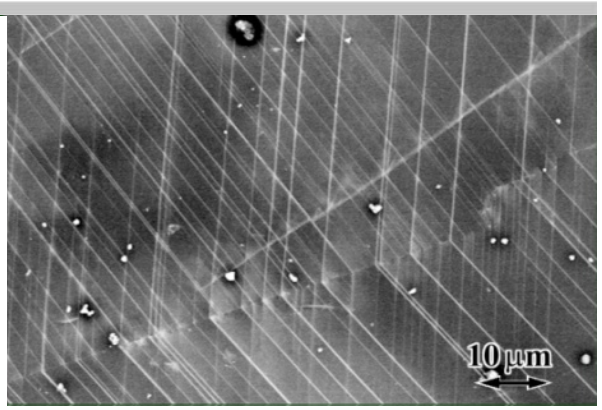
Requirements:

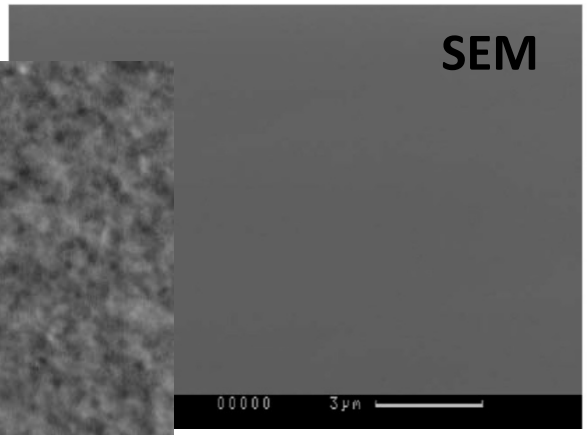
- High brightness electron gun (like for FEG-SEM)
- small beam convergence angle ~ 8mrad
- low beam divergence
- BSE detector with a large solid angle of collection ~ 0.6 π str
- Capability of collecting channeling patterns to align the sample to channeling contrast conditions (selected area channeling patterns (SACPs) for polycrystalline samples)
- Sufficiently high probe current to resolve the channeling contrast ~ 2nA
- Fine control over the stage tilt angle (Sample tilt within ~ 30o° of normal)

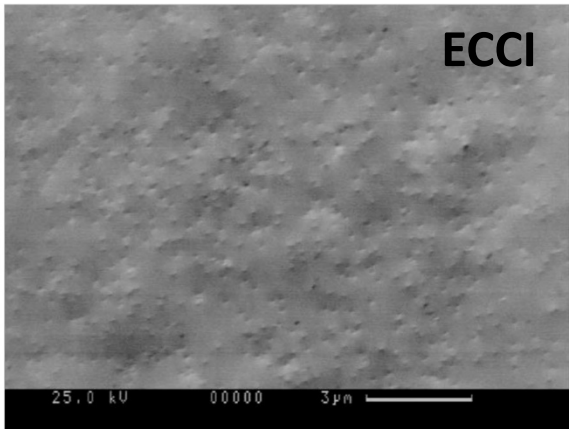
Electron Channeling Contrast Image (ECCI)

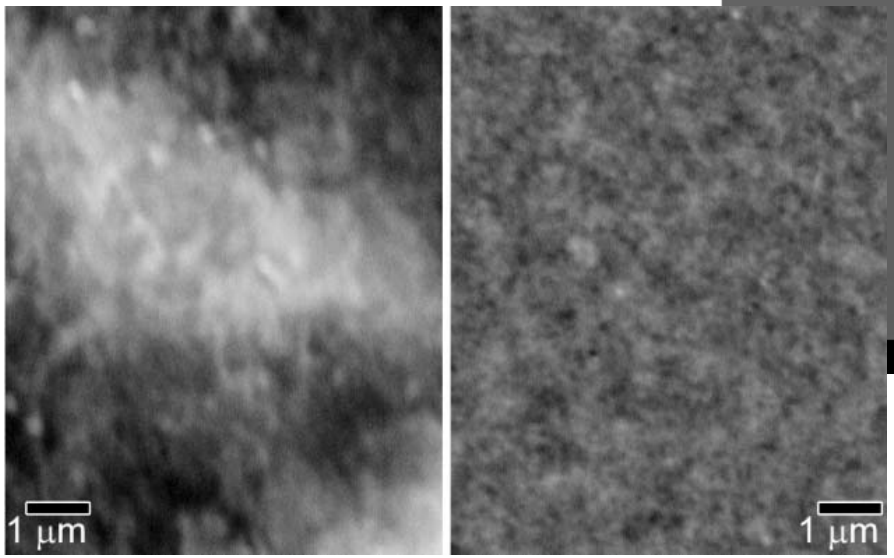
Imaging of fine scale crystalline defects such as dislocations and micro-twins.







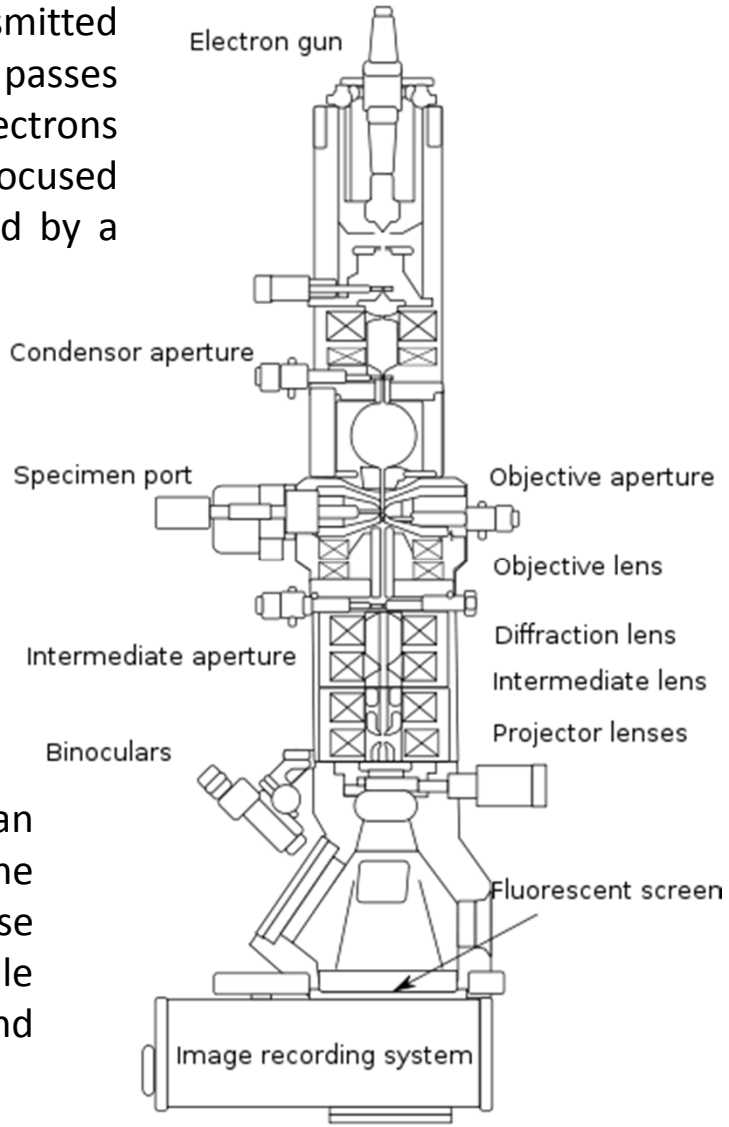




Dislocations imaged with ECCI in as-received ingot (left) and a recrystallized grain near weld (right).
D. Baars et al. Proceedings of SRF2007, Peking Univ., Beijing, China, TUP05

Transmission Electron Microscopy (TEM)

Microscopy technique whereby a beam of electrons is transmitted through an ultra thin specimen, interacting with the specimen as it passes through. An image is formed from the interaction of the electrons transmitted through the specimen; the image is magnified and focused onto an imaging device, such as a fluorescent screen or detected by a sensor such as a CCD camera.



Imaging

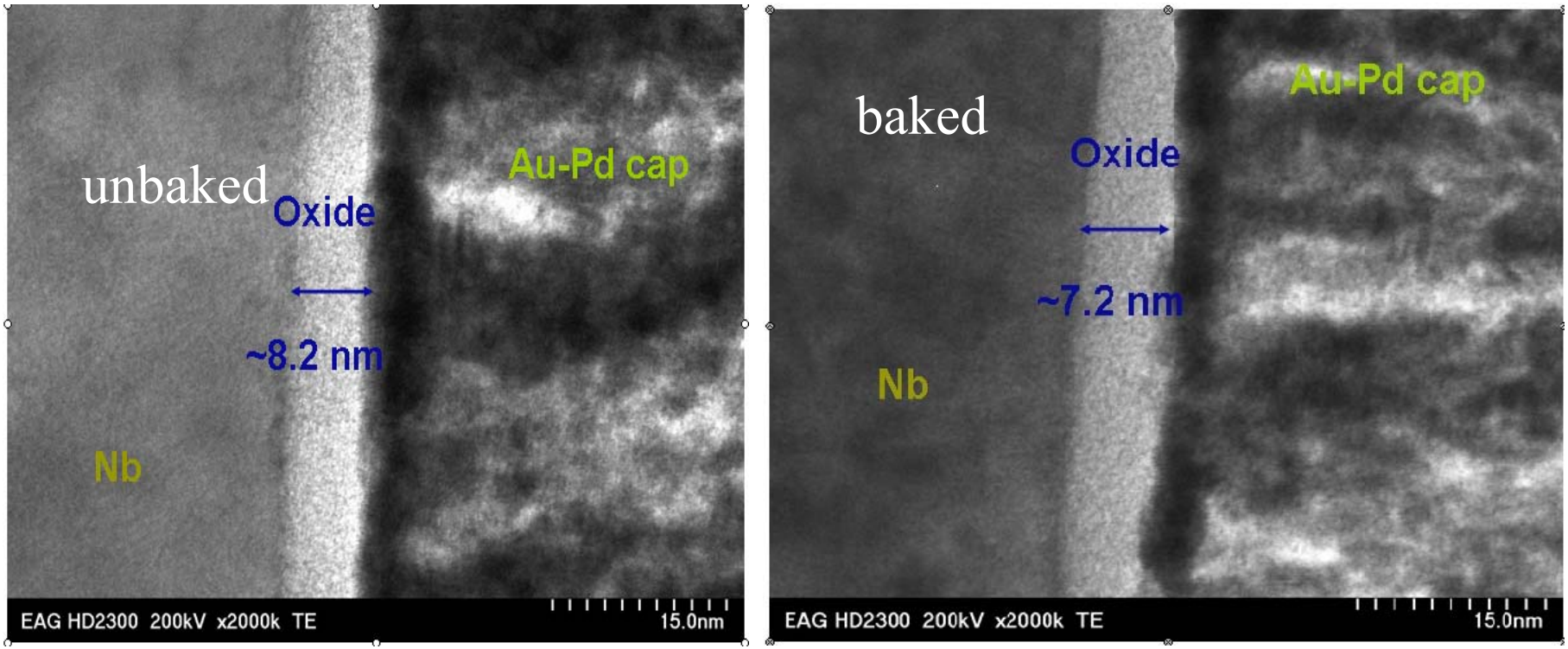
Bright Field
Diffraction contrast of dark field

Diffraction pattern

Sample preparation with electropolishing, ion milling, FIB requires time and labor and may introduce some artifacts.
Limited observation area (few μms)

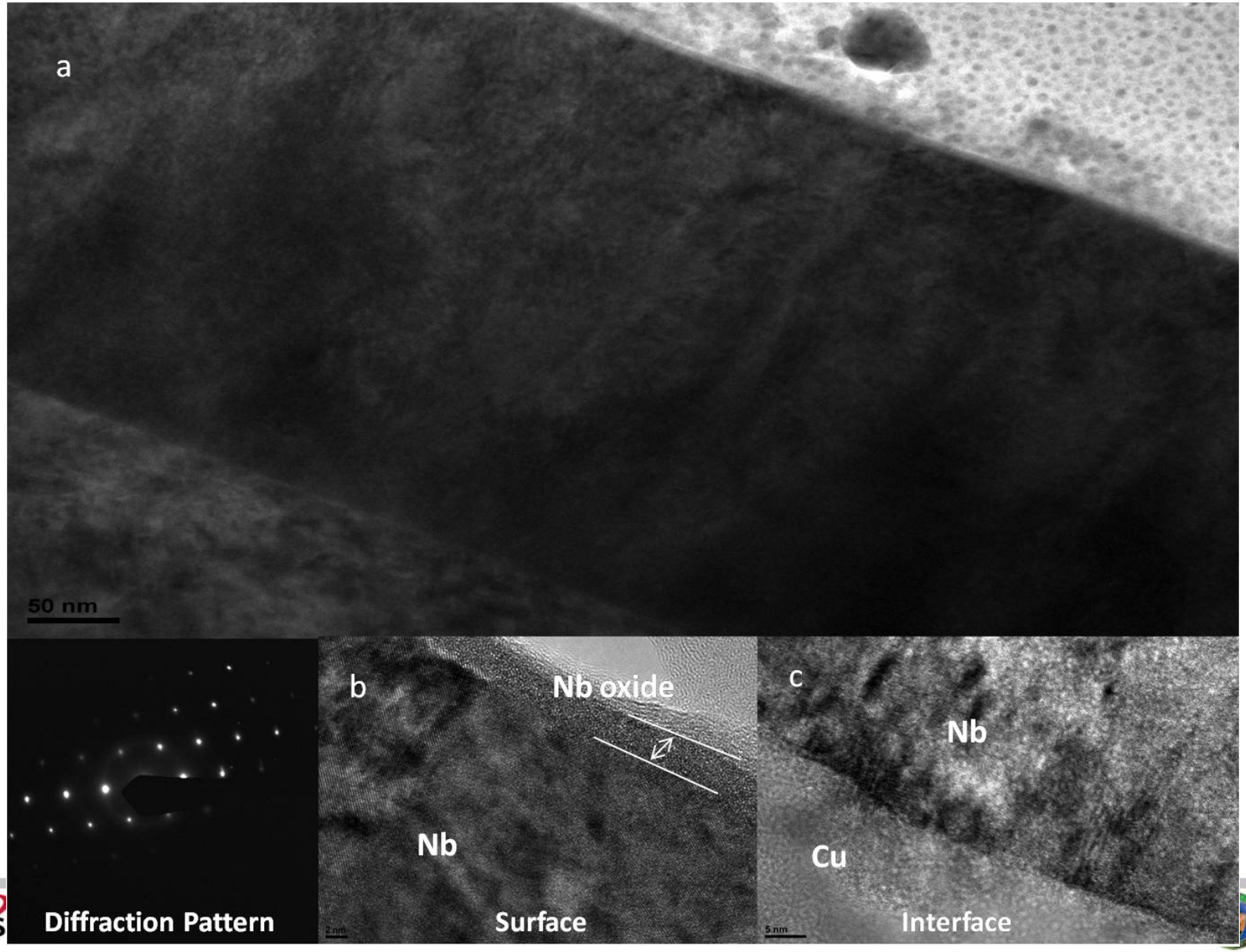
High-resolution transmission electron microscopy (HRTEM) is an imaging mode of TEM that allows the imaging of the crystallographic structure of a sample at an atomic scale. Because of its high resolution, it is an invaluable tool to study nanoscale properties of crystalline material such as semiconductors and metals. Highest resolution ~0.8 Å.

