Surface Studies of Niobium for Superconducting Radio Frequency (SRF) Cavities

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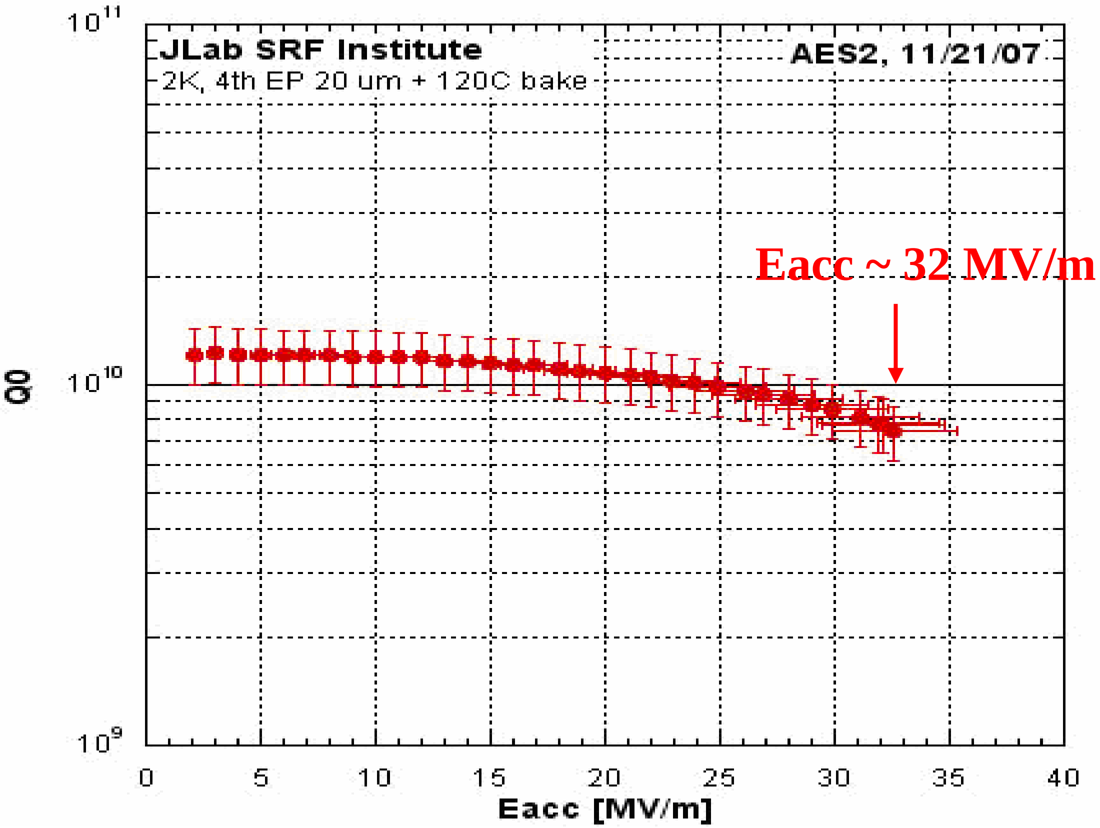
The Performance of SRF Cavity & Its Limitations



Q_0 *vs.* E_{acc} for an electropolished niobium 9-cell cavity. Courtesy of Jefferson lab

The SRF cavity performance is characterized by Q_0 *vs.* E_{ac} .

Various anomalous losses limit cavity performance:

-Thermal break-down; enhanced field emission; multipacting; Q-drop.

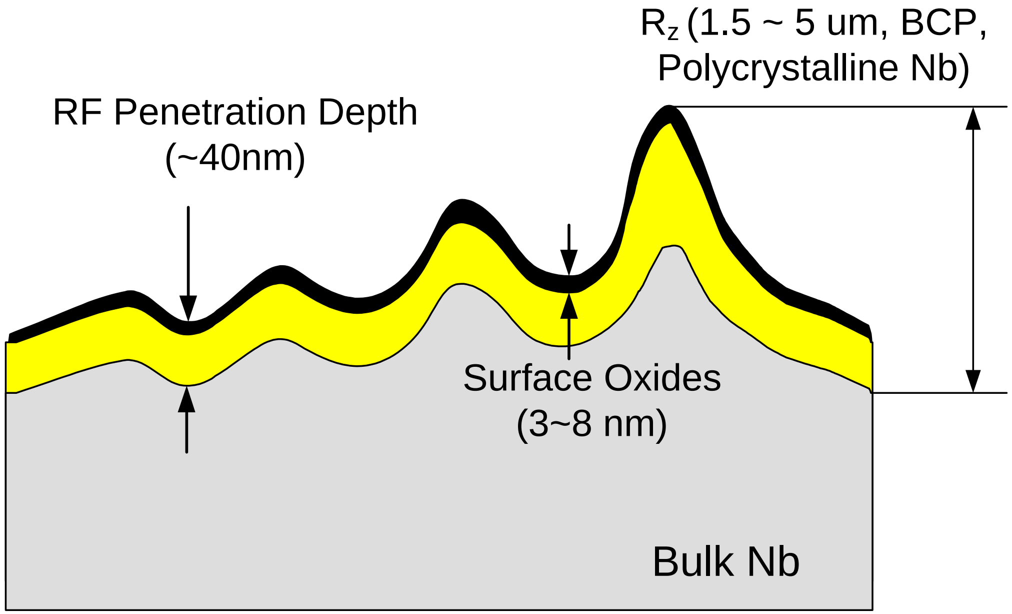
Current Nb SRF Cavity
Surface Treatment Methods Needs Improvement

Cavities Processing Recipe (courtesy of *www.linearcollider.org*)

1. Incoming cavity quality control checks.
2. Optical inspection of as-received cavity.
3. Bulk buffered chemical polishing(BCP)/electropolishing (EP)~150 μ m damage layer removal .
4. Ultrasonic degreasing.
5. High-pressure rinsing.
6. Hydrogen degassing at 600/800°C.
7. Field-flatness tuning.
8. 20 μ m buffered chemical polishing(BCP)/electropolishing (EP)
9. Ultrasonic degreasing.
10. Field-flatness verification and retuning if <95%.
11. High-pressure rinsing.
12. Assembly and vacuum leak testing.
13. 120°C bake.
14. Vertical dewar test.

Current technology of cavities' surface treatment- “ a series of removal steps + low T baking ”- mechanical damage; chemical residues; hydrogen (bulk); particulate + oxygen, hydrogen, structure…

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

Outline: Topography

1. **Motivation-Understanding for Improving Performance.**

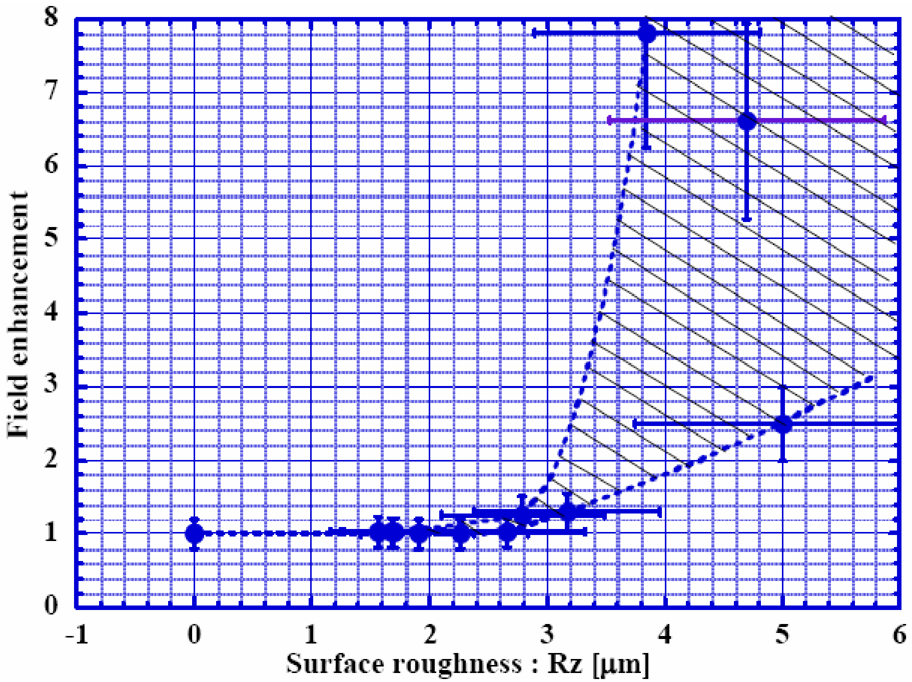
2. **Characterization of Niobium Surface Topography.**

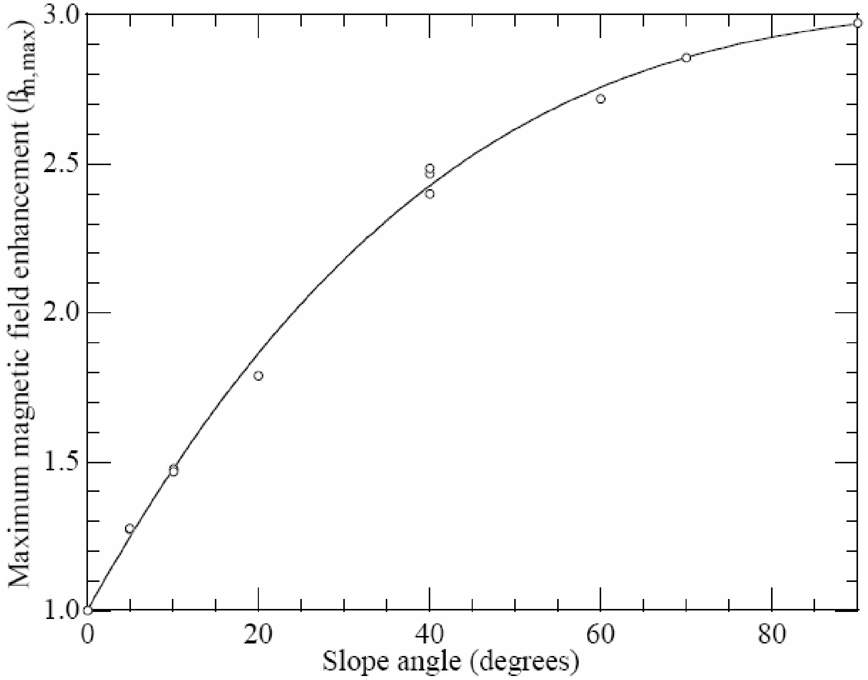
3. **X-ray Photoelectron Spectroscopy (XPS) Studies of Niobium Surface Oxide.**

4. **Surface Study of Niobium Buffered Chemical Polished (BCP) Under Conditions for SRF Cavity Production.**

5. **Characterization of Niobium Electropolishing (EP).**

Surface Topography Is a Critical Factor For Nb SRF Cavity





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

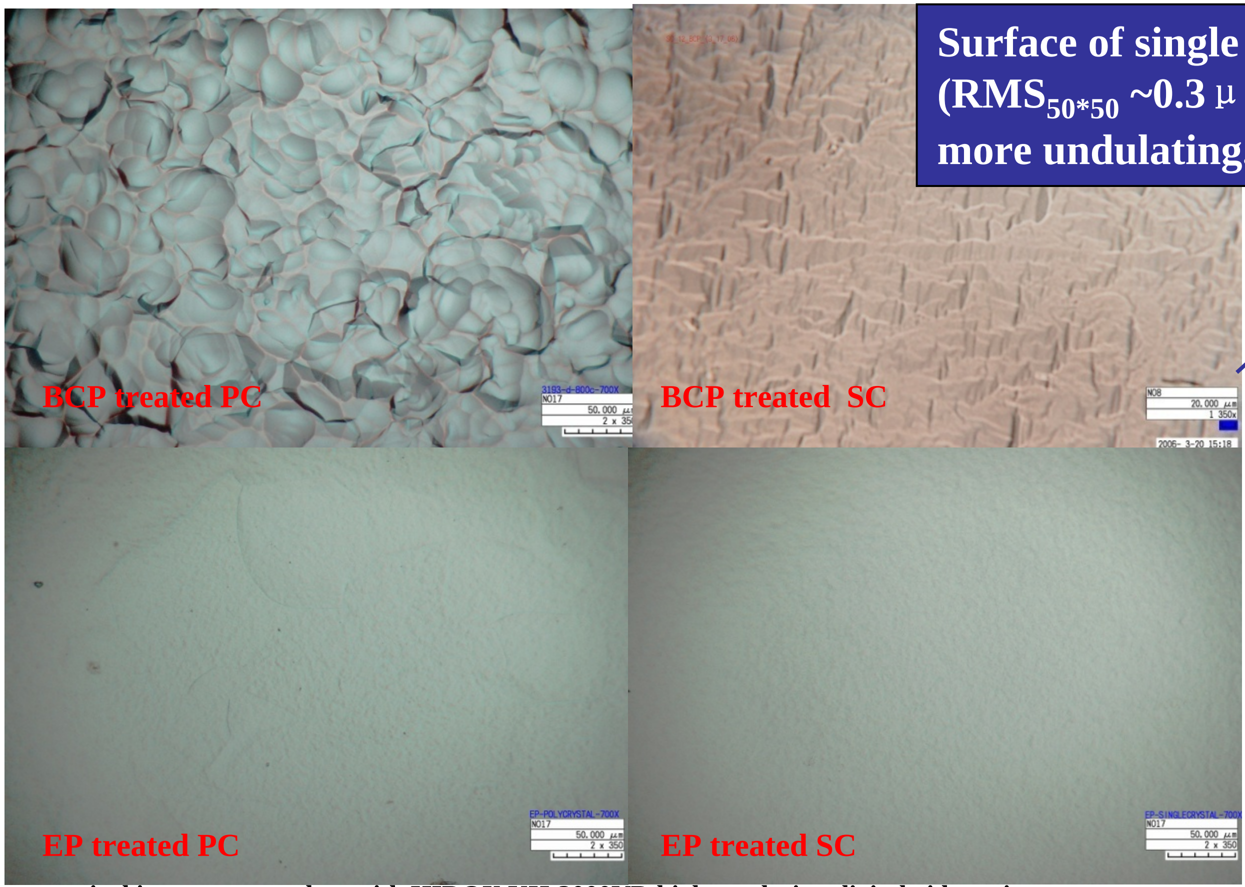
Magnetic field enhanced at the sharp protrusions. *Courtesy from J. Knobloch et. al, the 9th SRF workshop in Santa Fe, NM.*

Both vertical & lateral surface topography information are important for Nb cavity

Surface Topography of BCP/EP

Single Crystal and Polycrystalline Nb

Surface of single crystal BCP (RMS$_{50*50}$ ~0.3 μm) appears more undulating.