Nb oxides Structure (Unbaked/Baked)

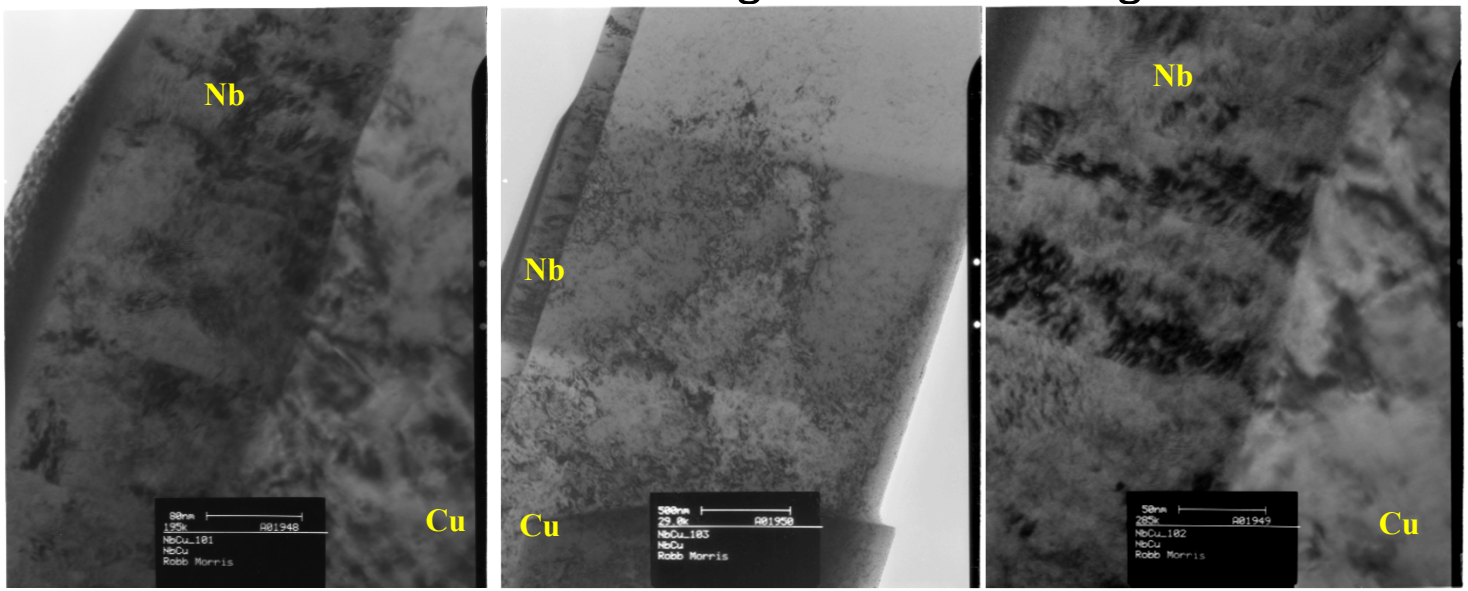


No clear structure change can be observed (suboxide, interstitial oxygen- cluster)

TEM of Nb/Cu Film



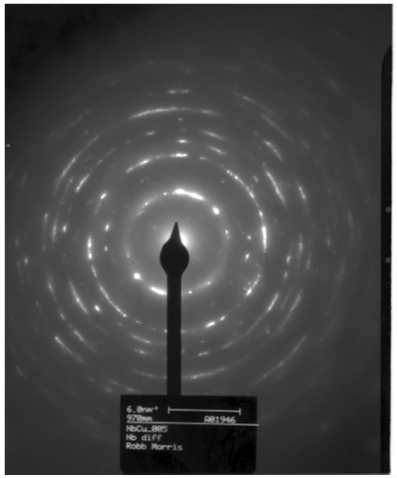
Nb on Cu substrate - Bright field TEM images



Diffraction patterns

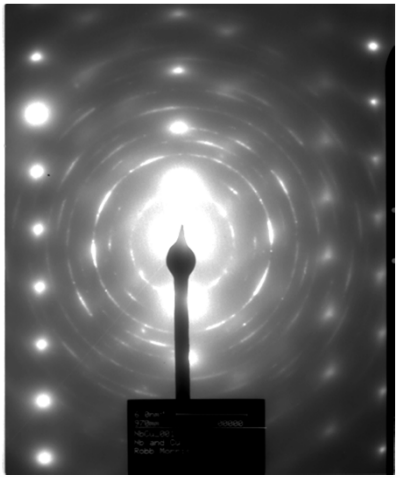
Electron diffraction of Nb layer

Wide spots/rings indicate small grain size

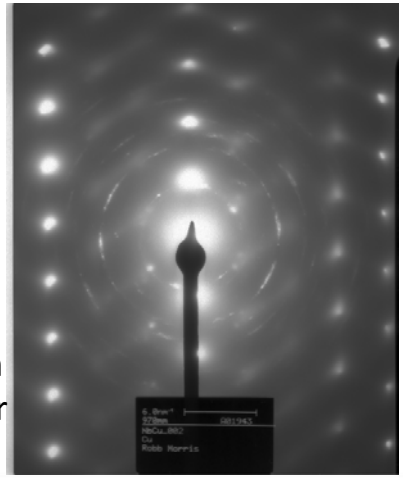


Electron diffraction of Nb and Cu

Strong tights spots indicate diffraction of single Cu grain

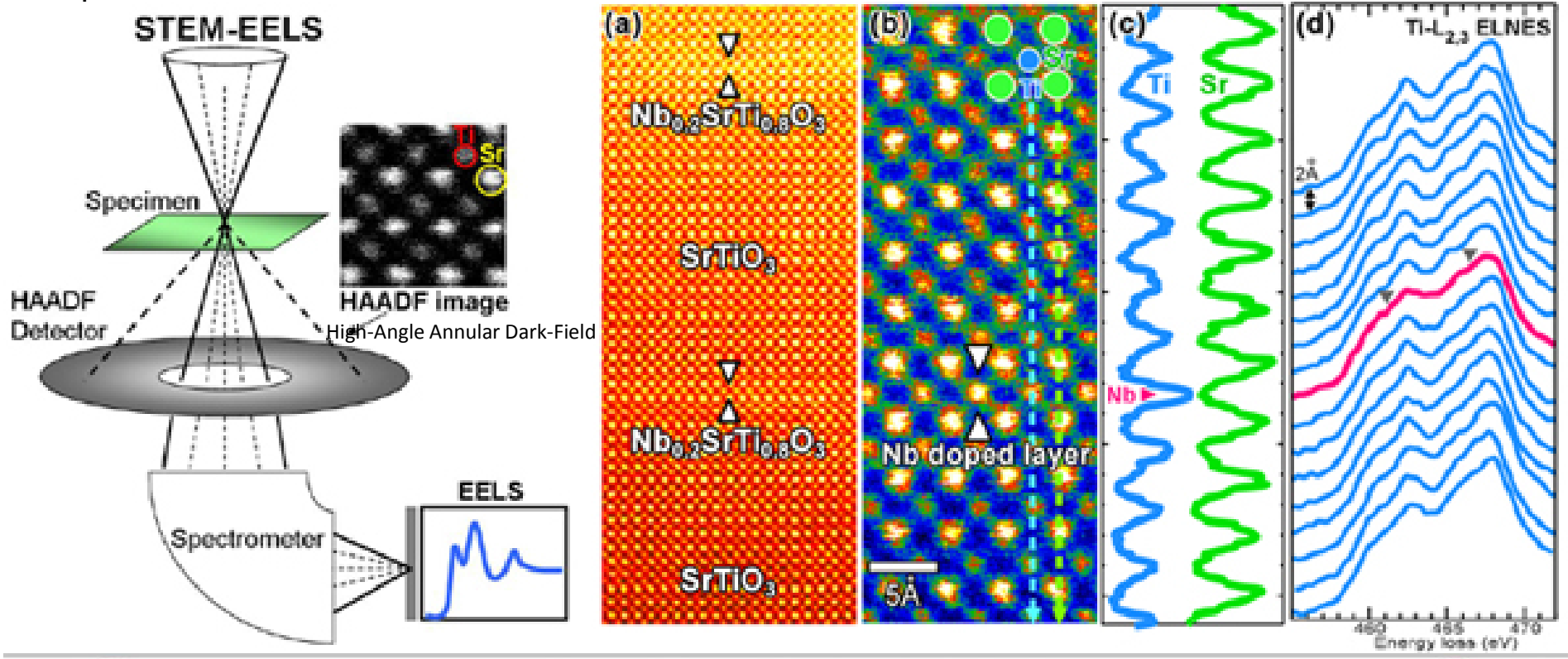


Electron diffraction of Cu layer

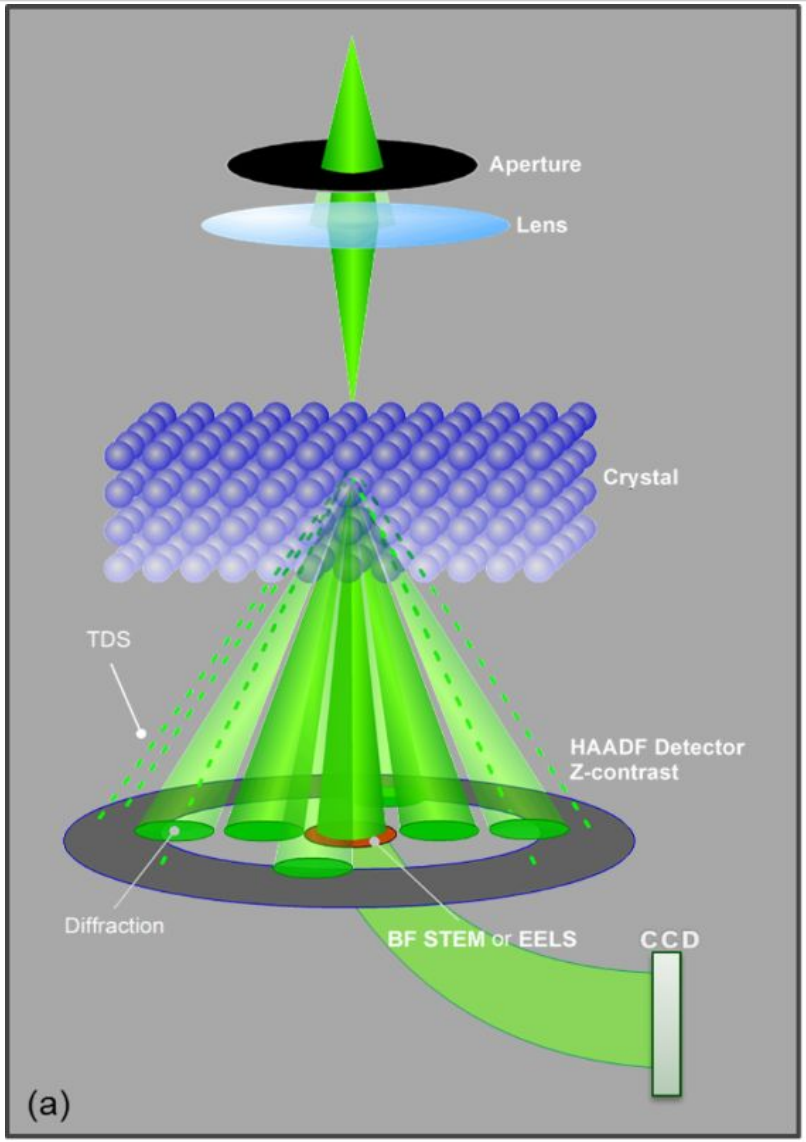


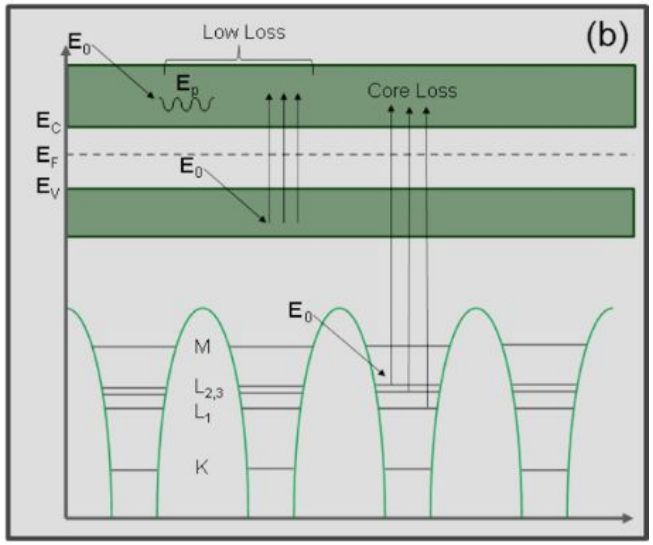
Electron Energy Loss Spectroscopy in TEM

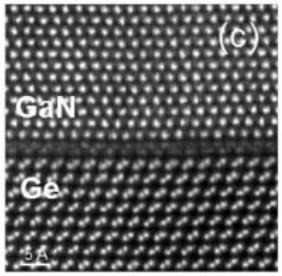
In electron energy loss spectroscopy (EELS) a material is exposed to a beam of electrons with a known, narrow range of kinetic energies. Some of the electrons will undergo inelastic scattering, losing energy and their paths are slightly and randomly deflected. The amount of energy loss can be measured via an electron spectrometer and interpreted in terms of what caused the energy loss. Inelastic interactions include phonon excitations, inter and intra-band transitions, plasmon excitations, inner-shell ionizations, and Cherenkov radiation. The inner-shell ionizations are particularly useful for detecting the elemental components of a material.

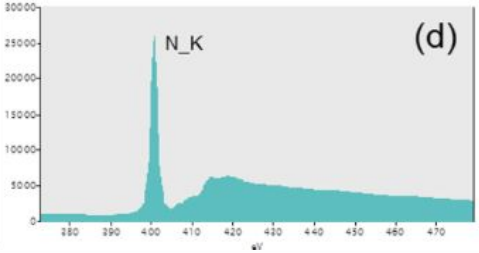


Electron Energy Loss Spectroscopy in TEM



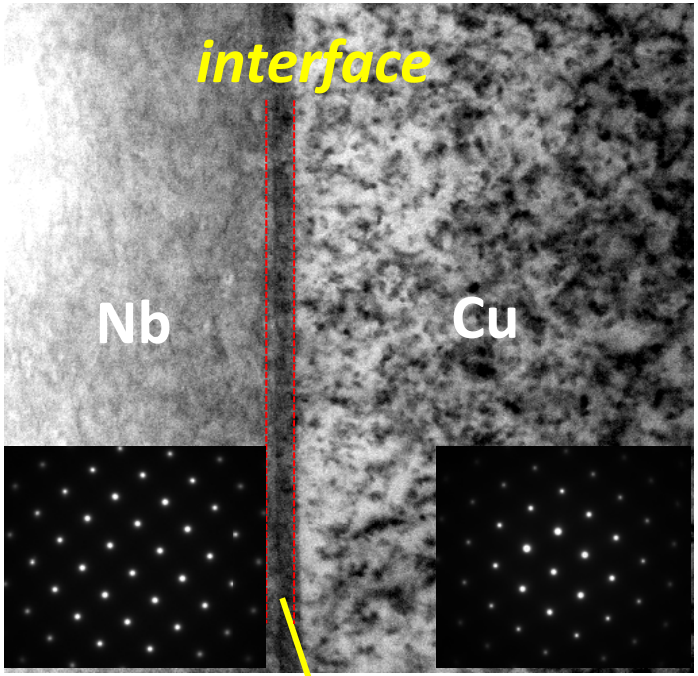


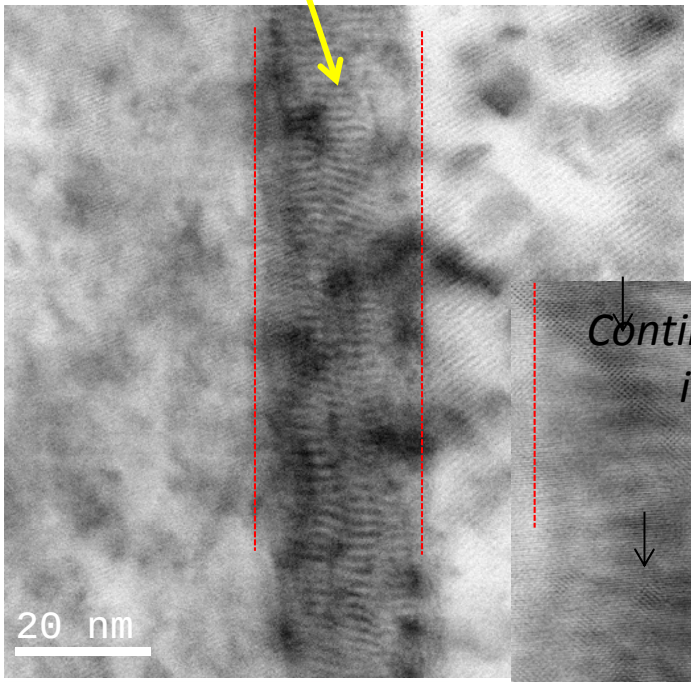


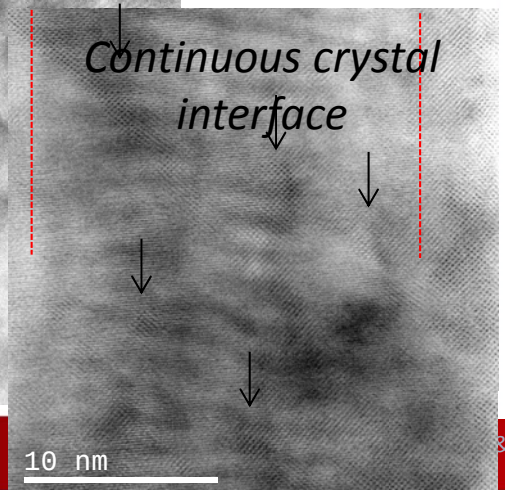


(a) the microscope configuration in the STEM mode; (b) the inelastic scattering processes in the TEM sample contributing to the low-loss and the core-loss EELS signals; (c) an atomic-resolution STEM-HAADF image of a GaN–Ge interface; (d) a EELS core-loss spectrum showing the N_K edge of gaseous N2.

EELS plot for Nb/Cu signal across interface

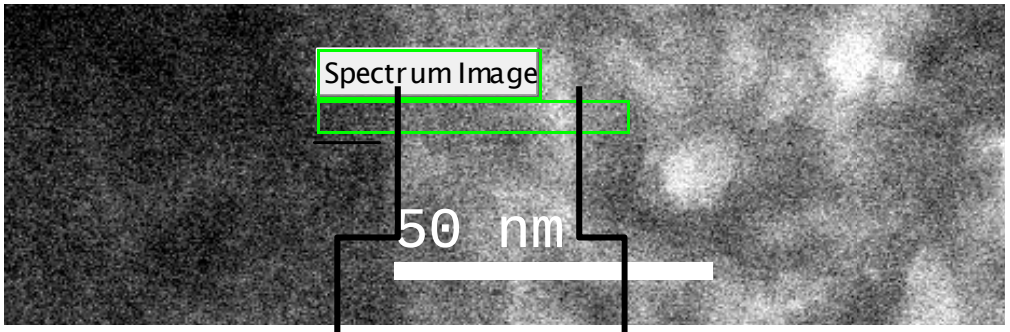


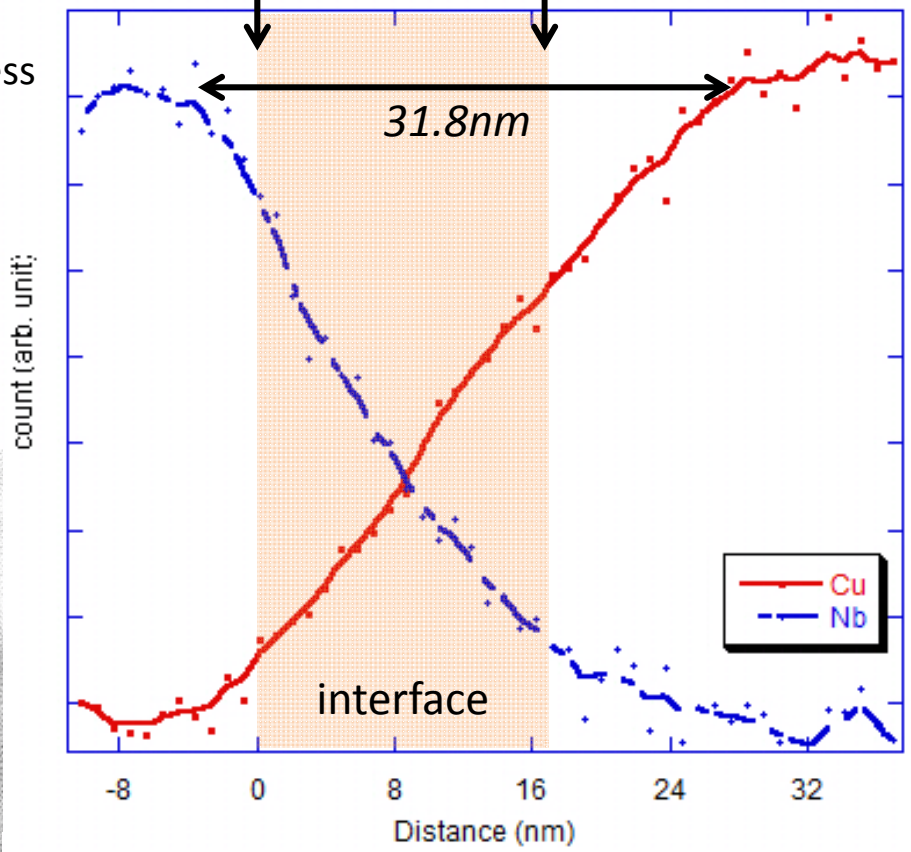




Interface thickness (e^{-1} of highest density)

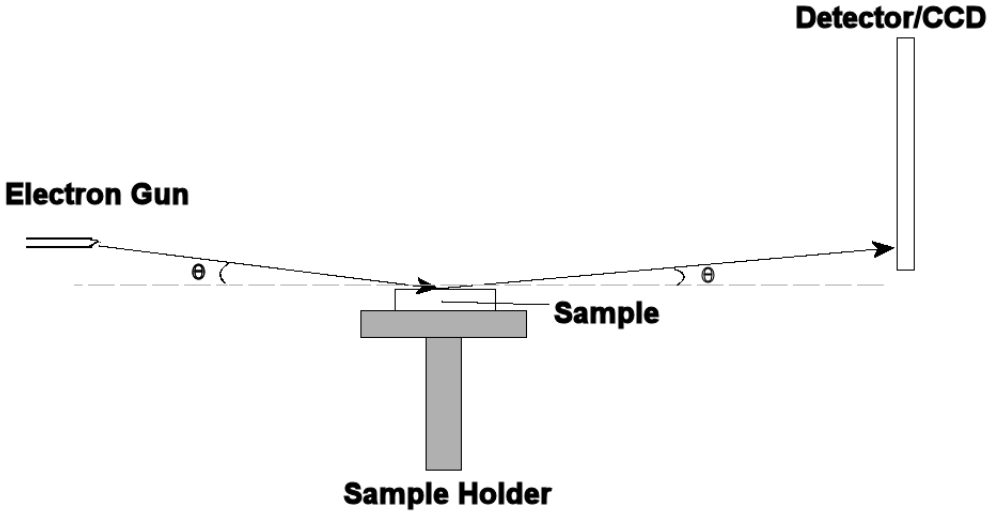
Nb: 12.5 nm
Cu: 20.1 nm

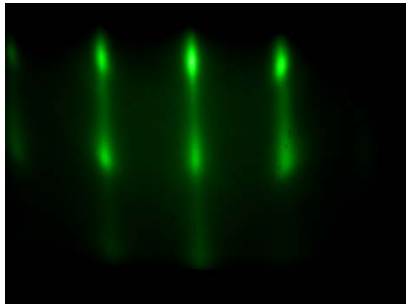




Reflection High Energy Electron Diffraction(RHEED)

RHEED is a useful in-situ and real-time diagnostic tool.
RHEED is used to characterize the surface of crystalline materials, monitor epitaxial growth, strain and thin film composition analyzing the time evolution of the lattice constant. RHEED oscillations can aid in establishing the thin film growth mode, e.g. the evolution of island formation
RHEED systems gather information only from the surface layer of the sample, which distinguishes it from other materials characterization methods that rely also on diffraction of high-energy electrons.



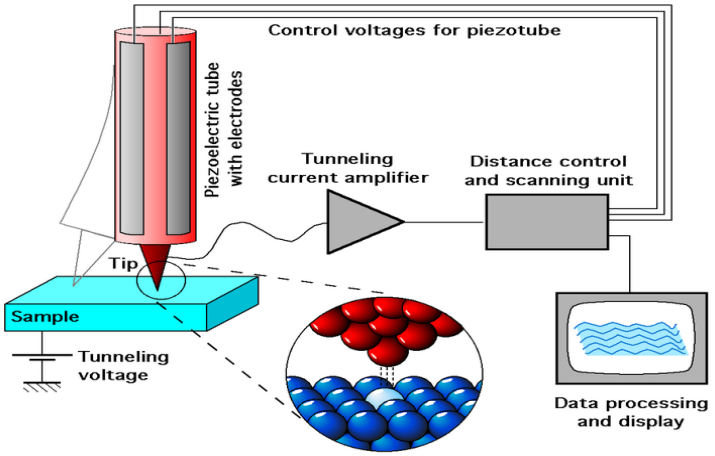


A RHEED system (MBE) requires an electron source (gun), photo-luminescent detector screen and a sample with a clean surface. The electron gun generates a beam of electrons which strike the sample at a very small angle relative to the sample surface. Incident electrons diffract from atoms at the surface of the sample, and a small fraction of the diffracted electrons interfere constructively at specific angles and form regular patterns on the detector. The electrons interfere according to the position of atoms on the sample surface, so the diffraction pattern at the detector is a function of the sample surface.

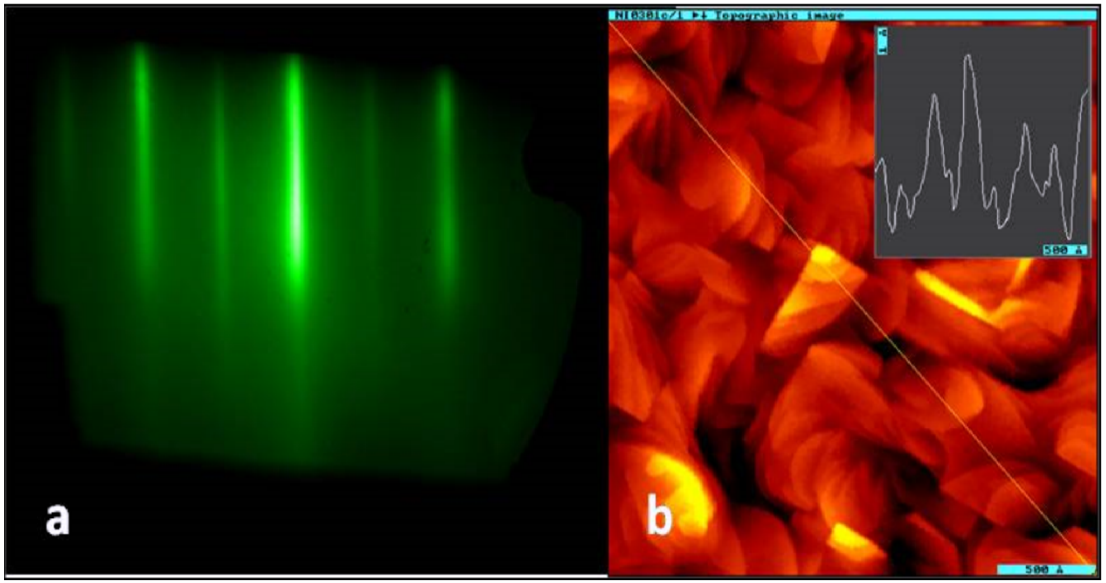
Scanning Tunneling Microscopy (STM)

Visualization tool often used to complement quantitative information gathered during wide-beam analyses such as RHEED.

A conductive probe is scanned over the sample, without contact, to map out the surface by maintaining a fixed current between the probe and the sample. Quantum tunneling of current from the tip to the sample allows the STM to map the topography of the sample. STM is a UHV technique that requires vacuum levels on the order of 10^{-10} Torr.