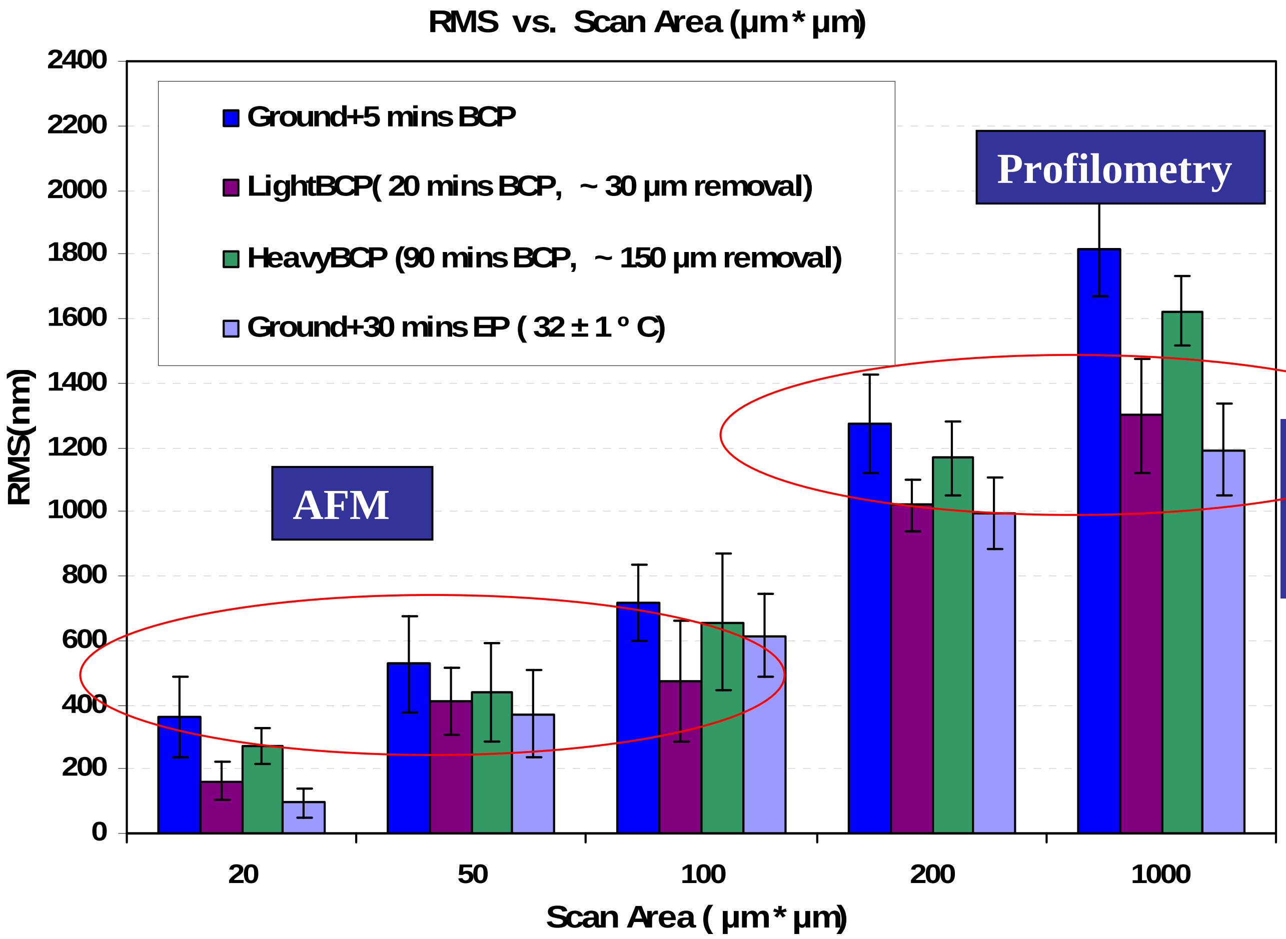


The above optical images were taken with HIROX KH-3000VD high resolution digital video microscopy system

Compared with EP treated poly-Nb (RMS$_{30*30}$ ~0.34 ± 0.11 μm, 50 μm × 50 μm), grain boundaries and other features of BCP treated poly-Nb are heavily etched (RMS$_{30*30}$ ~1.6 ± 0.42 μm, 50 μm × 50 μm)

EP single crystal surface <0.1 μm RMS$_{50*50}$ values (* well -control condition)

RMS Roughness Alone Is Not Sufficient to Characterize Nb Surface Topography



RMS measurements are scale dependent.

$$RMS = \sqrt{\frac{1}{n}\sum_{i,j}(z_{i,j} - \bar{z})^2}$$

Useful to get the average information about a surface variation .

No information about the lateral dimension of surface features.

Power Spectral Density (PSD) Provided a Promising Solution

$$PSD(f_x, f_y) = \lim_{L \to \infty} \frac{1}{L^2} \left| \int_{-L/2}^{L/2} \int_{-L/2}^{L/2} h(x,y) e^{-2\pi i (f_x x + f_y y)} dxdy \right|^2$$

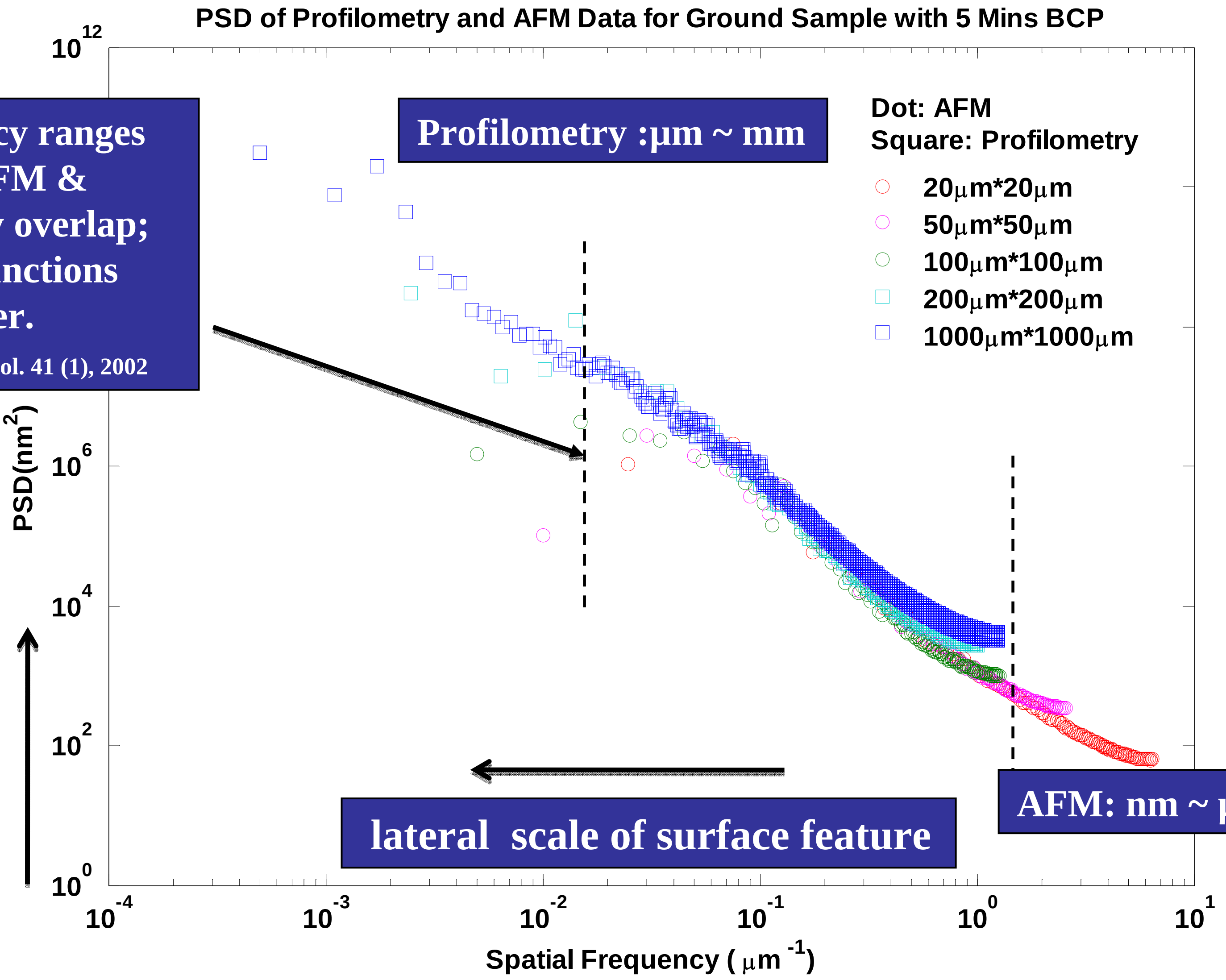
$$PSD(f_x)_N(m) = \left| (\frac{\Delta x}{N}) \sum_{n=0}^{N-1} h(x)_n \exp(-i2\pi nm/N) \right|^2 K(m)$$

➢**Square of the Fourier transform of the surface height data; describes how the height varies according to spatial frequency; gives information regarding both lateral and vertical roughness.**

➢**Related to RMS roughness, autocorrelation length and fractal dimension.**

➢**Maximum and minimum frequencies in data are set by the Nyquist limits(**$\left[\frac{1}{2N\Delta x}, \frac{1}{2\Delta x}\right]$**).**

PSD Allows Integration of the Nb Surface Topographic Measurements from AFM to Profilometry


PSD of Profilometry and AFM Data for Ground Sample with 5 Mins BCP

The spatial frequency ranges corresponding to AFM & profilometry largely overlap; the different PSD functions agree with each other.

A. Duparré, et. al., Appl. Opt. Vol. 41 (1), 2002

Profilometry :µm ~ mm

Amplitude of surface height.