Description Scanning Tunneling Microscope schematic.png Schematic diagram of a scanning tunneling microscope; Date 2005-Jun-07; Source Michael Schmid, TU Wien;

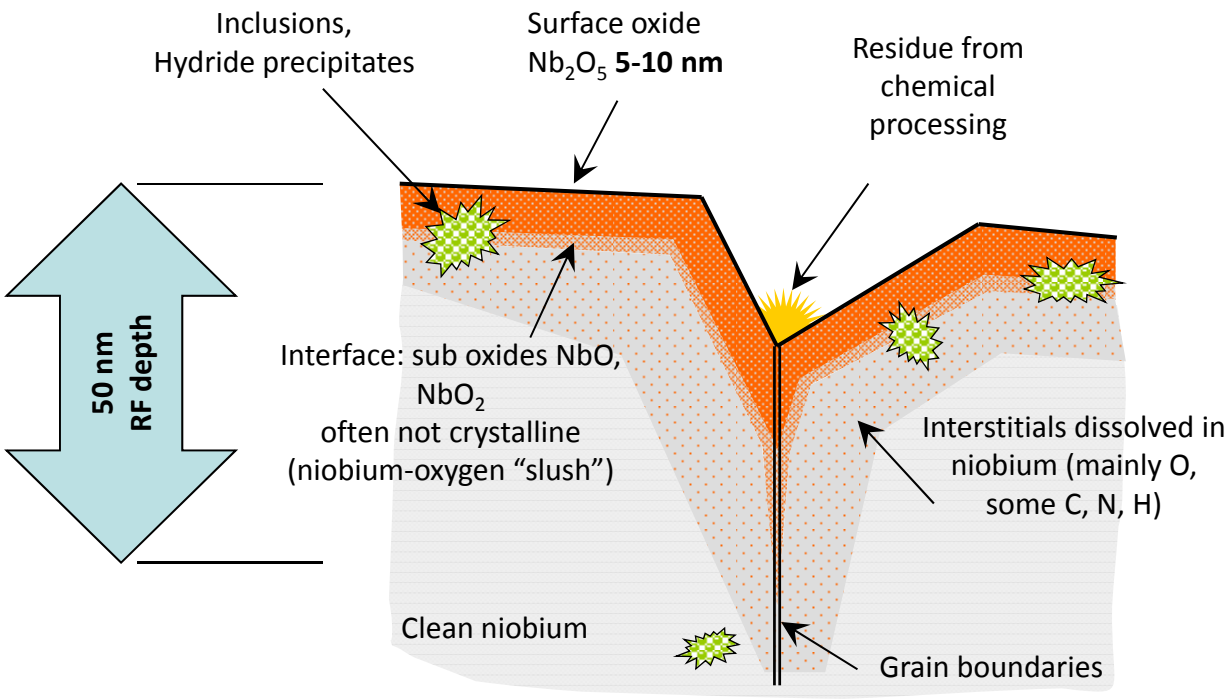


lateral resolutions ~ 0.1 nm

vertical resolution ~ 0.01 nm.

SURFACE & BULK CHEMISTRY

Niobium surfaces are complex



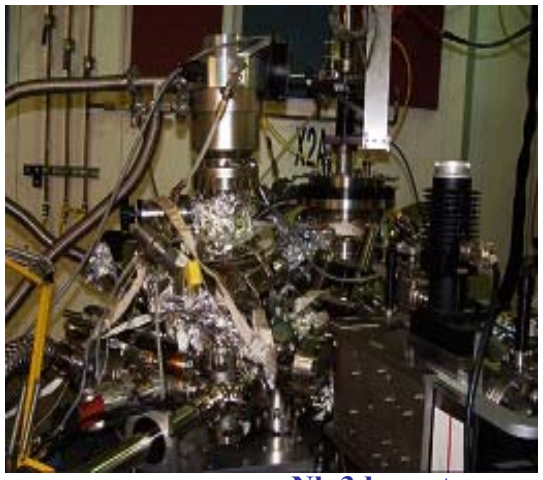
Surface composition (Nb oxides)
Species adsorbed on surface
Impurities dissolved or trapped in the bulk (O, H …)

X-ray Photoelectron Spectroscopy

- XPS reveals the surface chemistry non-destructively to study effect of cavity processing

  •XPS detects all elements with an atomic number(Z) of 3 and above. It cannot detect H or He

  •Detection limits for most of the elements are in the parts per thousand range. Detections limits of parts per million (ppm) are possible, but require special conditions: concentration at top surface or very long collection time (overnight).



Nb 3d spectrum

XPS is routinely used to determine:

Elements and the quantity of these elements that are present within ~10 nm of the sample surface

Contamination, if any, exists in the surface or the bulk of the sample

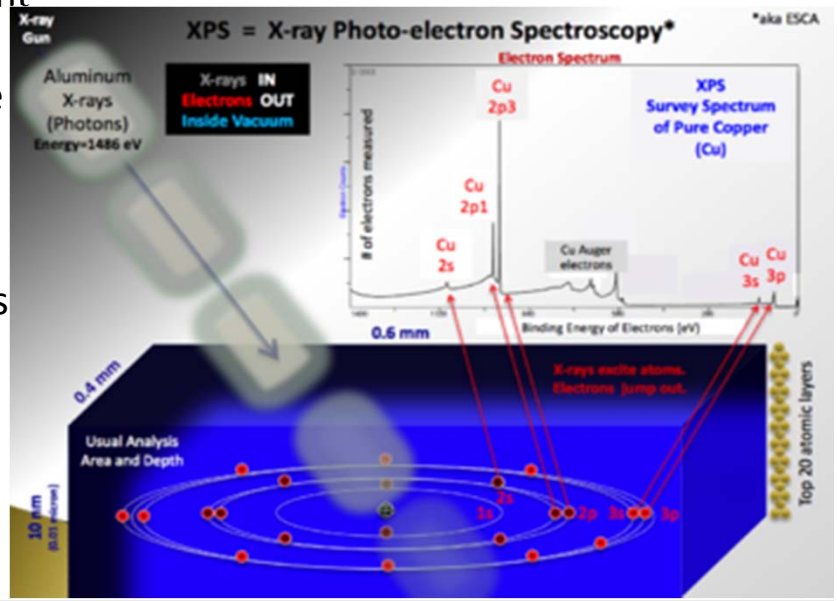
Empirical formula of a material that is free of excessive surface contamination

Chemical state identification of one or more of the elements in the sample

Binding energy of one or more electronic states

Thickness of one or more thin layers (1–8 nm) of different materials within the top 10 nm of the surface

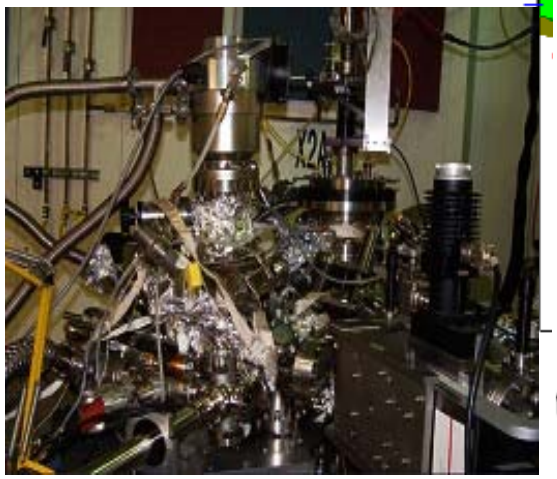
Density of electronic states

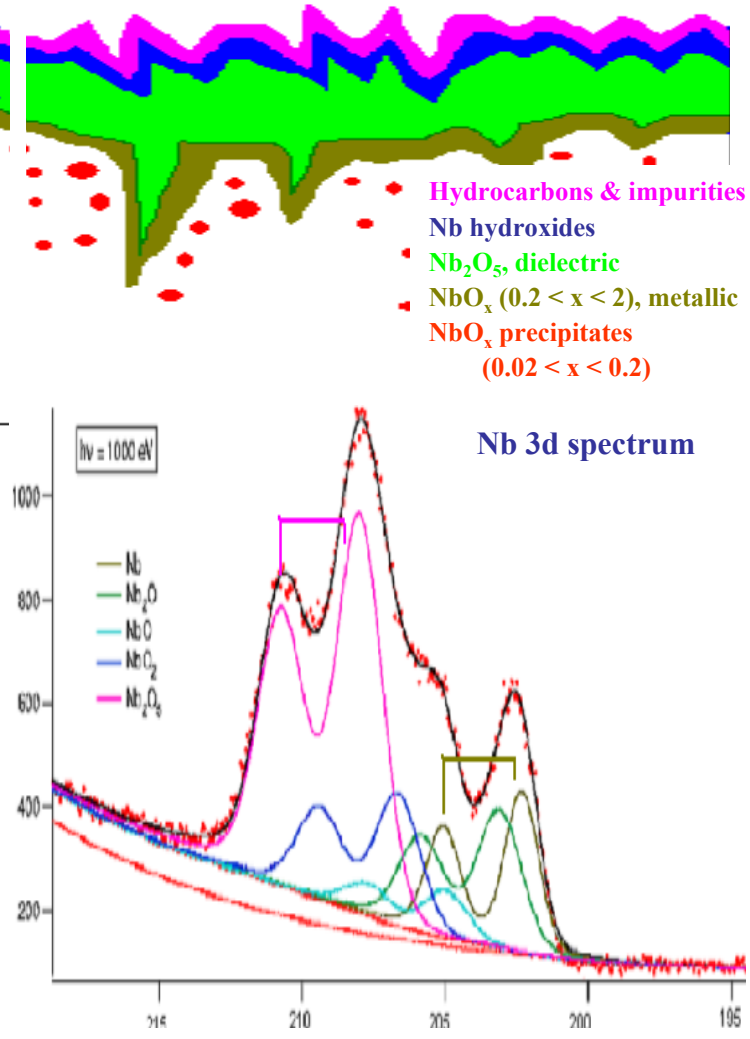


X-ray Photoelectron Spectroscopy

XPS reveals the surface chemistry non-destructively to study effect of cavity processing

All elements except for H and He can be detected at concentrations above 0.05 to 1.0 atom. % Sampled area varies from 1mm down to 30 µm in diameter.

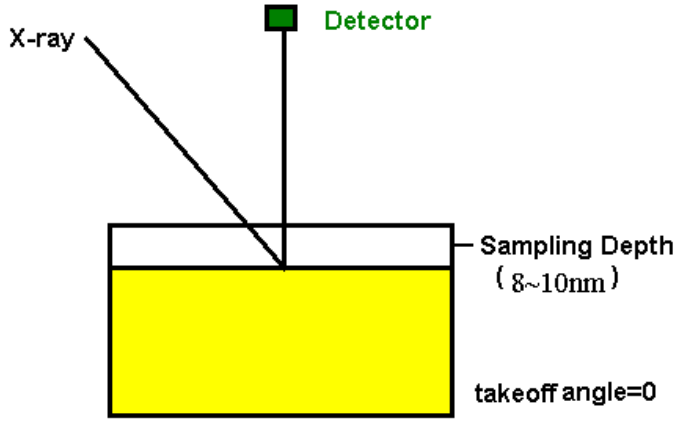




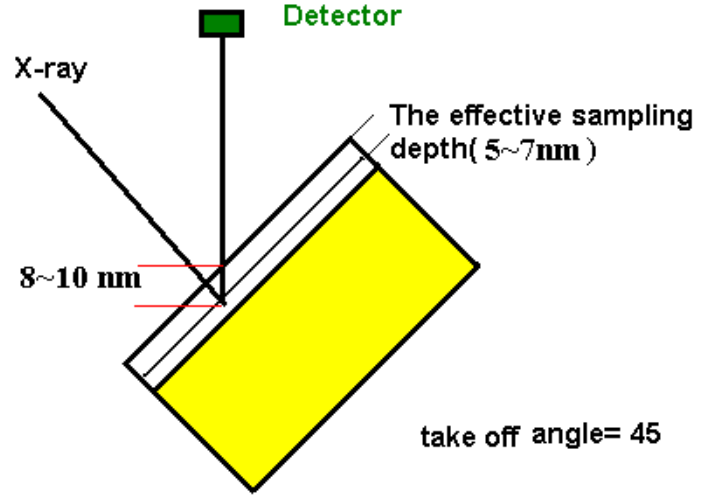
- Oxide thickness is less with EP than BCP and single than poly crystal
- Low-T bake decreases oxide thickness and creates more sub-oxides. Vacuum preserves the baked state, but sustained air exposure restores it

H. Tian & C. Reece/ JLab - CWM - BU - NSLS-BNL)

Angle Resolved (AR) *vs.* Energy Resolved (ER)XPS



AR

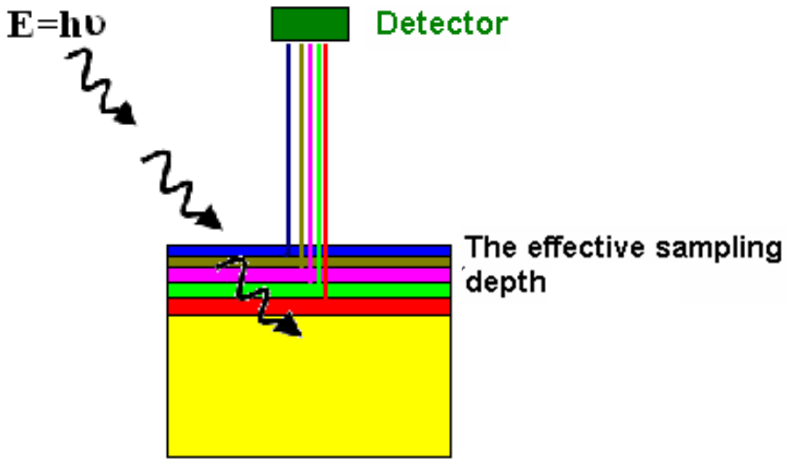


At the normal incident angle (Nb_2O_5: 3 ~ 8 nm+ metal)

$$\lambda = E / \{E_p^2[\beta_m \ln(\gamma E) - C/E + D/E^2]\}$$

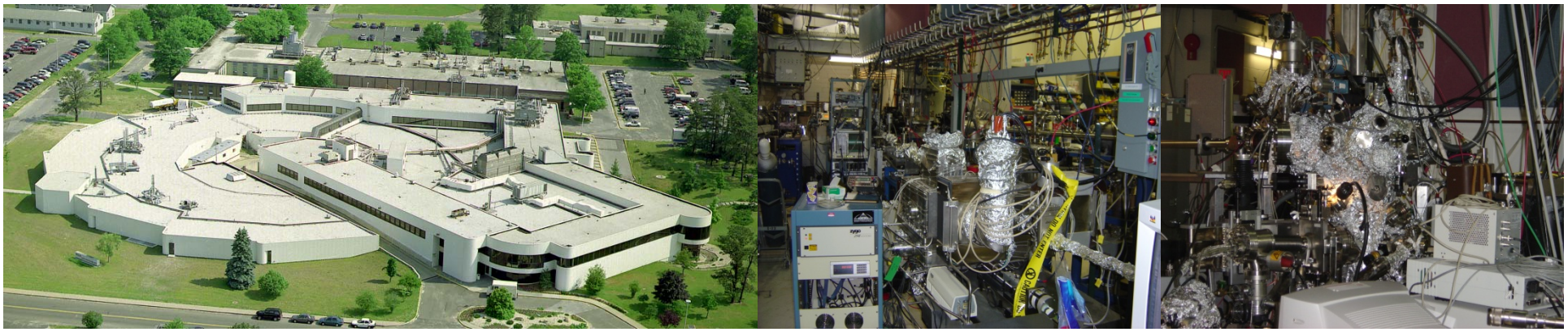
E=hυ(eV)	Sampling Depth (nm) Nb_2O_5
300	2.8
550	4.2
750	5.3
1254(Mg)	8.1
1486(Al)	9