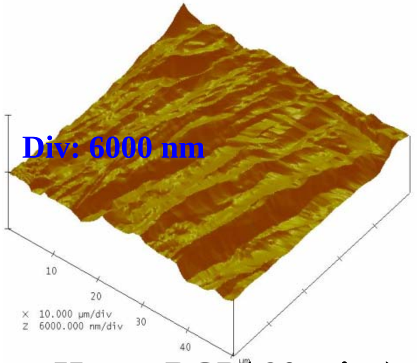
lateral scale of surface feature

AFM: nm ~ µm

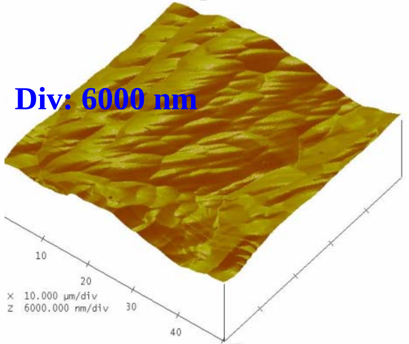
H. Tian, G. Ribeill, C. Reece, M. Kelley. Proceedings of 13th Workshop on RF Superconductivity

Surface Topography of Niobium Samples after BCP/EP Treatment

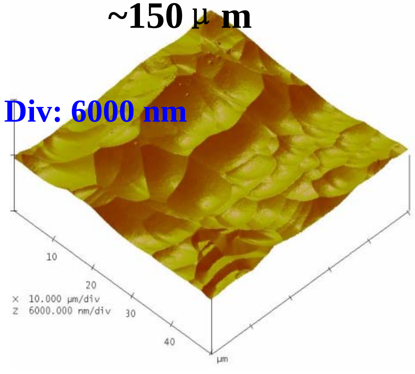
Ground



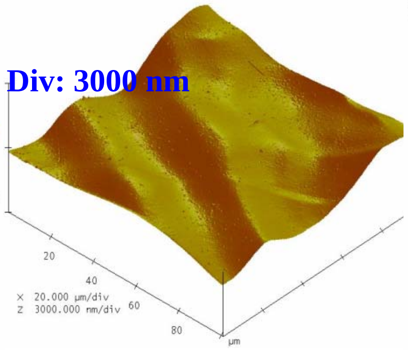
light BCP(20 mins) ~30 µ m

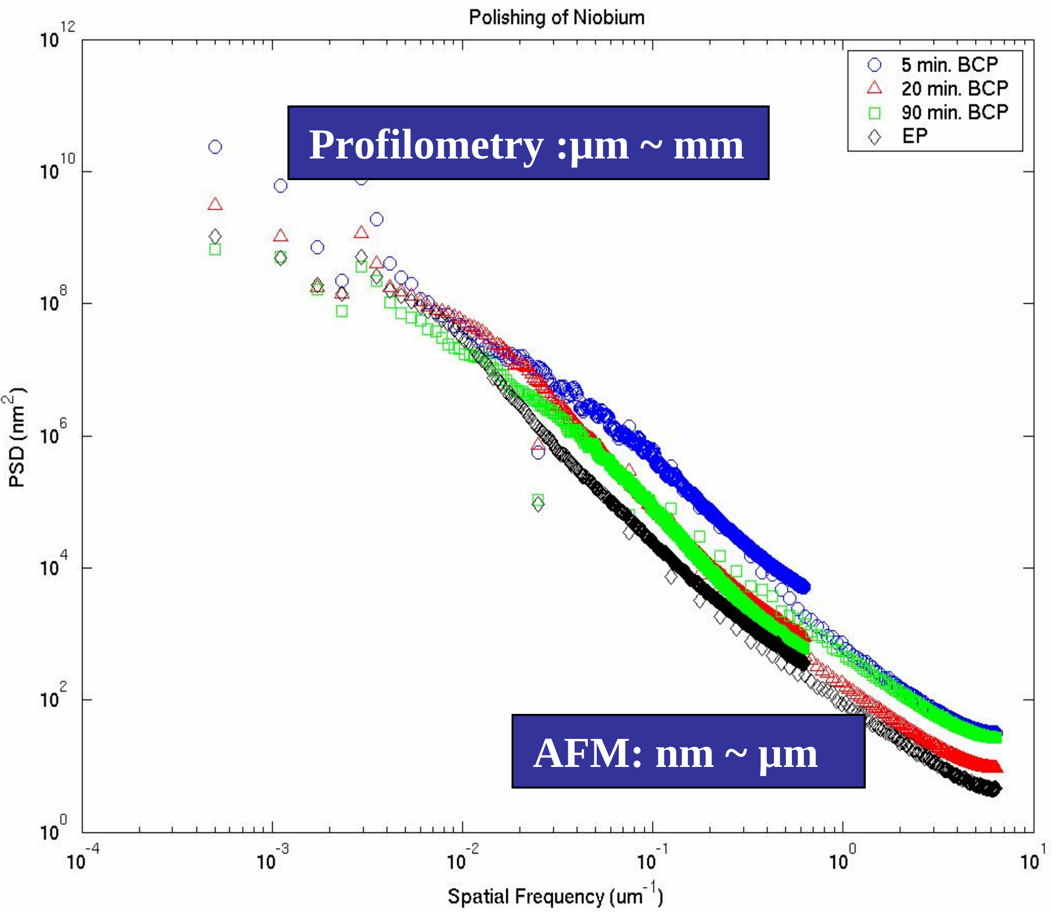


Heavy BCP(90 mins) ~150 µ m



EP (30 mins)~15 µ m





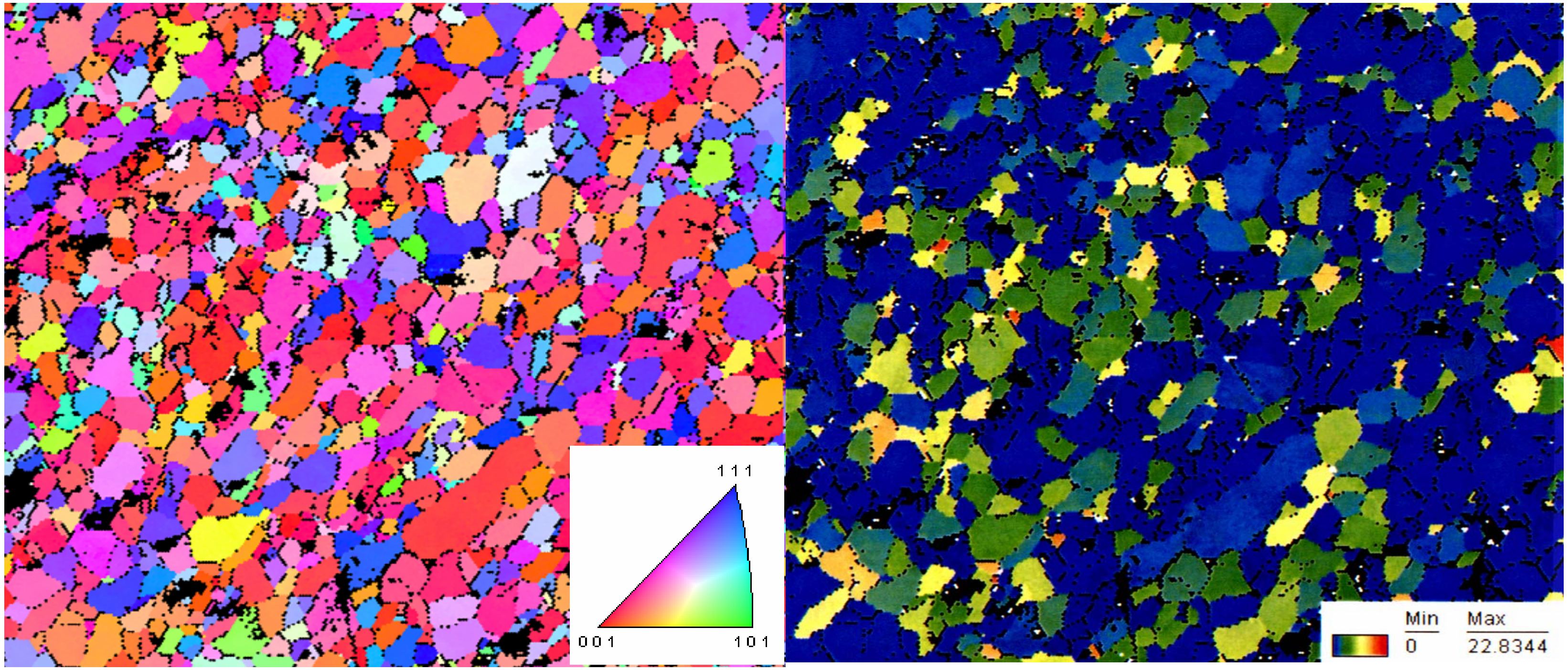
Profilometry :µm ~ mm

AFM: nm ~ µm

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

EP has smaller PSD and the longest correlation length- better macro & micro polish.

Electron Backscattering Diffraction Clearly Revealed Surface Grains Sizes & Orientations aft. BCP



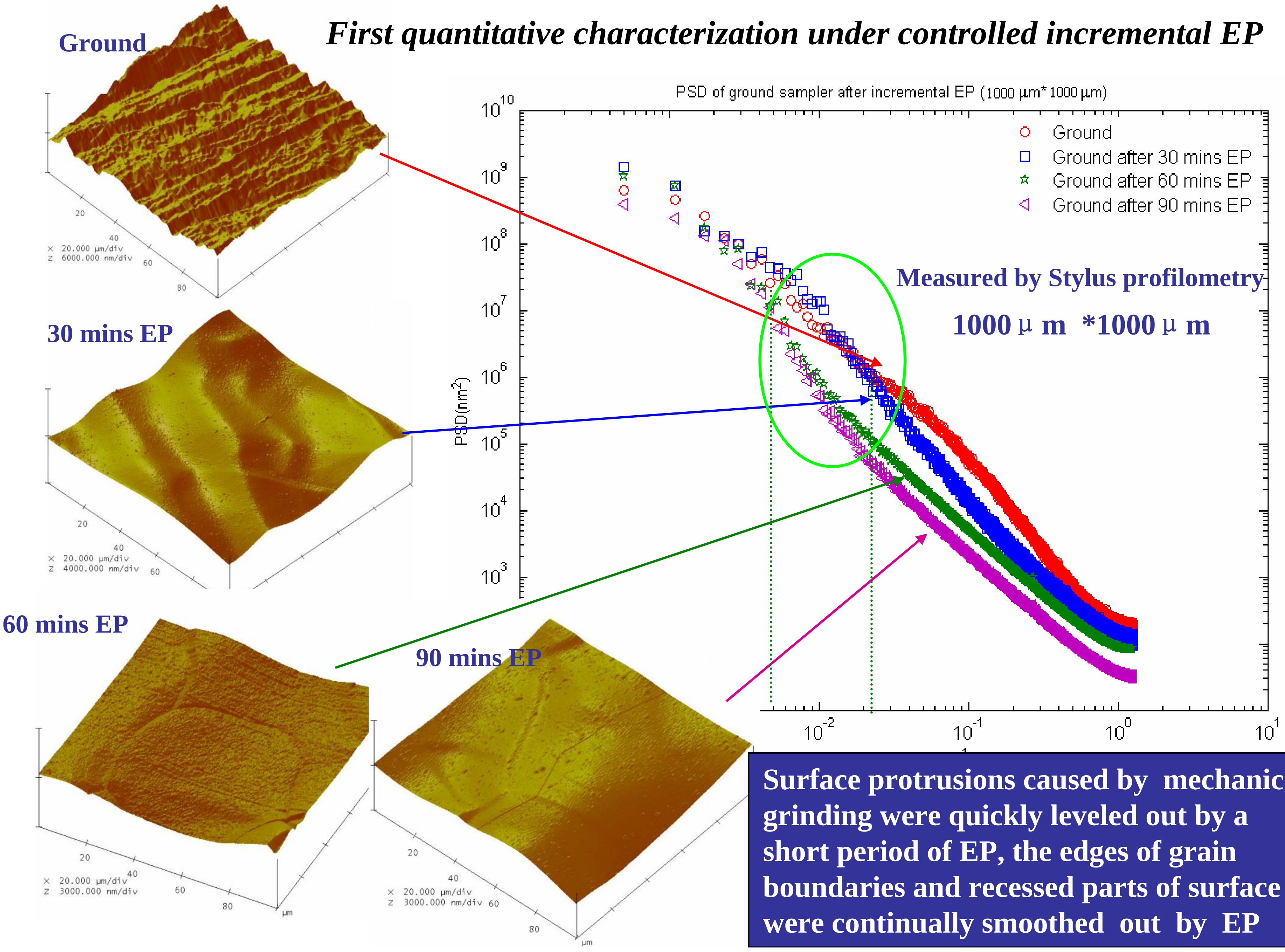
Grain orientation & mis-orientation deviation map(1.5 mm * 1.5 mm)

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.

The dominant grain orientation for BCP treated polycrystalline Nb is [100] .

Nb Surface Topographic Variation Under EP

First quantitative characterization under controlled incremental EP



Ground

30 mins EP

60 mins EP

90 mins EP

Measured by Stylus profilometry

1000 µ m *1000 µ m

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

Summary and Future Work

The first use of power spectral density (PSD) in quantitatively characterizing the surface topography of niobium has been demonstrated. The effect of preparation variables on Nb surface topography has been studied systematically for the first time.

Longer BCP removes the mechanical damages but leaves a rougher surface. First quantitative characterization under controlled EP shows longer EP smoothes out the surface variations caused by different pre-treatments.

Future:

In parallel with EP study, a systematic Nb surface topography study is required for optimizing EP process.

Understand at what scales roughness is most important to cavity performance, then optimize process to those requirement.

Outline: XPS

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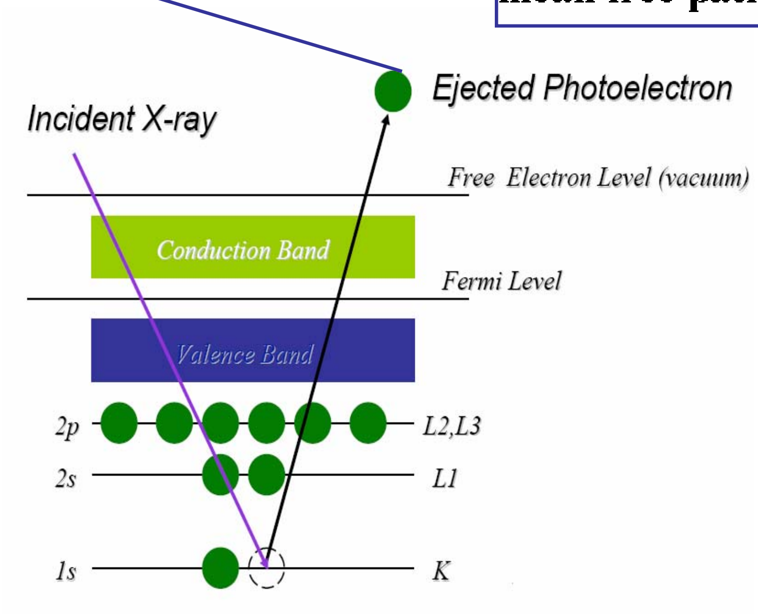
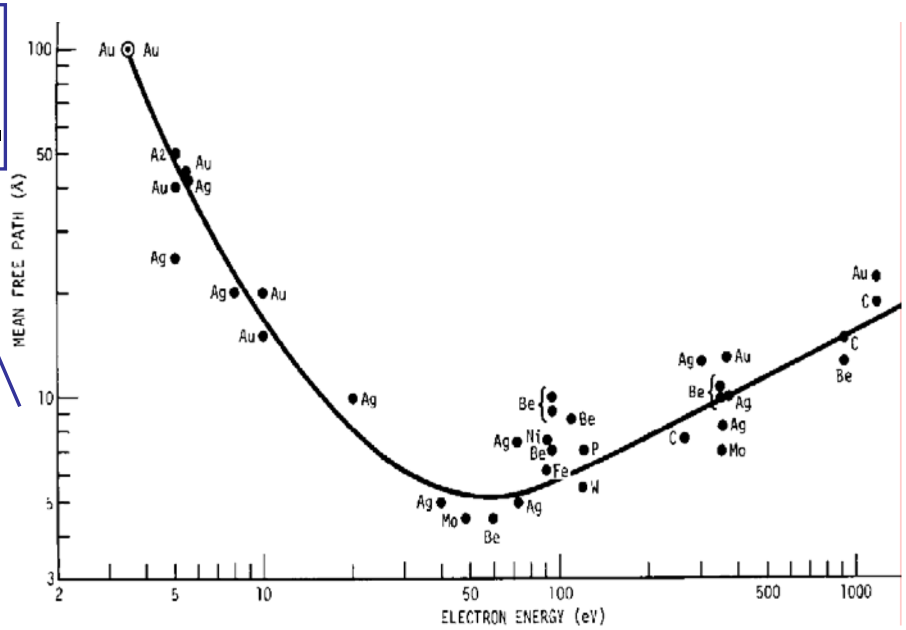
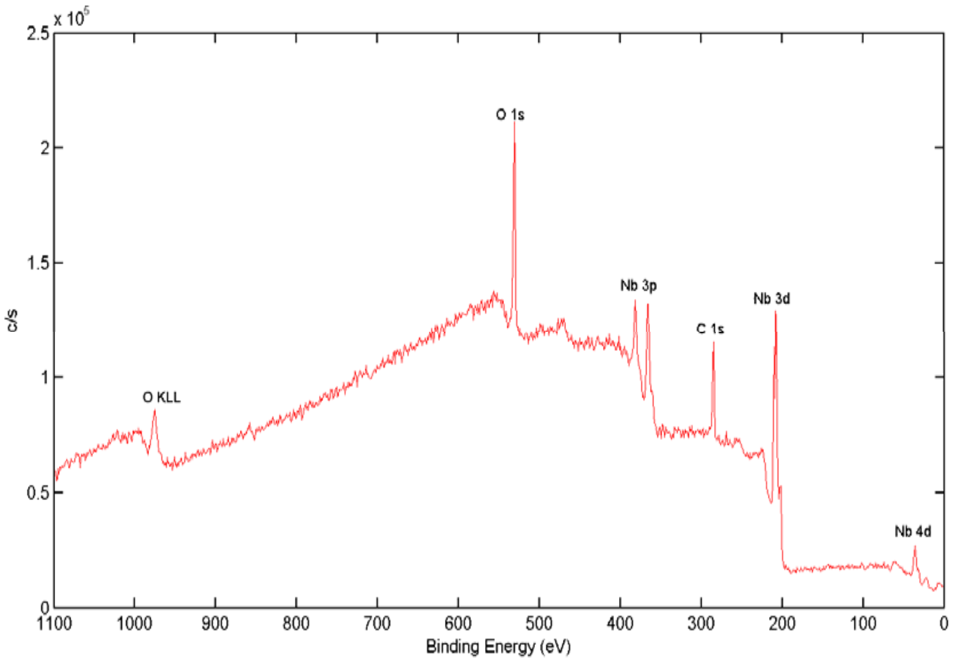
X-ray photoelectron spectroscopy (XPS)

$KE = h\nu - BE - \Phi_w$

Electrons ejected from depth < ~ 1 inelastic mean free path (IMFP)



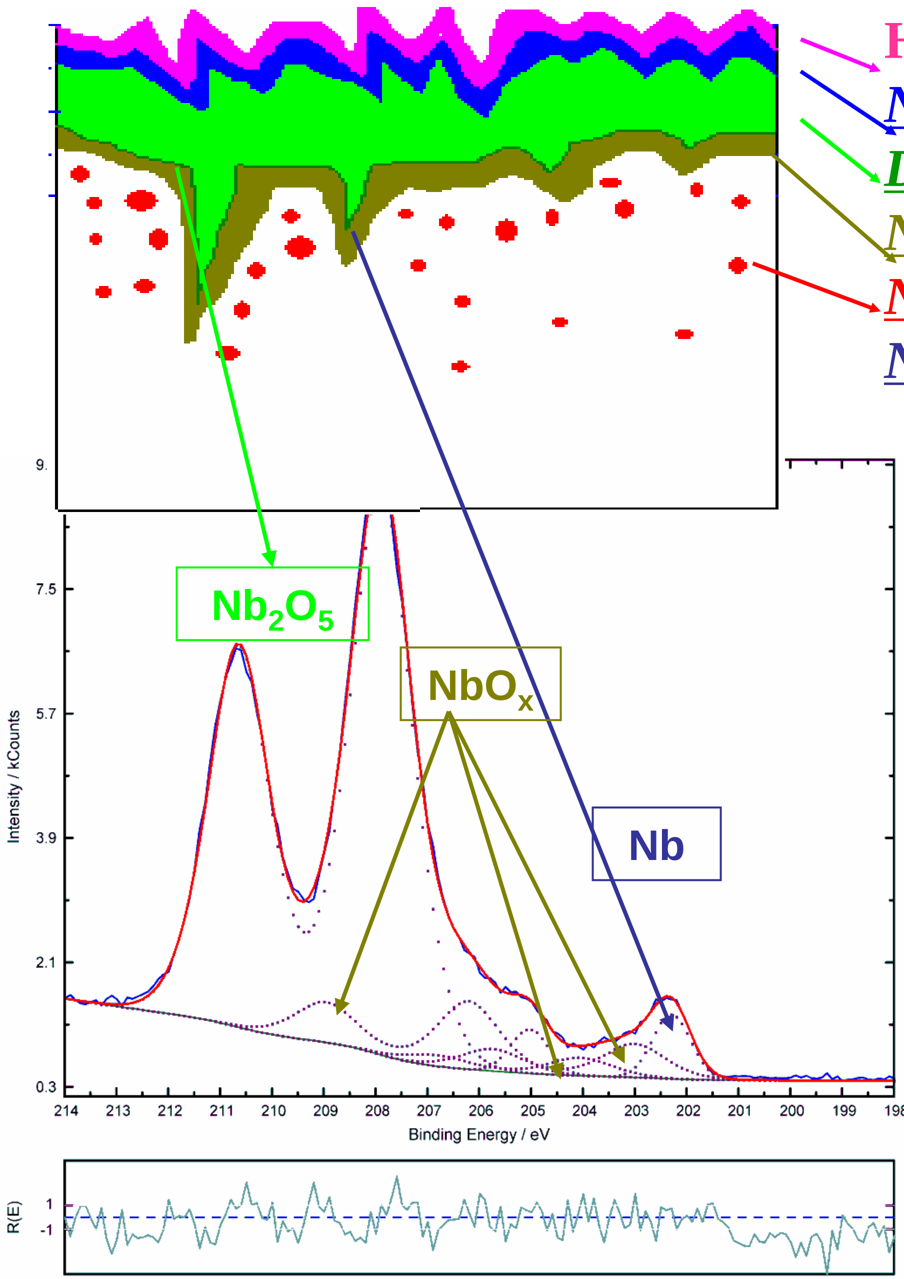




What information can you obtain from XPS?

- Identification of elements near the surface and surface composition
- Local chemical environments
- Oxidation states

Introduction



Hydrocarbons & impurities (<1nm)

Nb hydroxides (< 1 nm,?)

Dielectric Nb_2O_5(3~8 nm)

$NbO_{x-(0.2 < x < 2)}$-metallic(1~2 nm,?)

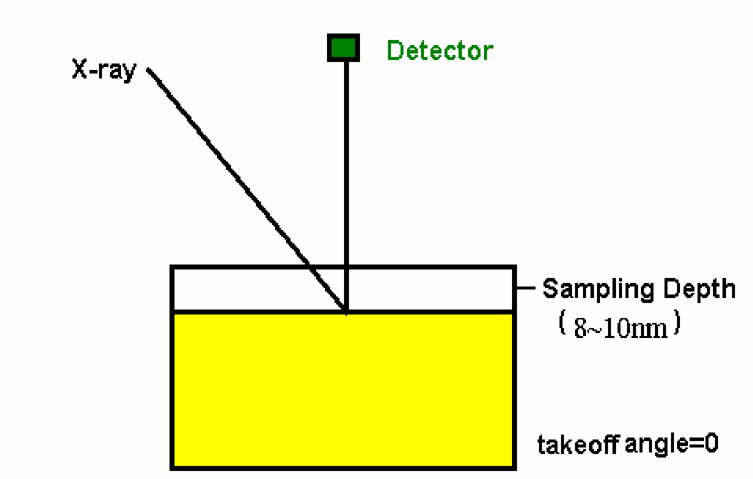
NbO_x precipitates (0.02 < x < 0.2,?)

Nb (RF penetration depth : ~ 35 nm)

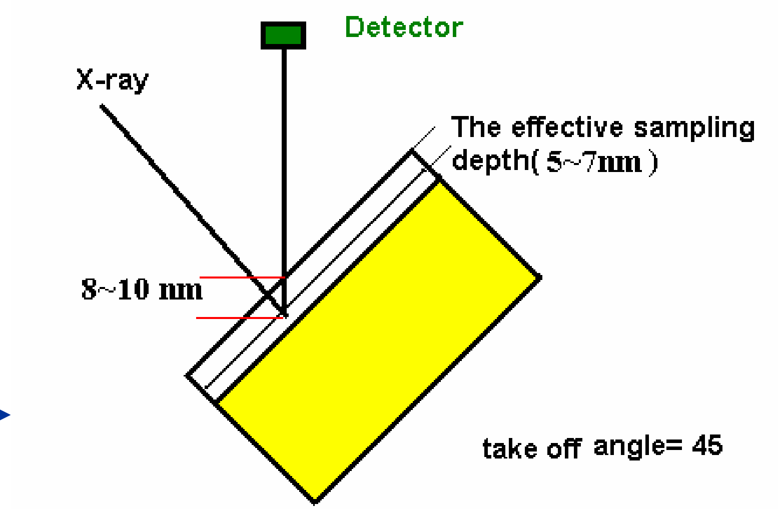
The surface chemistry of Nb is dominated by the high reactivity to oxygen; the outermost oxides layers are always found to be Nb_2O_5.

Suboxides in various combinations and morphologies are proposed to be between the Nb_2O_5 and the underlying metal.