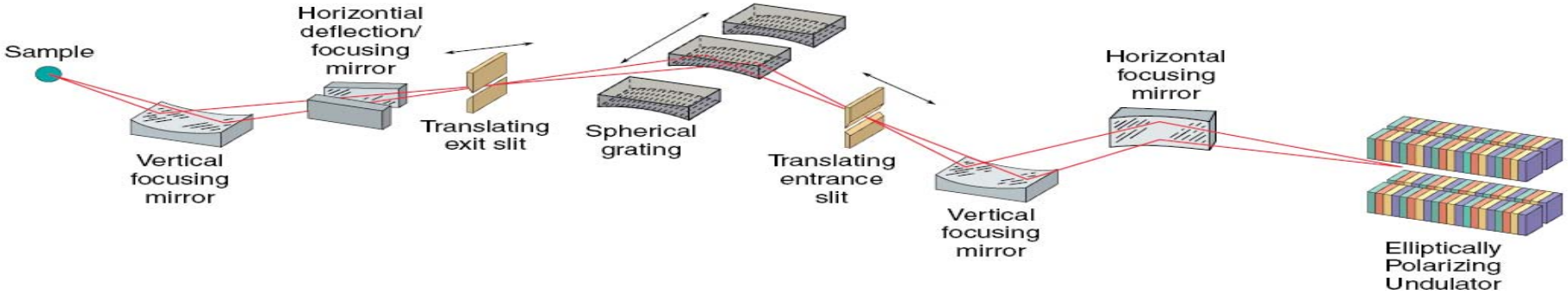
ER



Surface topography has less impact on variable photon energy XPS. AR + ER XPS provides the most surface sensitive information.

Energy Resolved XPS -BNL, NCLS, X1B





hυ = 300 eV, 550 eV , 750eV(100 ~ 1600 eV)- energy resolved XPS
Take off angle = 0° , 41° , 60° …-angle resolved XPS.
Spot size < 250 µm with enough intensity, total energy resolution can be less than 0.1eV.

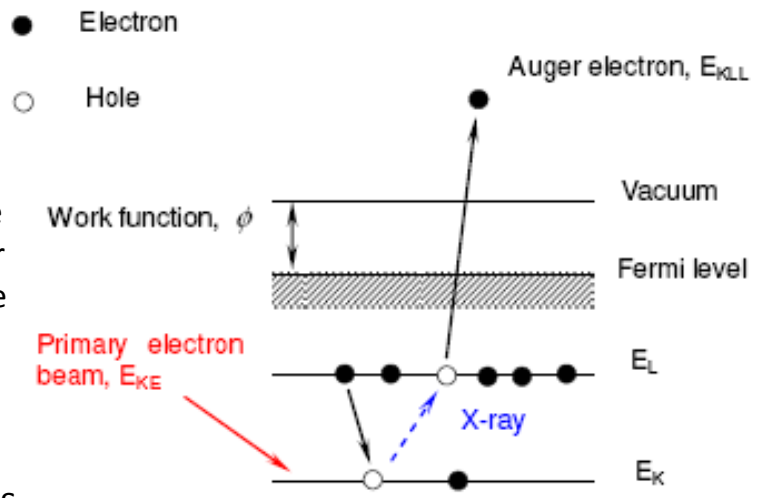
Scanning Auger Microscopy – SAM/AES

AES measures the chemical composition of the outermost 100 Å of a sample.
All elements except for H and He can be detected at concentrations above 0.1 to 1.0 atom %, depending on the element. In addition, elemental concentration versus depth (up to 2 µm) information can be obtained by ion sputter etching while monitoring every element of interest. Only conductive samples can be measured with this technique. The sampled area varies from 1 mm down to 2 µm in diameter.

Auger electron spectroscopy (AES) uses a scanned focused high energy electron source to excite atoms from the surface of a solid sample.
An excited atom will then relax by electron shell to shell transition and the energy difference between the 2 shells must be released, emitted as either an x-ray out outer shell electron emission-the so called Auger electron. The kinetic energy of these Auger electrons are measured and are elementally characteristic. The low escape depth of Auger electrons means that AES analysis only the top few atomic layers of the sample material.
For analysis beyond the top 1-5 nm an inert gas ion gun (normally Argon) can be used to sputter off the surface layers. Alternating sputtering and AES spectral acquisition permits chemical depth profiles to be obtained down to depths of about 1 µm into the bulk.

An emitted Auger electron will have a precise kinetic energy E_k

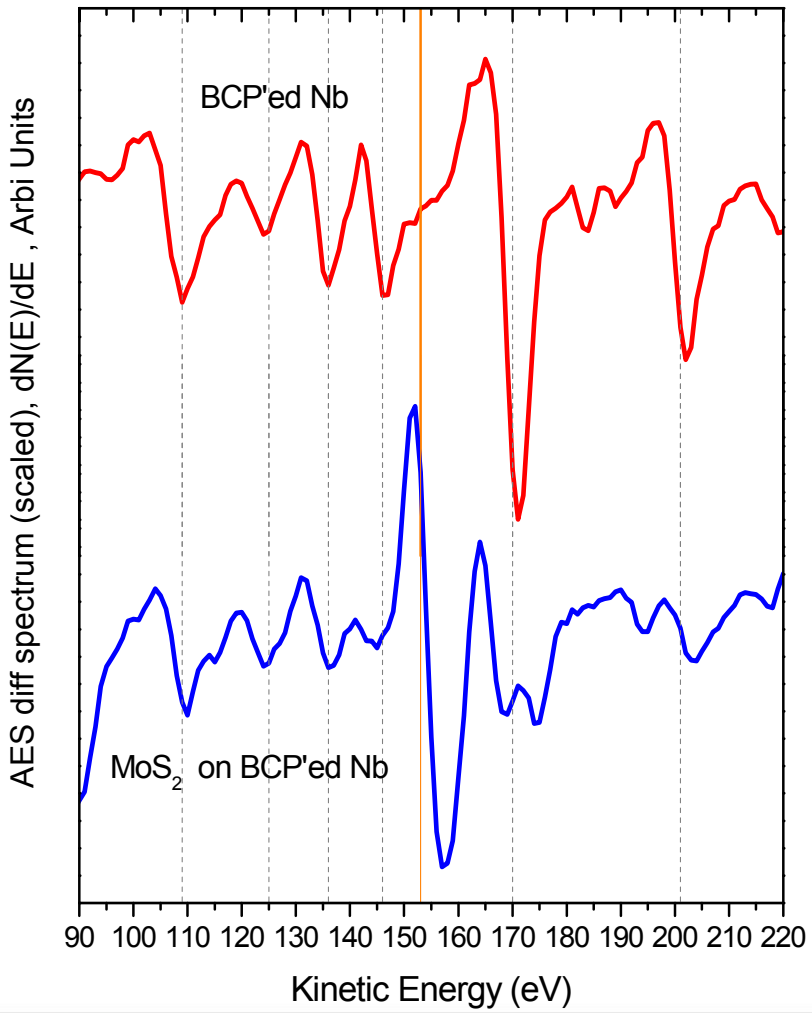
$$E_k = E_{\text{Core State}} - E_B - E_C'$$



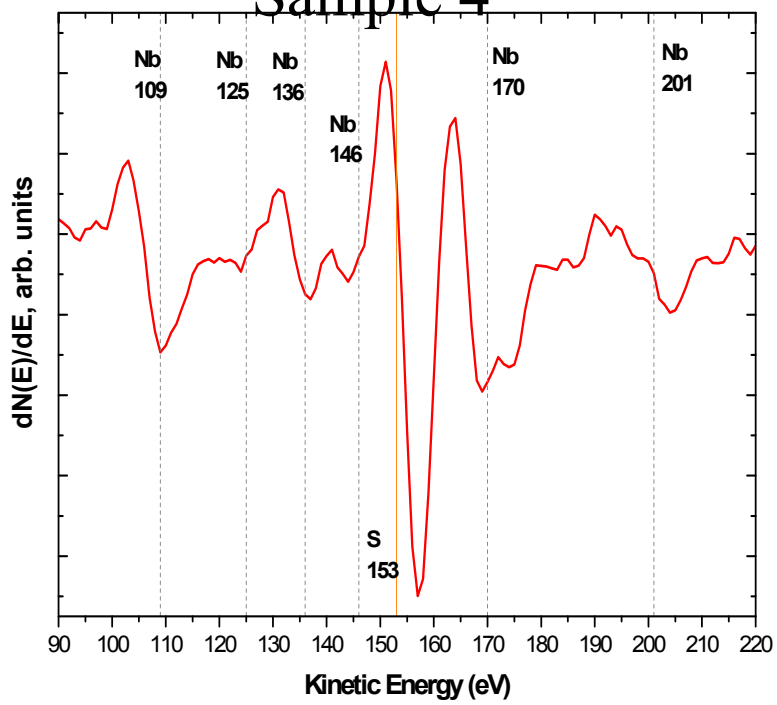
Schematic of Auger Effect

Sulfur Revealed by AES

System Calibration via BCP Nb and MoS_2

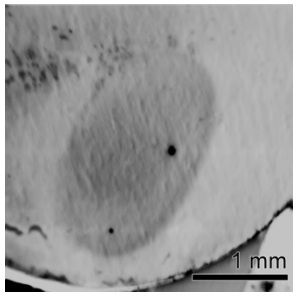


Sample 4

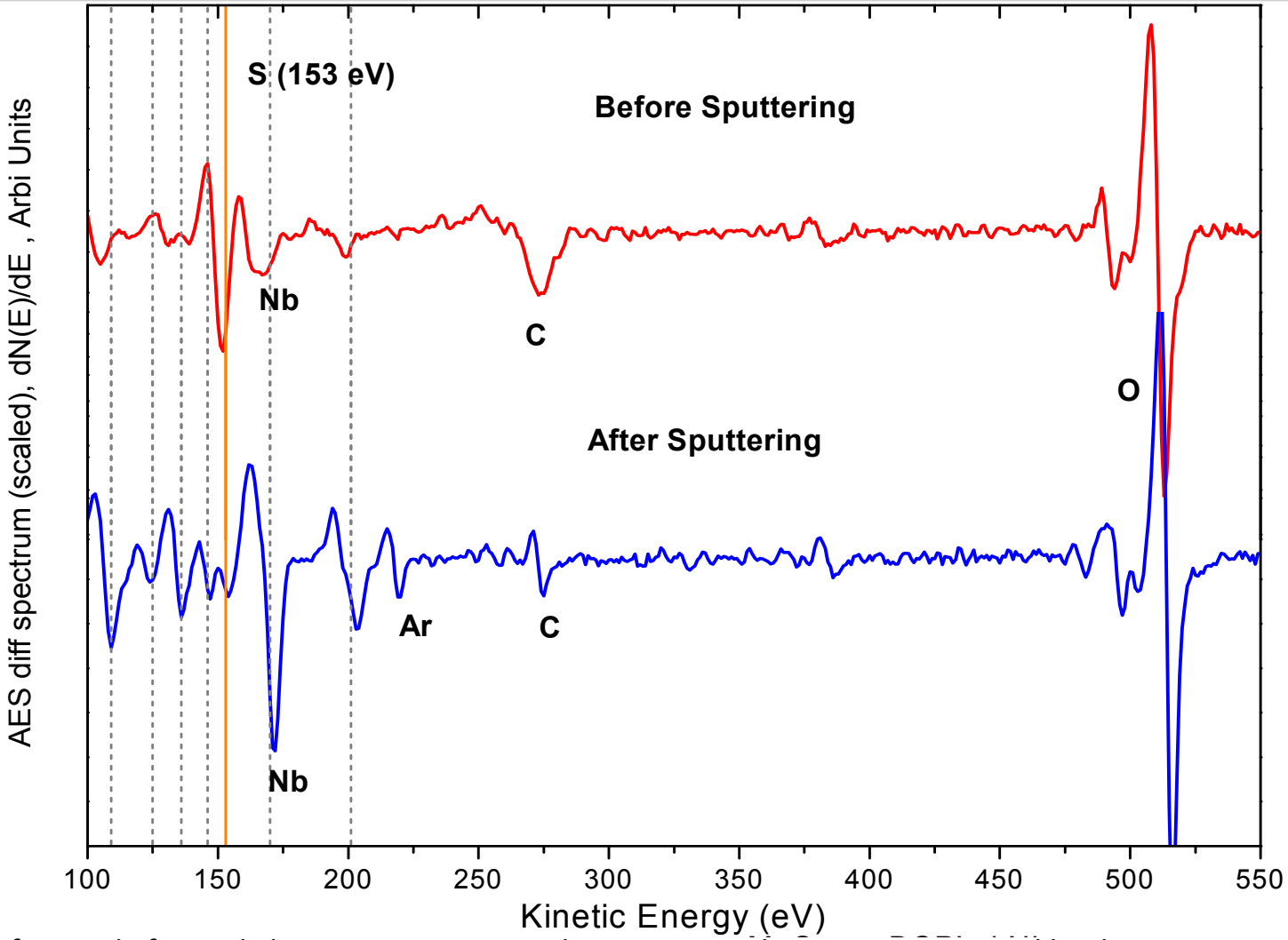


AES spectrum collected on spot1. (Sample 4).The theoretical sulfur peak position is labeled in orange. The Nb:S atomic ratio is 3:1 after RBD *Augerscan*™ quantification evaluation