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



AR

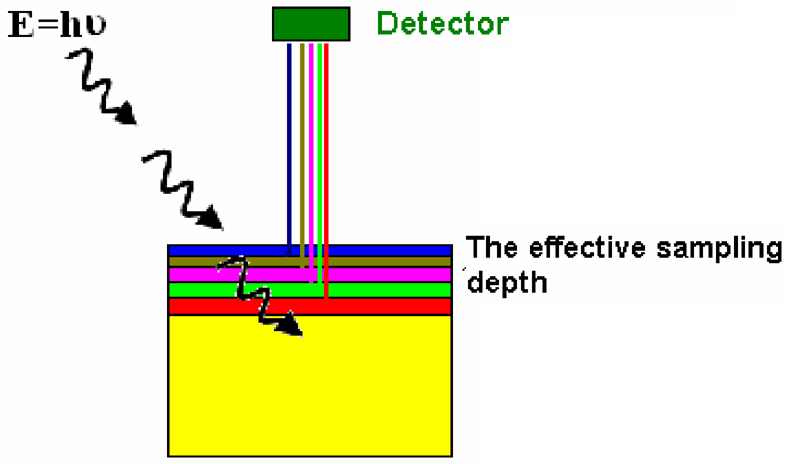


At the normal incident angle **(Nb_2O_5: 3 ~ 8 nm+ metal)**

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

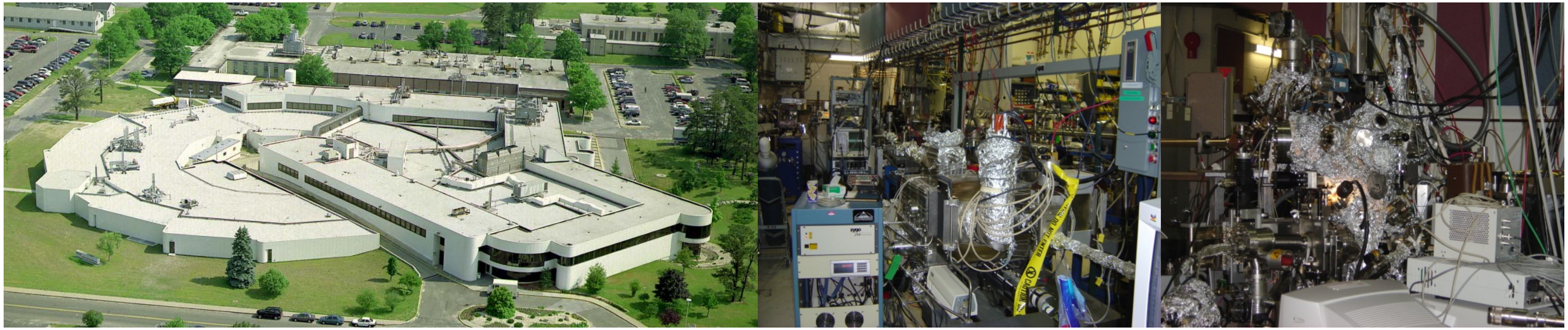
E=h υ (eV)	Sampling Depth (nm) Nb_2O_5
300	2.8
550	4.2
750	5.3
1254(Mg)	8.1
1486(Al)	9

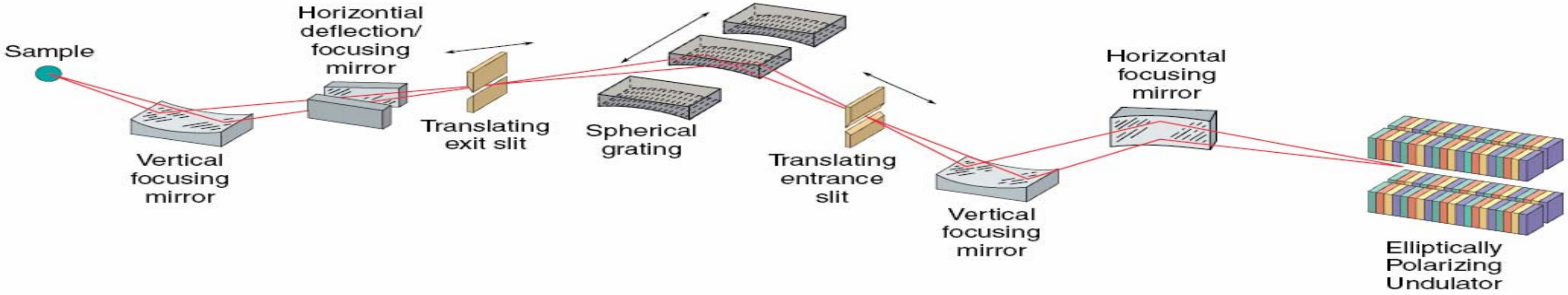
ER



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

Energy Resloved XPS -BNL, NSLS, X1B



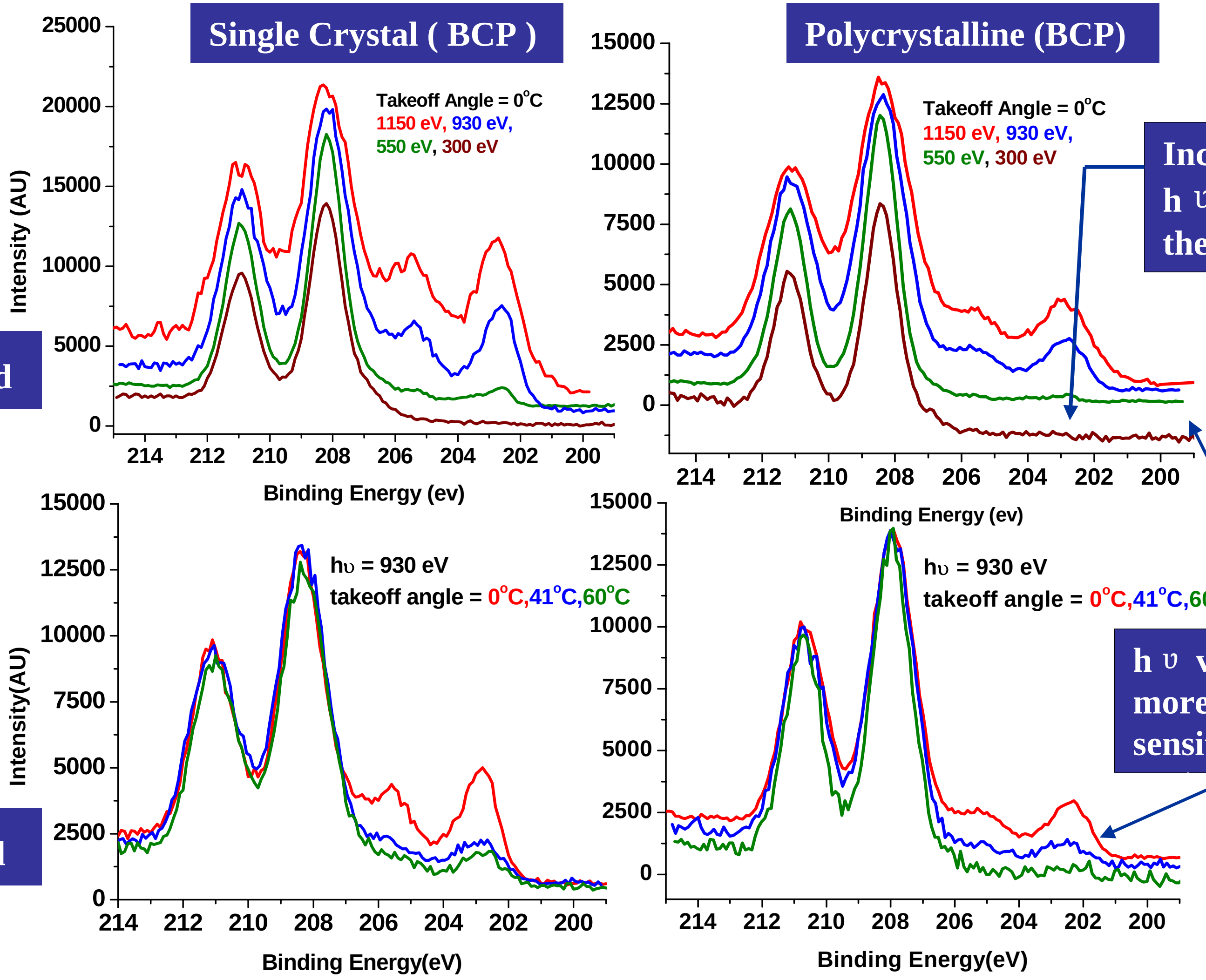


h υ = 300 eV, 550 eV , 750eV(100 ~ 1600 eV)- energy resolved XPS

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.

Depth Profiling : Angle Resolved *vs.* Energy Resolved XPS



Energy Resolved

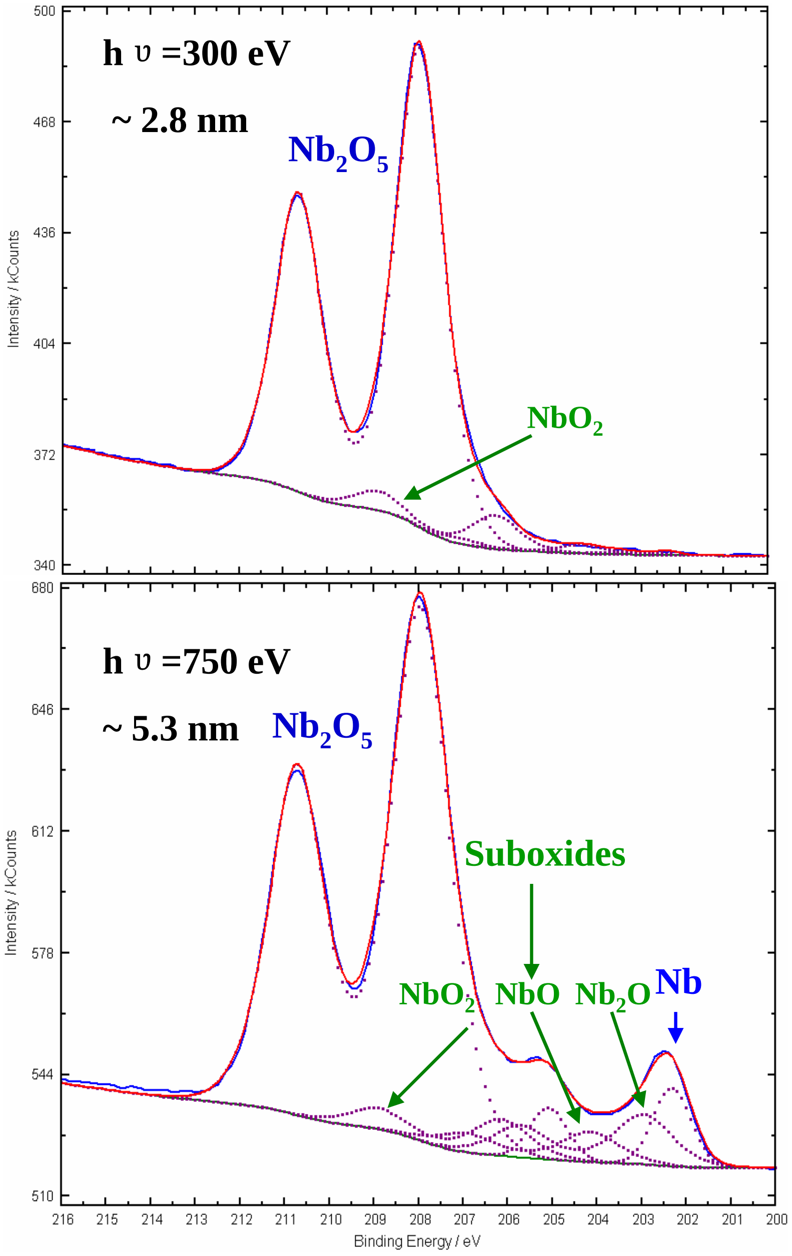
Angle Resolved

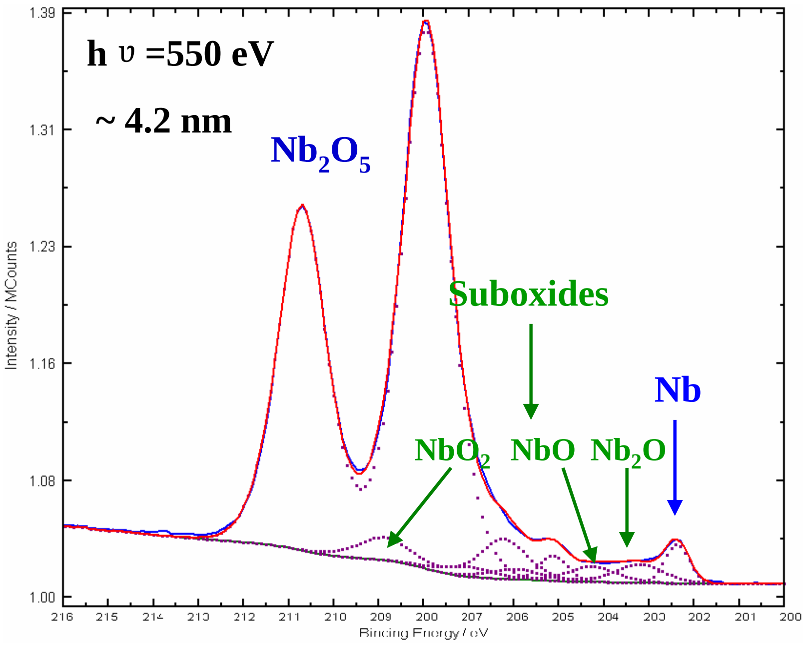
Increasing h υ ,“see though” the surface Nb_2O_5

h υ variation is more surface sensitive than angle

Variable photon energy XPS probes the near-surface composition more incisively and provides better depth analysis than angle-resolved XPS.

Niobium Oxide Profiling of Single Crystal Nb by Energy Resolved XPS

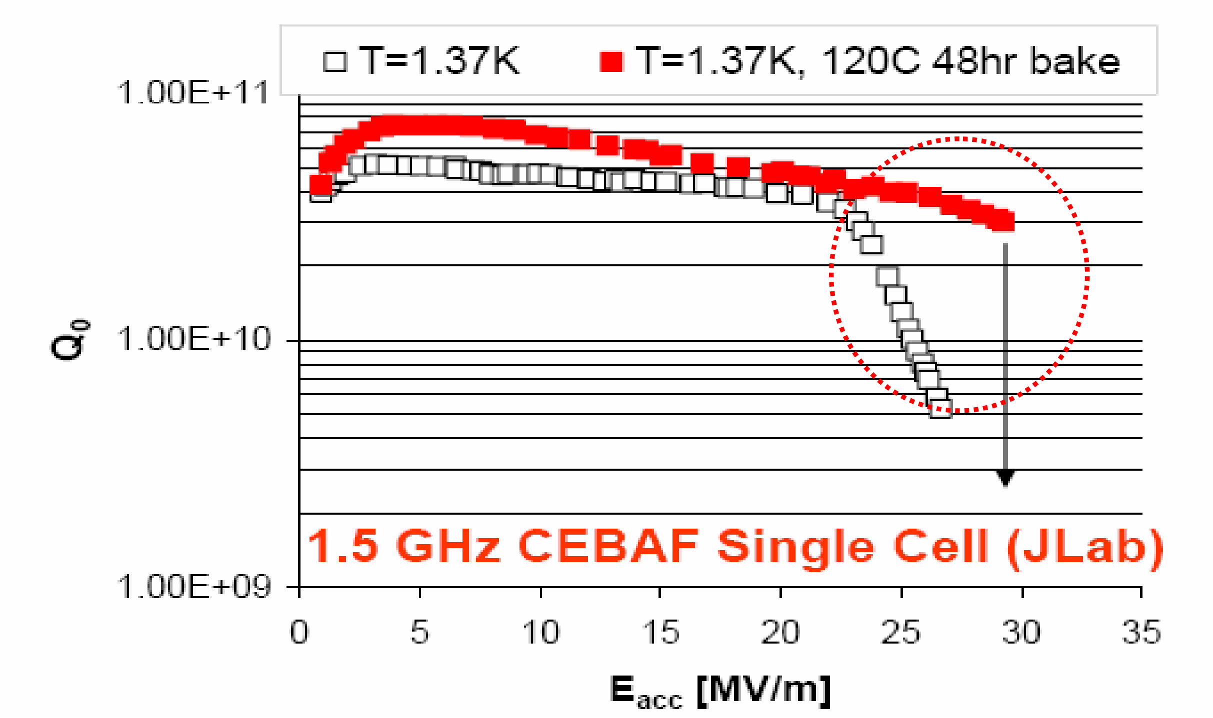




Energy Resolved XPS clearly reveals that between 2~3 nm Nb_2O_5 and the underlying metal is the structural transition zone of suboxides (NbO_2, NbO and Nb_2O) with a thickness not larger than one nanometer.

Low Temperature “in situ” Baking & Q-Drops

Low	Medium	High



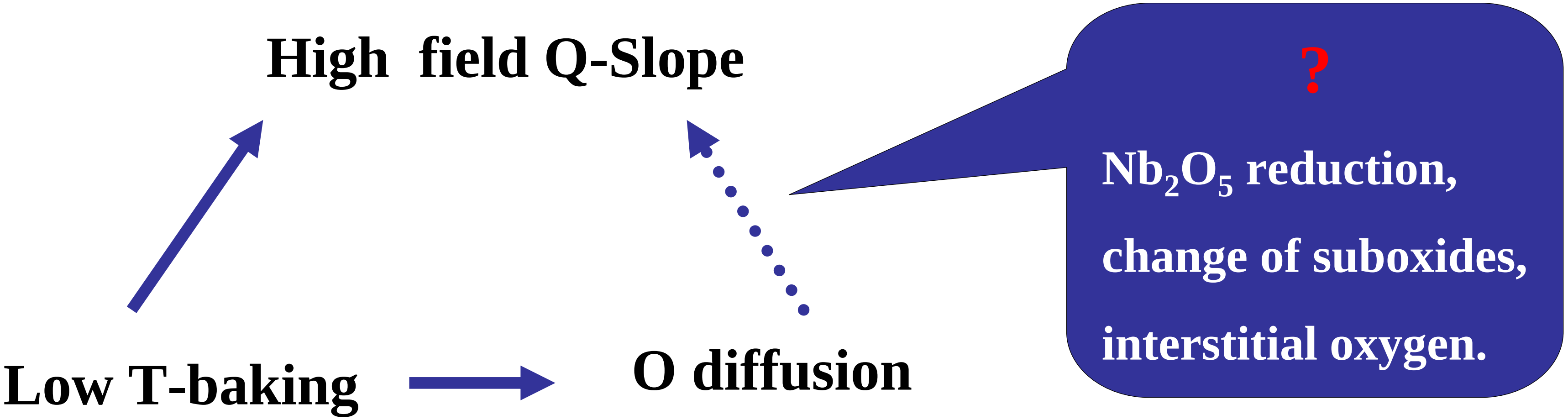
Q_0 *vs.* E_{acc} for a niobium single cell cavity before & after baking. Courtesy of G. Ciovati , Jefferson lab

Enhancement @ low field	**Slight flattening @ medium field**	**Strong improvement @ High field**

Q-drops & improvement @High Field after Low T baking: theory & question

	Q- drop	Improvement (after low T baking)
Theory 1	Tunnel exchange at Nb-Nb_2O_5 interface	Nb_2O_5 (localized states) reduction ? Additional HF –new oxides layer, preserve performance
Theory 2	Magnetic field enhancement (β_M H) : correlation exist between Q-drop origin & surface roughness	Hc increase ? Before/after baking , similar Q- drops /improve for BCP & EP , polycrystal & single crystal cavities
Theory 3	Oxygen (Nb_2O_5 , sub-oxides, interstitial oxygen)	R_{BCS} , ℓ decrease related to baking temperature (time) ? Suboxides? Interestital oxygen

Possible Mechanisms about Q-drop & Low-T Baking



High field Q-Slope

Low T-baking

O diffusion

?

Nb_2O_5 reduction,

change of suboxides,

interstitial oxygen.

Low temperature (100~140°C, 12~ 24 hrs) baking at high vacuum becomes an indispensable process to be applied to high RRR bulk niobium cavities (BCP/EP, SC/ PC). The performance enhancement from baking remains even after several days of air exposure.

Present Baking Recipes :

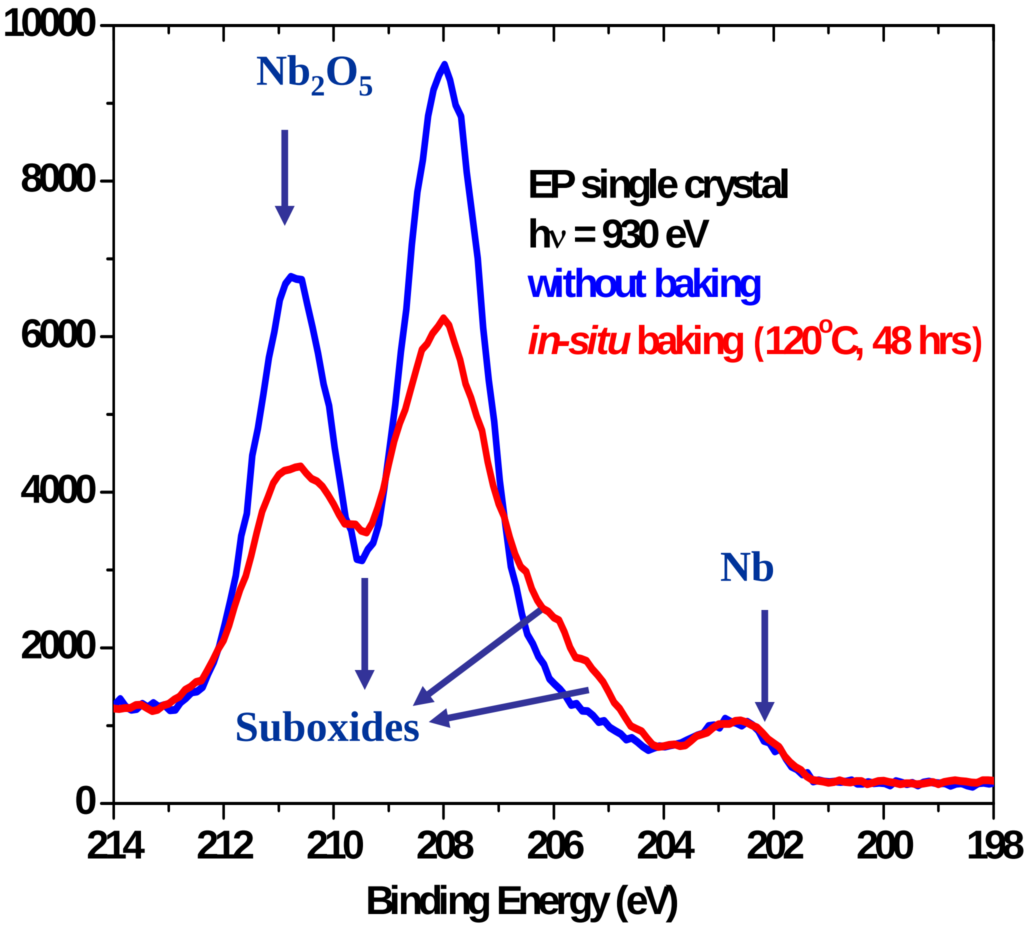
Classic: 110~120°C (< 150°C), 24~48 hrs, high vacuum

B. Visentin et, Saclay: 145°C, 3 ~6 hrs, Air; 120°C, >24hrs, Ar.

G. Ciovati et, J-lab: 120°C, 3~6 hrs, large grain, high vacuum

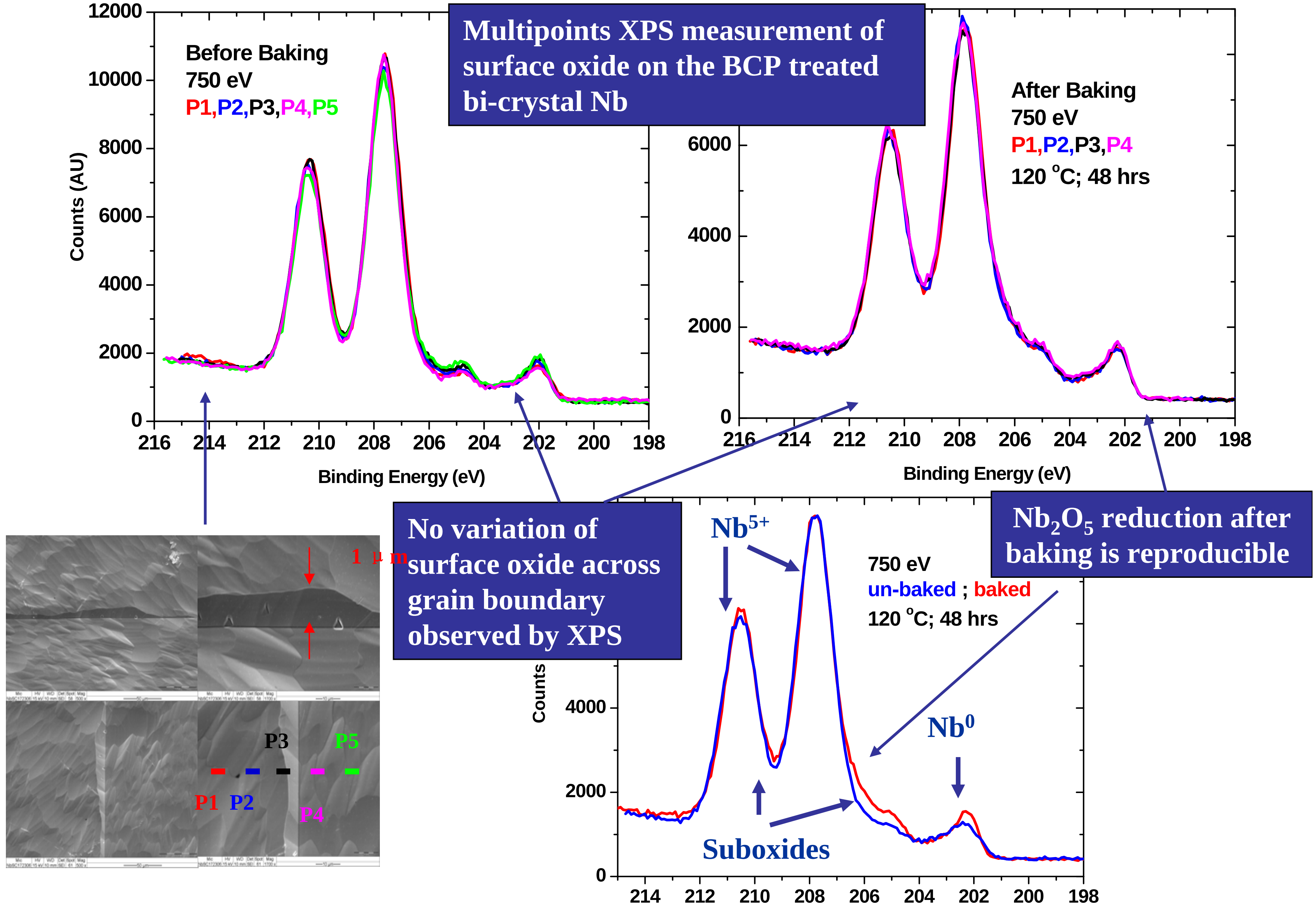
Niobium Surface Oxide

Before/ After Low T Baking



XPS study about BCP/ EP Nb surface show that Nb_2O_5 is partly transformed into suboxide.