Sulfur Revealed by AES and Depth Profiling



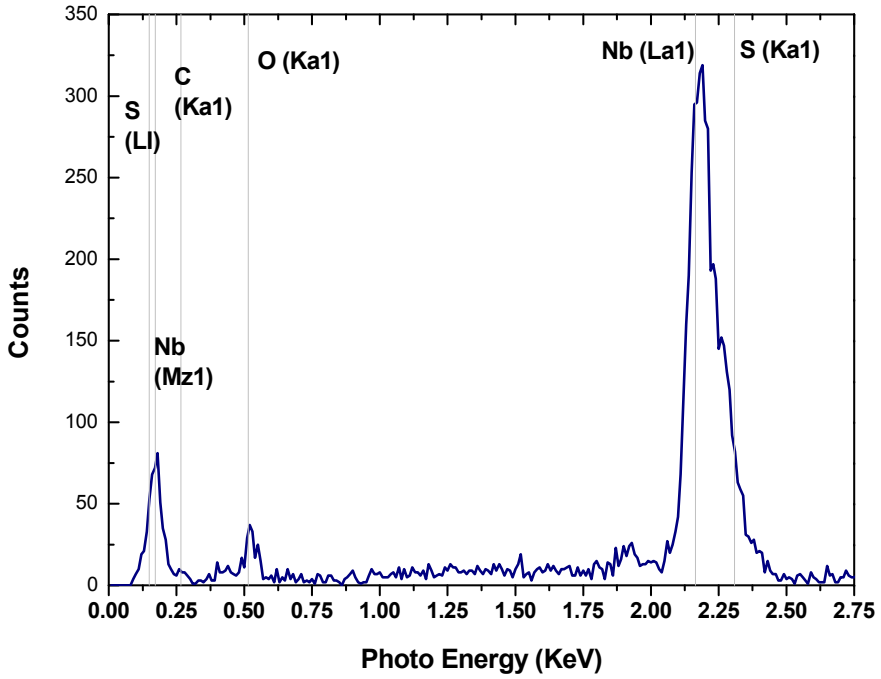
ABS images of the sputtered spot. It seems the Ar^+ beam cleaned the surface charging layer

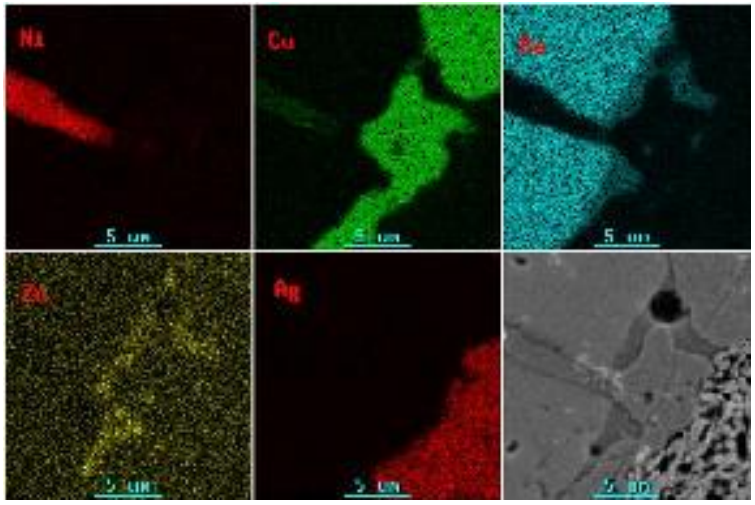


AES spectra of a spot before and after a slight sputtering. Fewer than 10 atomic layers were removed by the Ar^+ beam. The sulfur peak was greatly reduced after sputtering, which indicated sulfur coverage is ultra-thin.

Energy-Dispersive X-ray Spectroscopy – EDS(X)

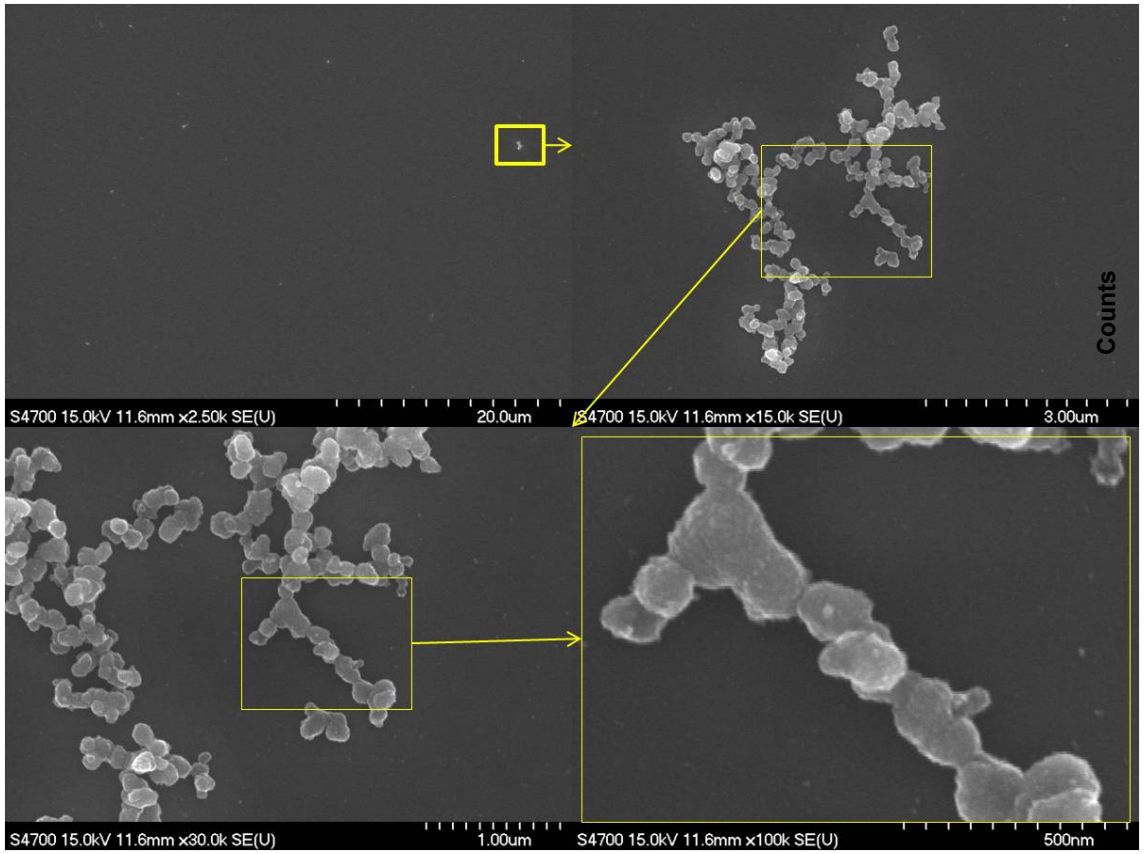
In an SEM, an electron beam strikes the surface of a conducting sample. The energy of the beam is typically in the range 10-20keV. This causes X-rays to be emitted from the point the material. The energy of the X-rays emitted depend on the material under examination. The X-rays are generated in a region about 2 μm in depth, and thus EDX is not a surface science technique. By moving the electron beam across the material an image of each element in the sample can be acquired in a manner similar to AES. Due to the low X-ray intensity, images usually take a number of hours to acquire. Elements of low atomic number are difficult to detect by EDX.

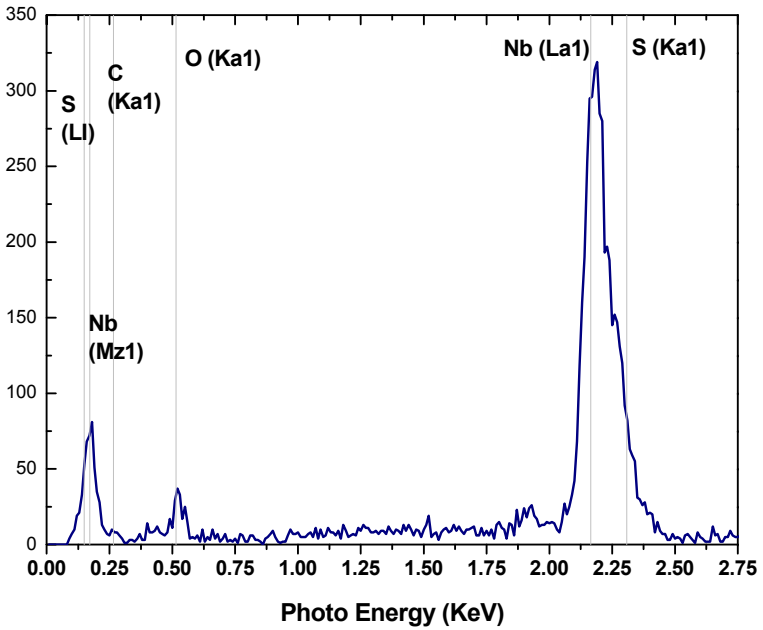




AMU Resolution ~1%
Sampling Depth ~3000 atomic layers (1μm)

Nb-Oxide Granules Produced by EP process observed via SEM/EDX

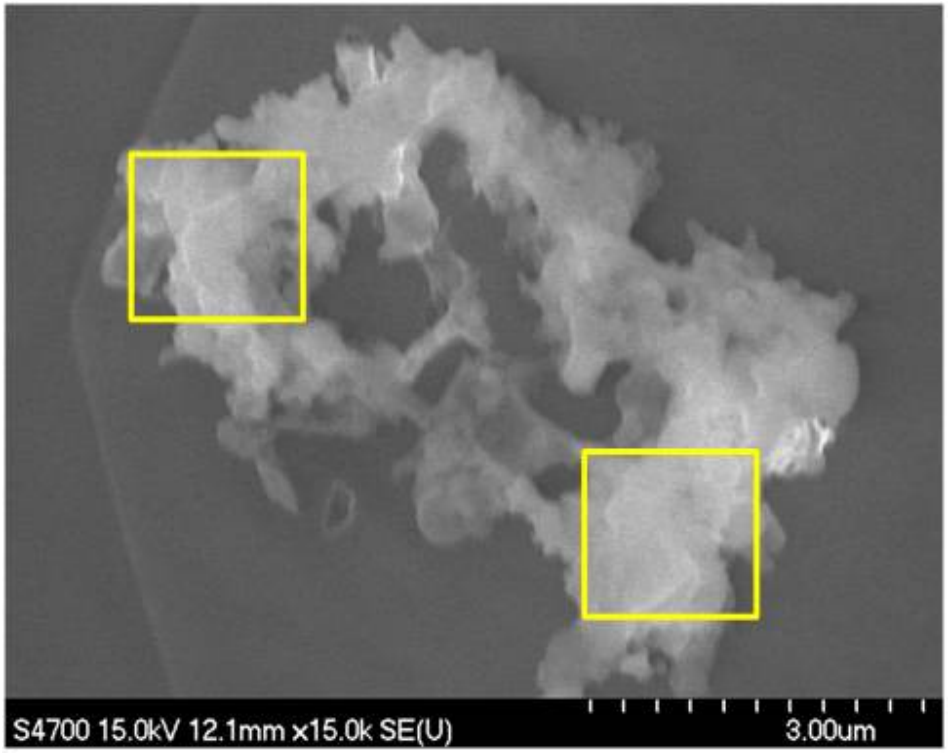




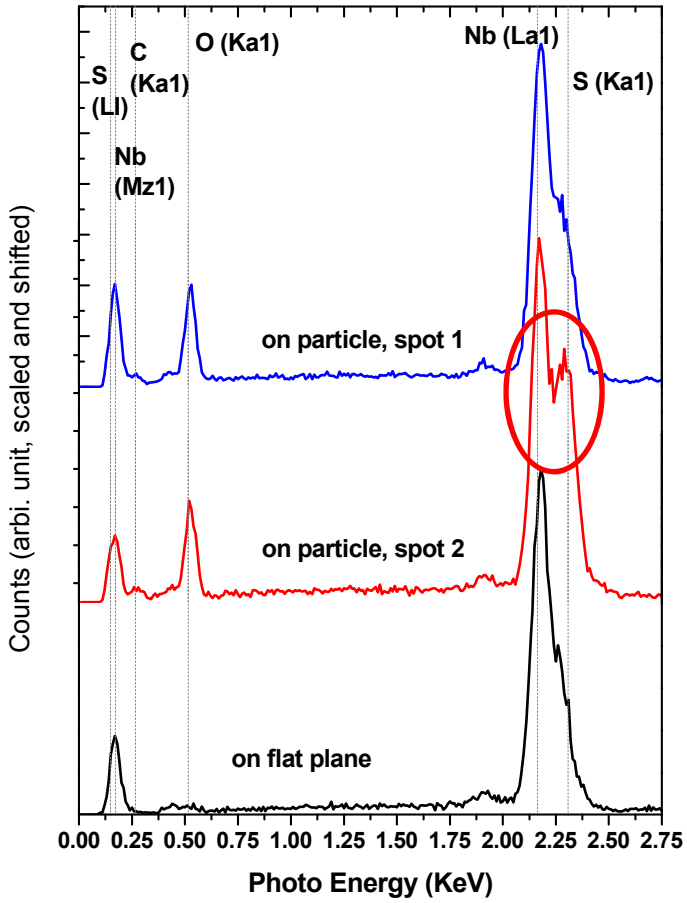
Sparsely distributed **Nb-O** granules were observed on Nb samples surfaces after EP. They reside on clear flat surface and their density is low.

EDX spectrum surveyed at a spot of the granule (survey area 300*200 nm^2). It suggests this granule only has **oxygen and niobium** elements.

Sulfur Revealed by SEM/EDX



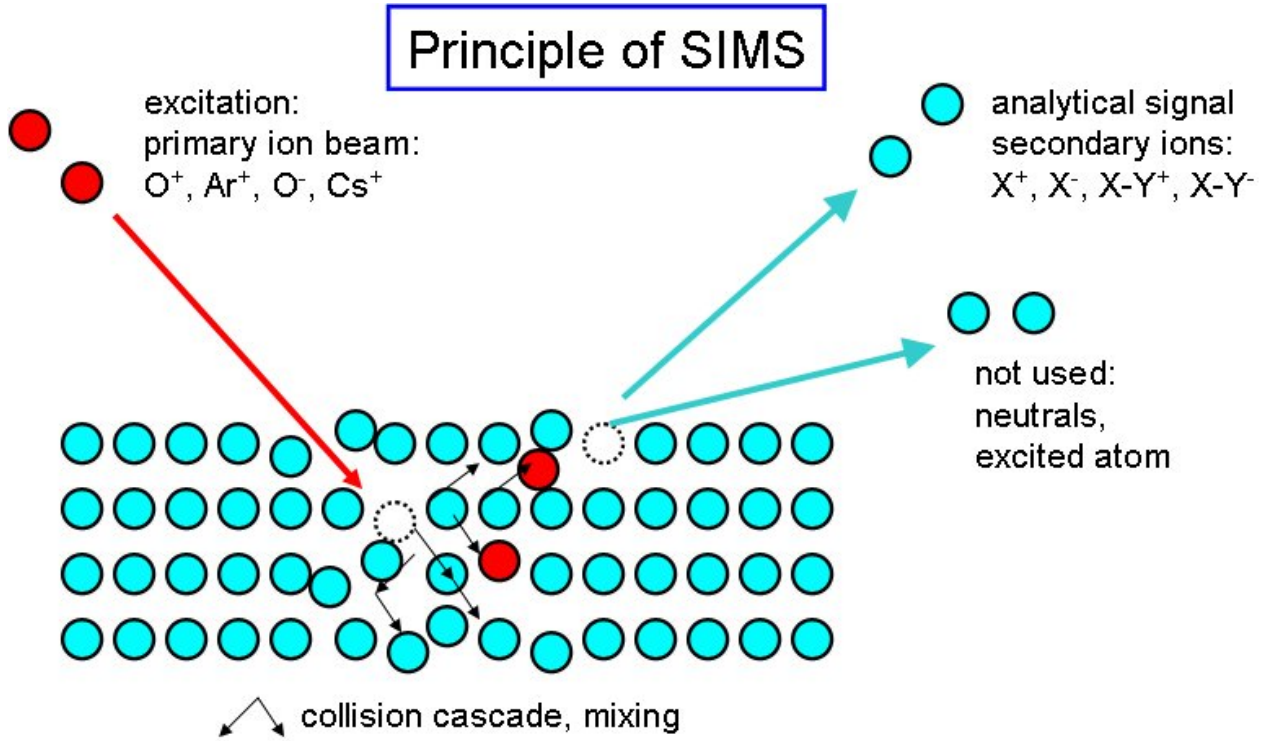
A sulfur-embedded granule observed on sample 6. Sulfur is enriched on one spot (spot2, bottom-right yellow window) but not at other spot (spot1, upper-left window). This granule is setting on a very smooth and flat plane



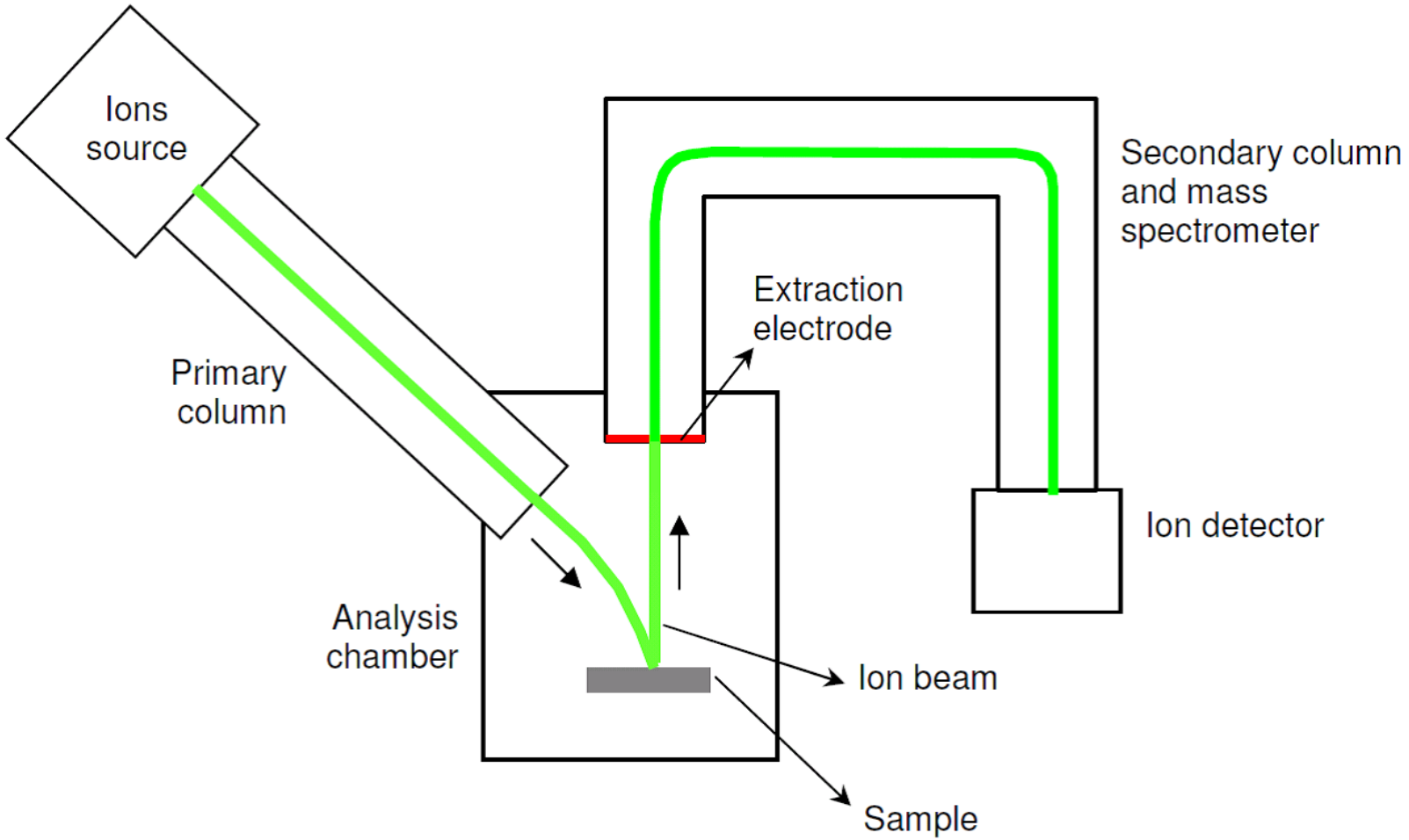
EDX spectrum surveyed from two spots on a granule and from off-granule flat plane (50 um away from the granule). Sulfur is enriched on spot 2 (red curve); oxygen to niobium ratio is much higher on the granule than that of a normal EP'ed surface (black curve).

Secondary Ion Mass Spectroscopy - SIMS

Analyze the composition of solid surfaces and thin films by sputtering the surface of the specimen with a focused primary ion beam and collecting and analyzing ejected secondary ions. These secondary ions are measured with a mass spectrometer to determine the elemental, isotopic, or molecular composition of the surface.
SIMS is the most sensitive surface analysis technique, being able to detect elements present in the parts per billion range.

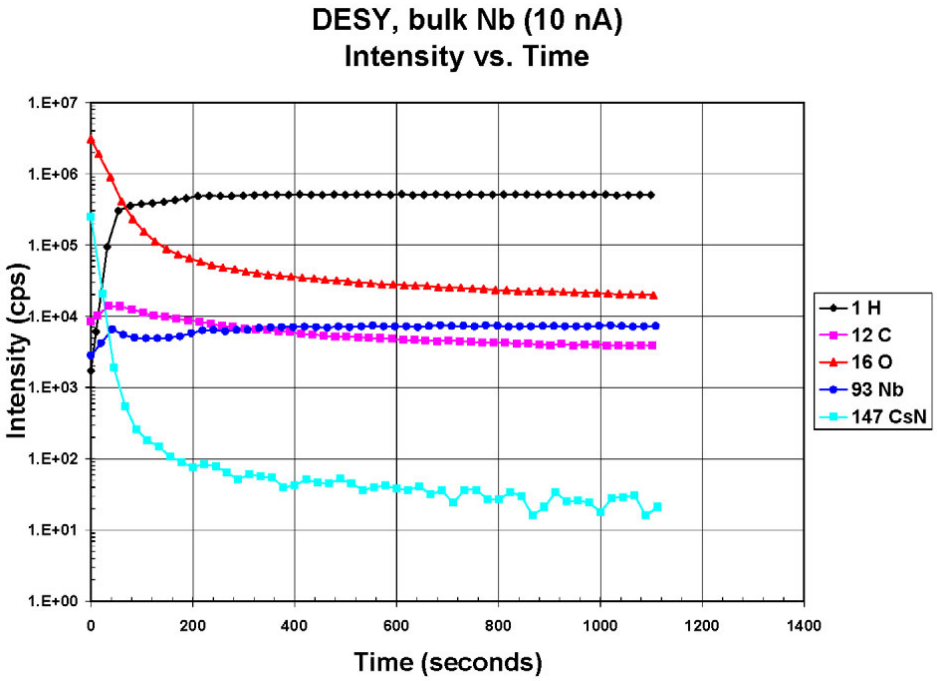


Secondary Ion Mass Spectroscopy - SIMS

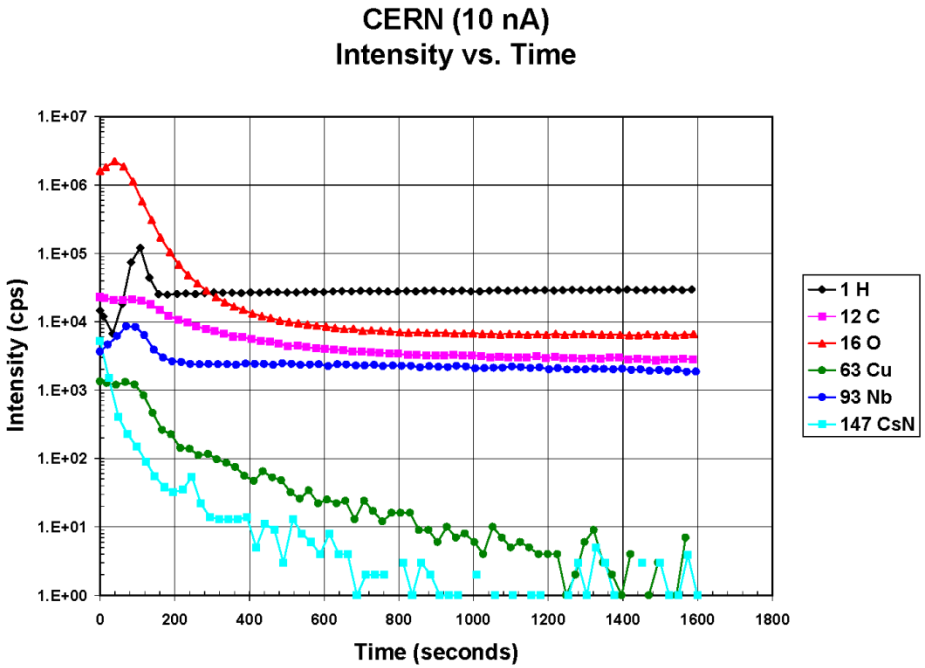


SIMS on Nb surfaces

Bulk Nb
From surface down to 70 nm

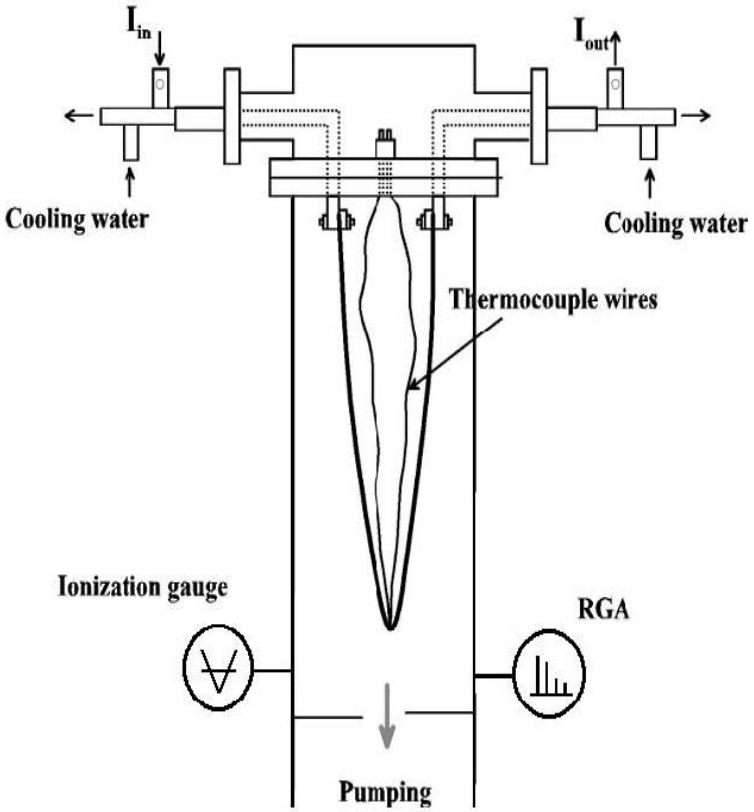


Nb/Cu film
From surface down to 100 nm



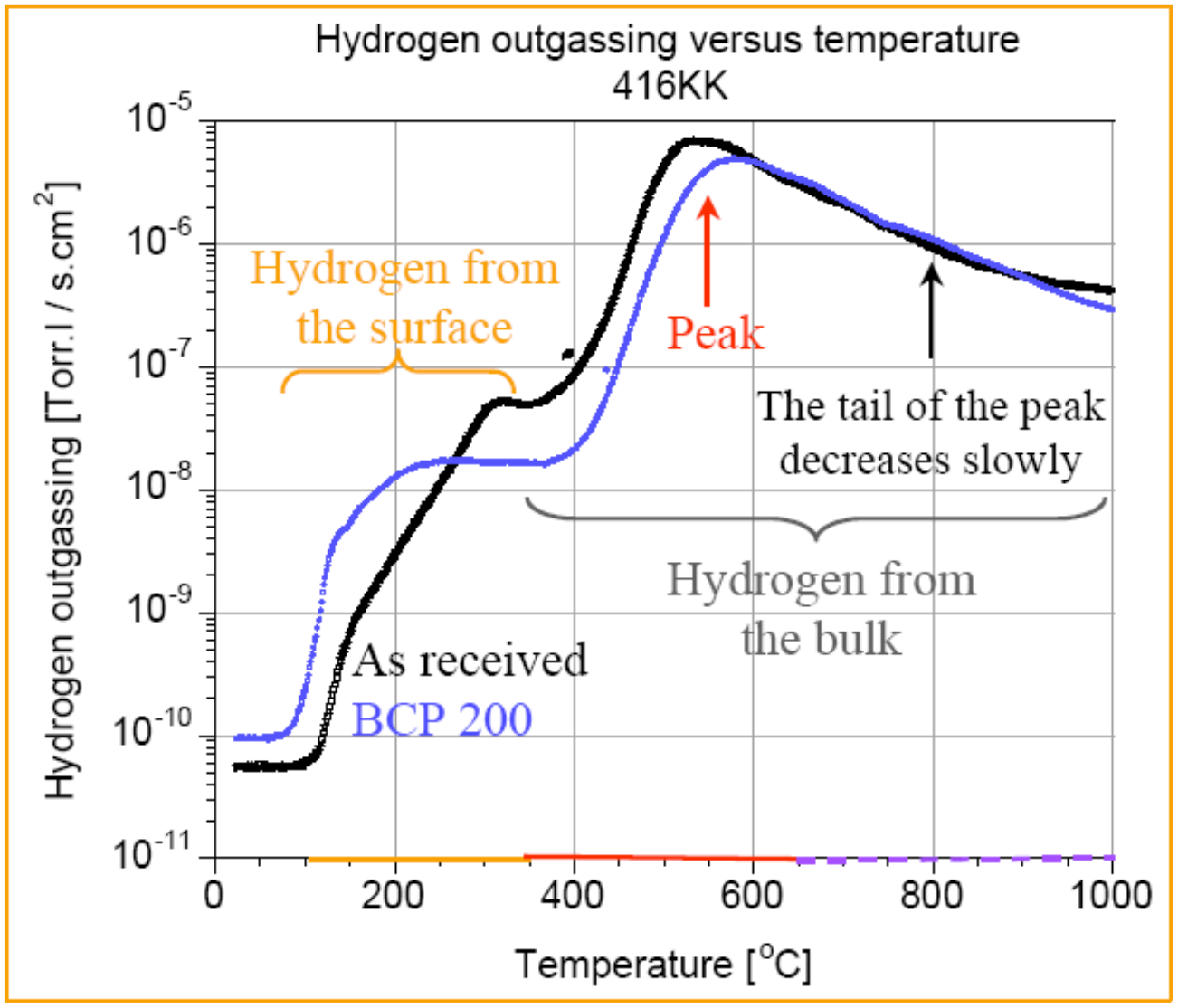
Thermal Desorption Spectroscopy (TDS)

TPS (also known as TPD) involves heating resistively a sample under UHV conditions and simultaneously detecting the residual gas in the vacuum by means of a mass analyzer. The heating of the strip (1-2°C/min). results in desorption of the gases from the surface, at temperatures depending on their characteristic desorption energies. Using a Residual Gas Analyzer (RGA) the degassed gases are identified and their rate of release is measured by using a known pumping speed applied to the UHV measurement chamber. In addition, the diffusible species, mainly hydrogen, are diffused from the bulk to the surface and finally degassed usually at higher temperatures. The position and the shape of the peak are related to the ramping speed. This can be used as a tool to distinguish the diffusion peak from the surface peaks, which are characteristic to their binding energy and therefore will remain stationary. The temperature of the peak maximum provides information on the binding energy of the bound species.