Reproducibility Study of Nb Oxide Before/After Baking

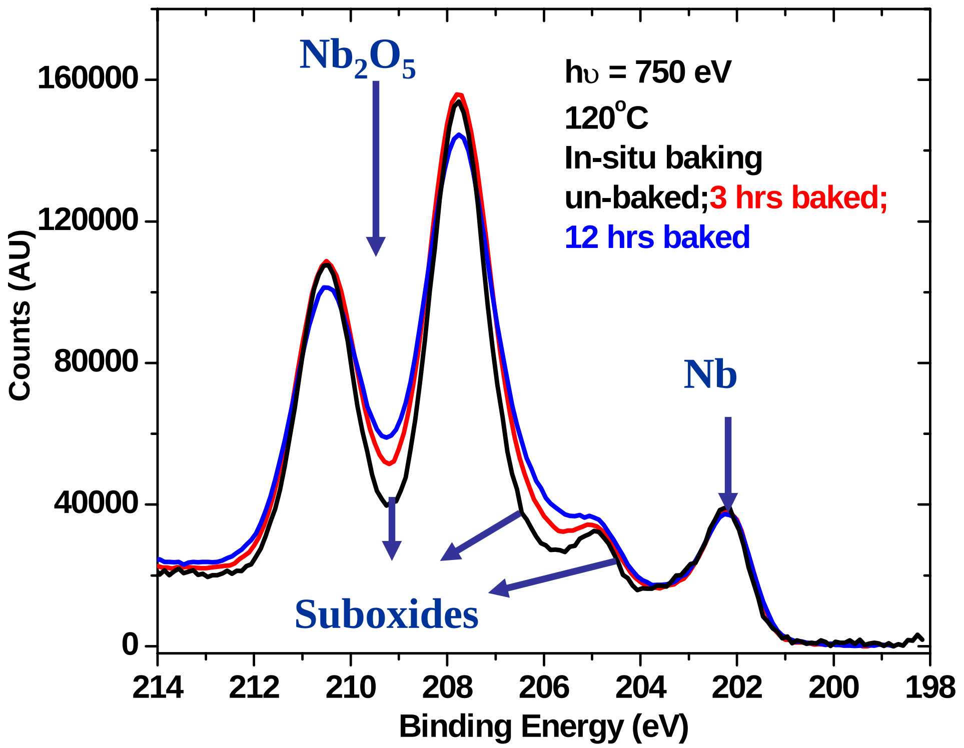


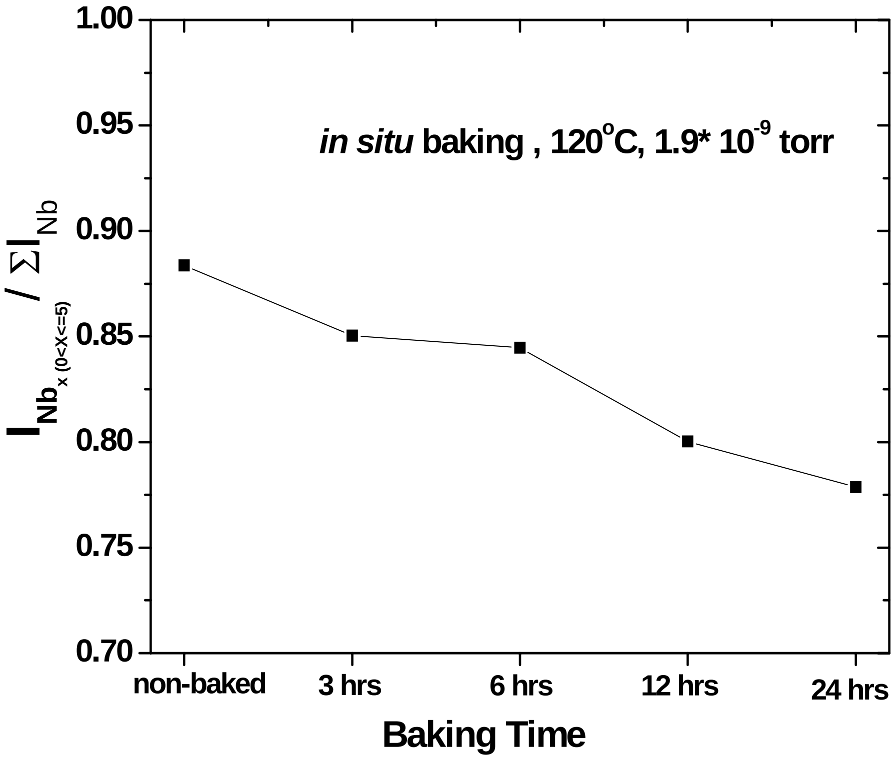
Multipoints XPS measurement of surface oxide on the BCP treated bi-crystal Nb

No variation of surface oxide across grain boundary observed by XPS

Nb_2O_5 reduction after baking is reproducible

Nb_2O_5 Reduction Increases with the Baking Time



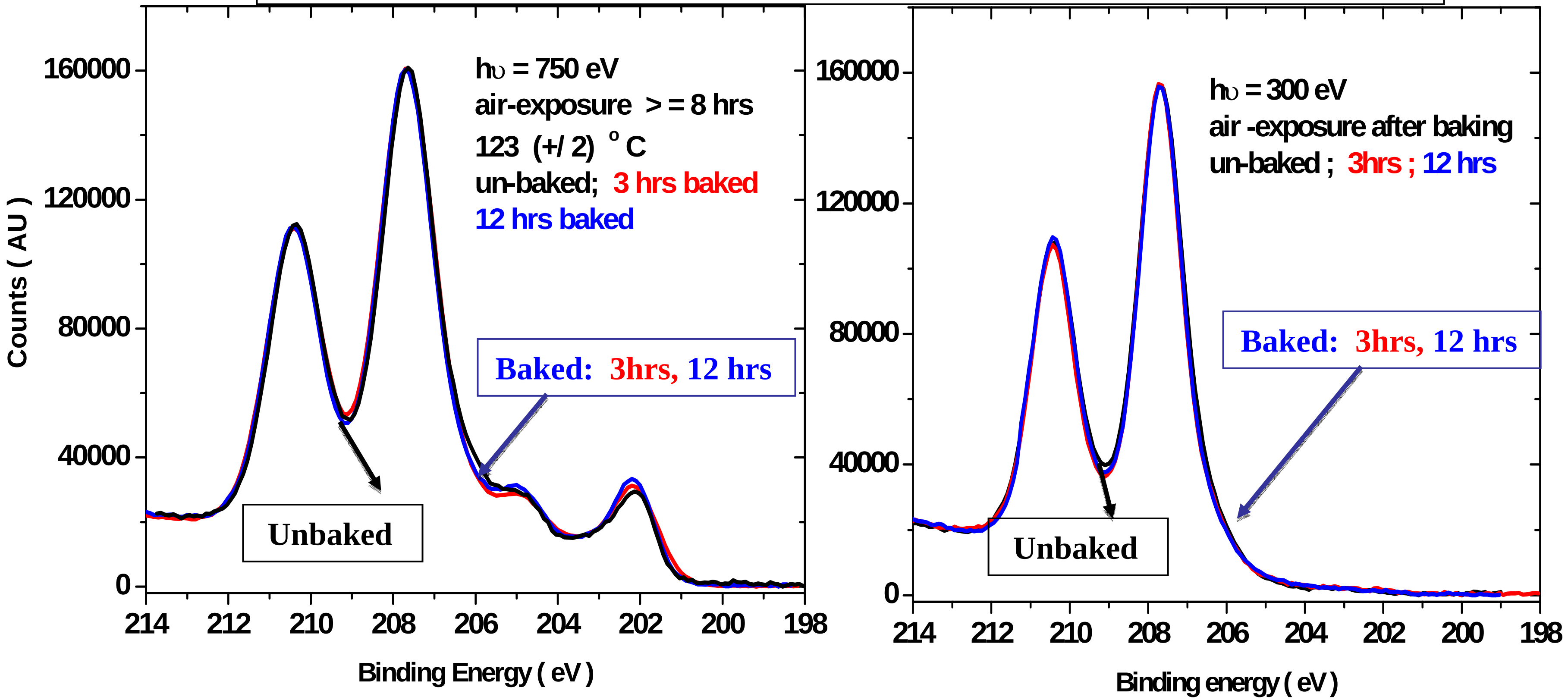


More Nb_2O_5 transforms into suboxides with the baking time

$I_{\text{total oxides}} / I_{Nb}$ decreases linearly with baking duration -surface oxide layer become thinner.

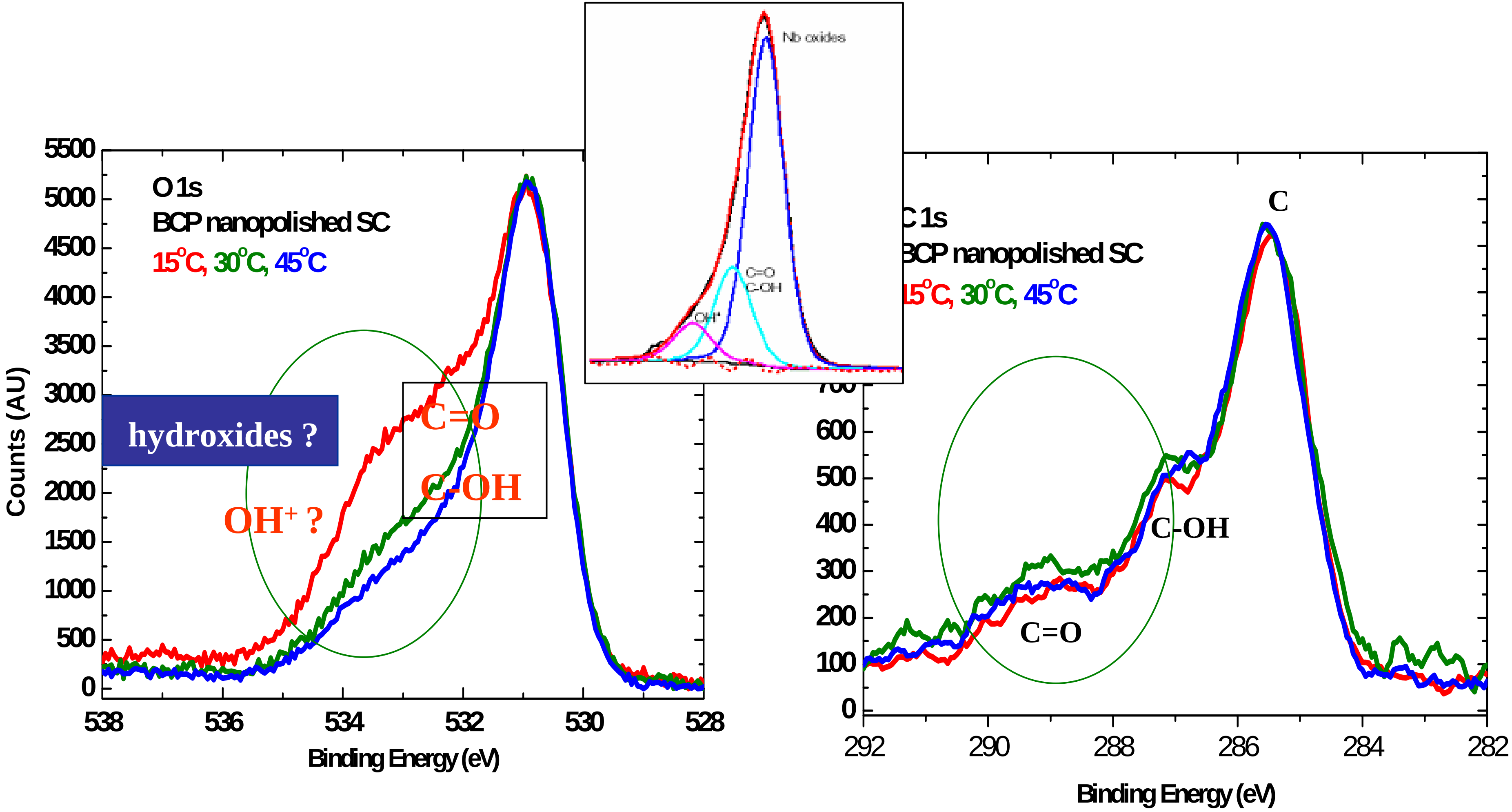
Air Exposure “Recovers” Nb Surface Oxide

The samples in this study were treated at the same condition: BCP 1:1:2, 120°C, 12hrs, air-exposure ~8hrs



No significant change in surface oxide layer can be observed after air exposure

Where is the Hydroxides-ARXPS?



hydroxides ?