CERN TDS Setup

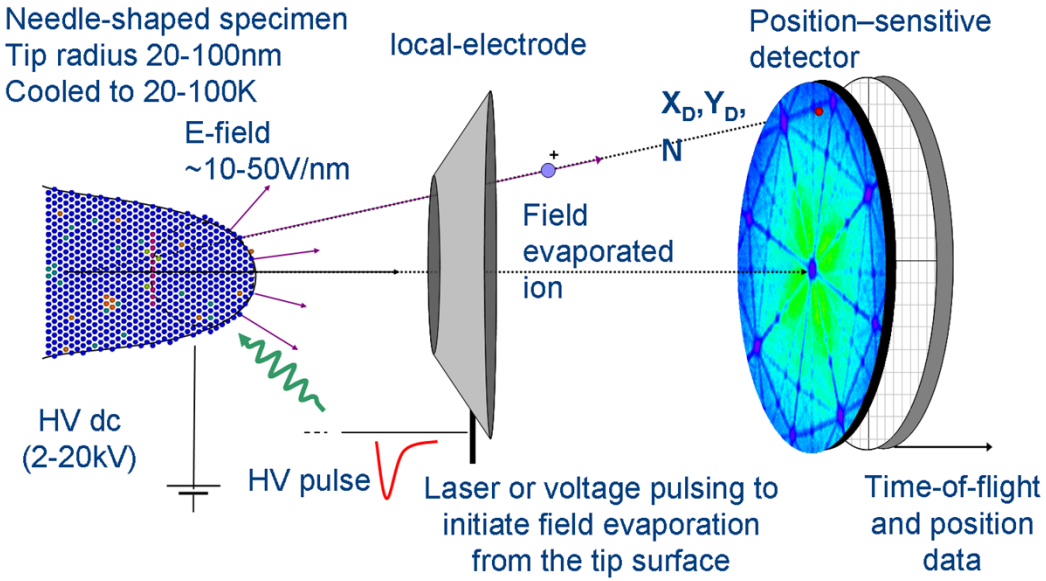
TDS of Nb

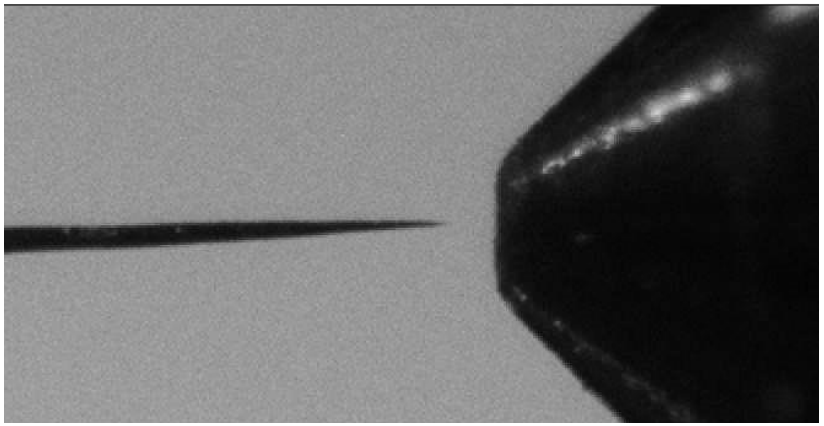

Hydrogen outgassing versus temperature
416KK
Hydrogen outgassing [Torr.l / s.cm^2]
10^{-5}
10^{-6}
10^{-7}
10^{-8}
10^{-9}
10^{-10}
10^{-11}
Hydrogen from the surface
Peak
The tail of the peak decreases slowly
Hydrogen from the bulk
As received
BCP 200
0
200
400
600
800
1000
Temperature [°C]

Atom Probe Tomography (APT)

An atom probe is an integrated point-projection microscope and time-of-flight mass spectrometer. The technique offers quantitative 3-D compositional imaging and analysis of small areas (precipitate, interface, defects…). Detection of all elements, isotopes, and higher-mass molecular ions.

Unique ability to tie compositional information to structure at sub-nm levels.



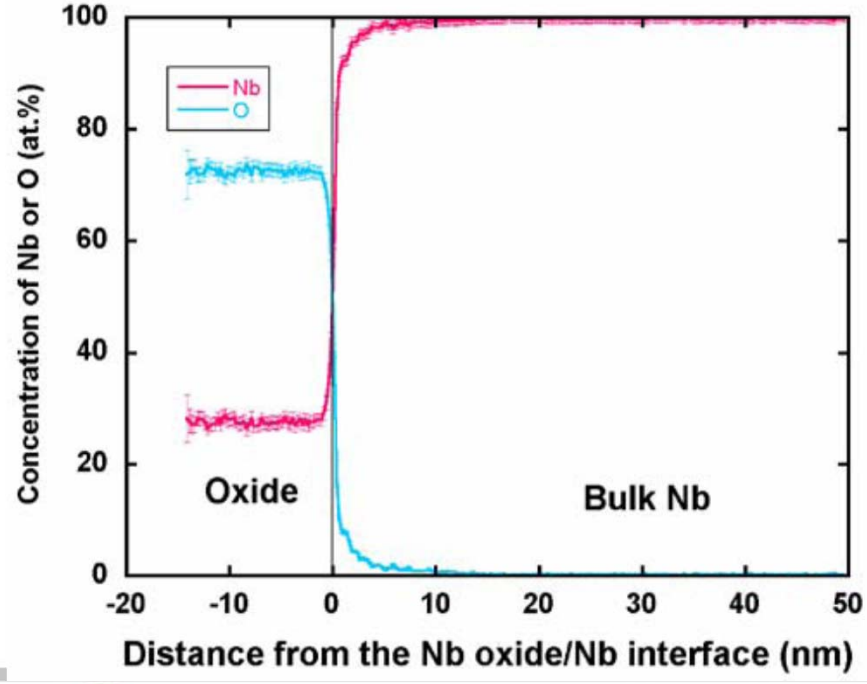


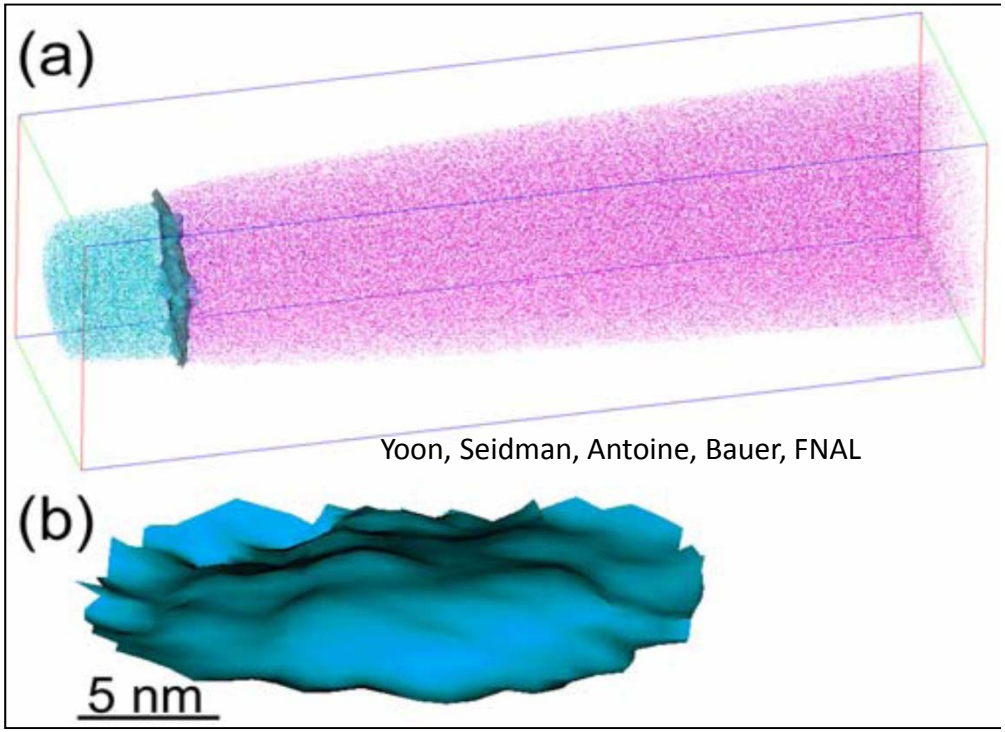
Pulsing the sharp, needle shaped target causes atoms to be evaporated as ions, which can be identified by time of flight. Their 2-D hit position on the detector is recorded along with a 1-D sequence number. The magnification is primarily a function of the geometry, and is determined by ratio of the tip to detector distance (~10 cm), to the tip radius, (~30 nm), giving values greater than 10^6. Highly-magnified projection of the atomic-scale structure of the specimen surface on the detector.

Cavity Grade Nb surface (Atom Probe)

(a) Atomic reconstruction of surface metal oxide layer on bulk Nb. The overall reconstruction dimensions are 33 x 32 x 111 nm^3, and the volume contains 2 million atoms. Sample is Fibbed from cavity grade Nb.

(b) The surface niobium oxide/Nb interface identified with an 30 at.% O isoconcentration surface. The RMS chemical roughness of the interface is 0.4 nm.





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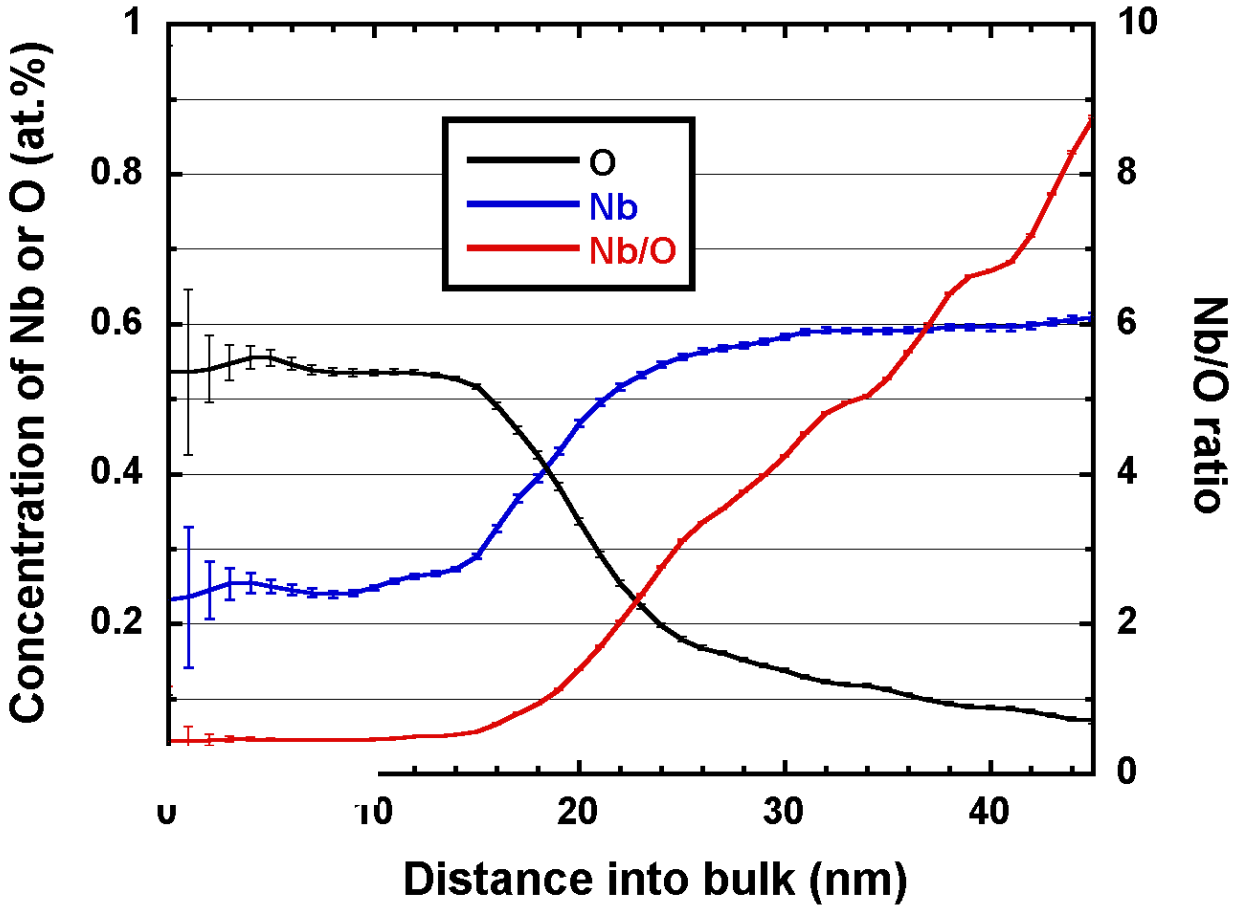
Reduced Data shows 15 nm ~Nb_2O_5 at surface

3D-AP: impurity profiles at the Nb surface (NU)

Atom Probe Tomography of EP'ed Nb (RRR300) tip:

1) Oxide Layer thickness: 25 nm
2) Interstitial O content: 15-8% in first 15nm at the surface



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CONCLUDING REMARKS

- There are a large number of surface and material analyses techniques useful for investigating SRF surfaces in terms of topography, structure, chemical composition of the top-surface and the material bulk.

- When investigating an SRF surface, one usually need to use more than one surface/material analysis technique.