OH^+ ?

C=O

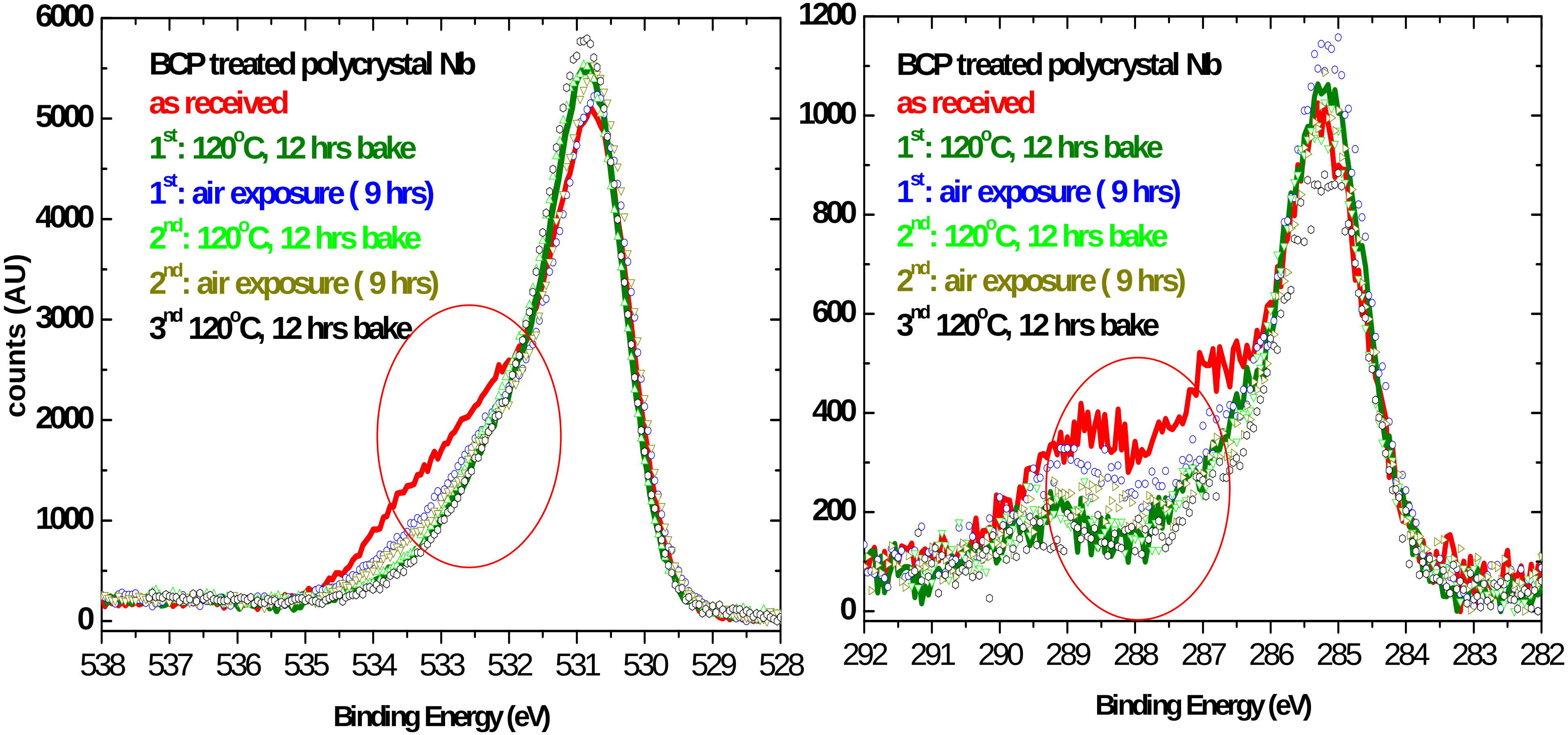
C-OH

C-OH

C=O

A less than nm hydroxide layer seems to lie below the hydrocarbons & impurities by ARXPS .

Where Does the Hydroxides Go After Baking & Air-exposure ?



Low-T baking helps to "remove" the top hydrocarbon layer?

Systematic Surface Oxide Study in Parallel with Practical SRF Cavities Baking Process

After baking, Nb_2O_5 is partially transformed into suboxides, the total oxide layer becomes thinner. But upon air-exposure, the change of oxide layer observed after baking disappeared . Cavities still kept good performance, therefore the suboxides created by in situ bake is irrelevant to SRF cavity performance.

Longer baking time at 120°C increases Nb_2O_5 reduction & transformation Large grain cavities after 3 hrs baking shows performance improvement, the reduction of Nb_2O_5 is irrelevant to SRF cavity performance.

Comparing with 120°C baking, higher baking temperature (160°C) helps more oxide transformation; Air baking produce thick oxide layer.

XPS studies show that the changes in the niobium oxide layer caused by low -T baking appears to not play a big role in cavities performance.

H.Tian, C. Reece, M. Kelley, A. DeMasi, L. Pipe, K. Smith, Proceeding of 13th workshop on RF superconductivity

Summary and Future Work

The ERXPS is used to probe Nb near-surface composition for the first time. It confounds the effect of surface roughness and provides better depth analysis than ARXPS .

The systematic surface oxide study show that the changes in the niobium oxide layer caused by low T baking does not relate with the observed performance improvement of niobium cavities.

Future work:

An explicit layer structure and discrete phases of suboxide requires further study.

Where does the oxygen go after baking-dissolution into metal?

Detailed SIMS depth profile is required before/after baking-O,H…

Re-baking study is required to investigate the possible enrichment of interstitial oxygen.

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What is Buffered Chemical Polish (BCP)

a most commonly employed Nb cavity surface treatment

1:1:1/1:1:2 (volume) mixture of HNO_3(69%) HF(49%) & H_3PO_4(85%), 10ºC

$$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$$

$$2Nb + 5H_2O \rightarrow Nb_2O_5 + 10e^- + 10H^+$$

$$6Nb + 10HNO_3 \rightarrow 3Nb_2O_5 + 10NO + 10H_2O$$

$$Nb_2O_5 + 14HF \rightarrow 2H_6NbO_2F_7 + H_2O$$

$$Nb_2O_5 + 12HF \rightarrow 2HNbF_6 + 5H_2O$$

$$Nb_2O_5 + 10HF \rightarrow 2NbF_5 + 5H_2O$$

$$Nb_2O_5 + 10HF \rightarrow 2H_2NbOF_5 + 3H_2O$$

Possible chemical reactions involved

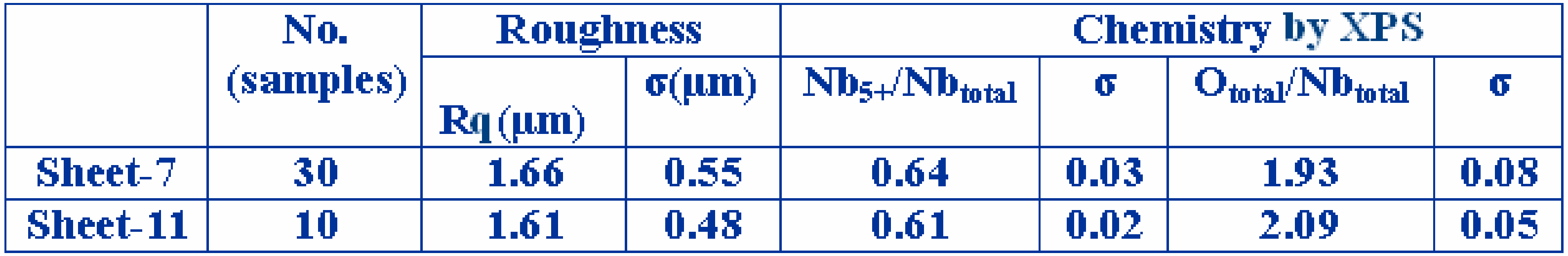
No a systematic surface study of BCP polycrystalline Nb has been done.

Different solution flow may cause a non-uniform surface finish.

First Reproducibility Studies of BCP Treated Polycrystalline Nb

What differences are due to experimental scatter?

Sample-to-Sample variation



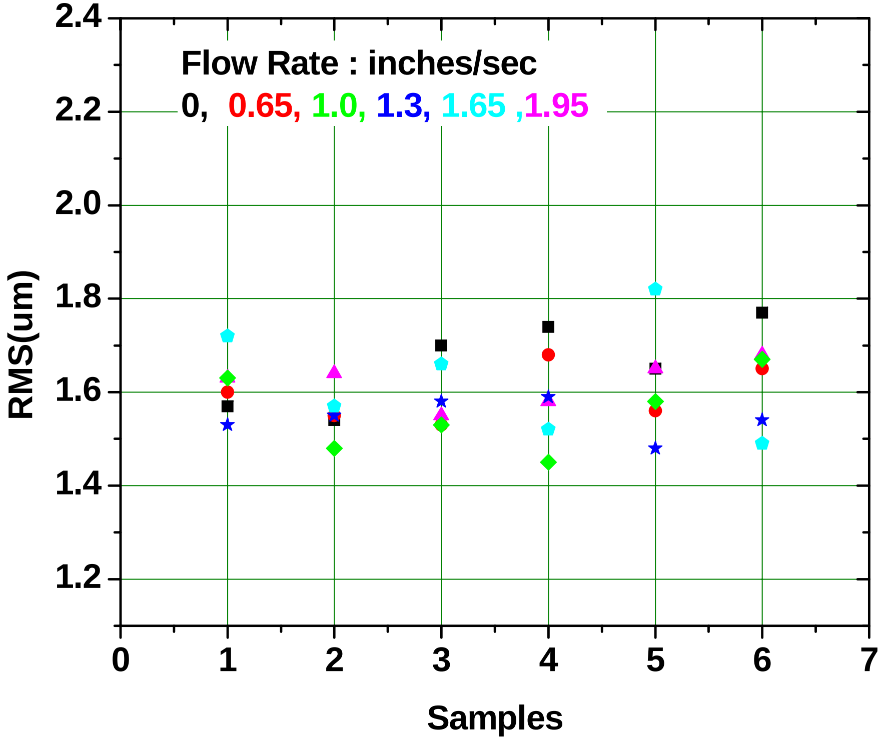
	No. (samples)	Roughness		Chemistry by XPS			
		Rq (µm)	σ(µm)	Nb_{5+}/Nb_{total}	σ	O_{total}/Nb_{total}	σ
Sheet-7	30	1.66	0.55	0.64	0.03	1.93	0.08
Sheet-11	10	1.61	0.48	0.61	0.02	2.09	0.05

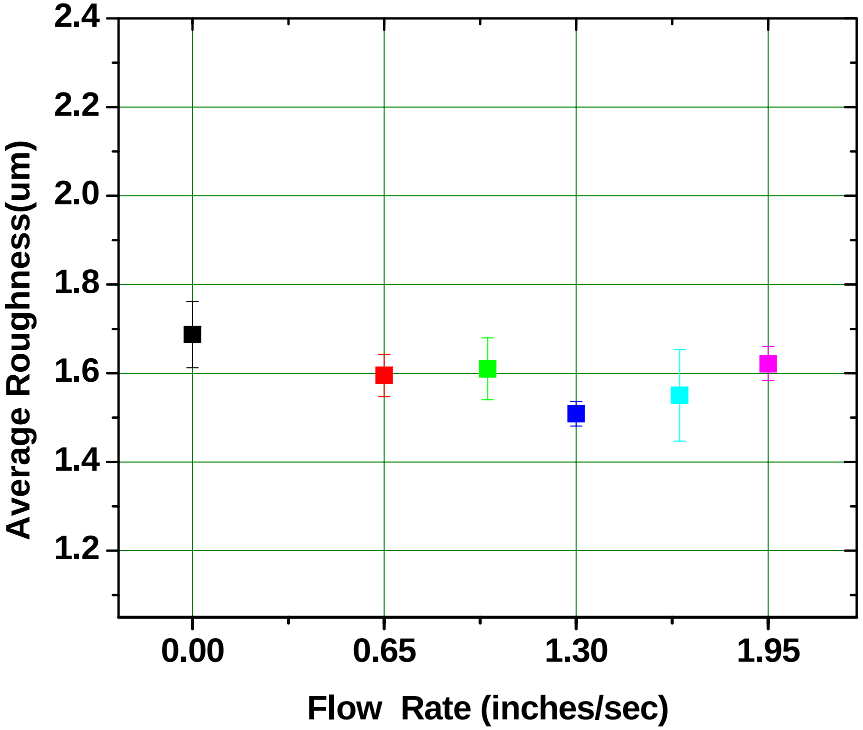
Batch-to-batch variation is comparable to sample-to-sample. Position-to-position variation within samples and sheet-to-sheet variation are less.

Roughness values and variation all exceed the few-nm escape depth of photoelectrons.

The average intensity ratios of O_{total}/Nb_{total} for each sample are much smaller than 2.5 (Nb_2O_5) .

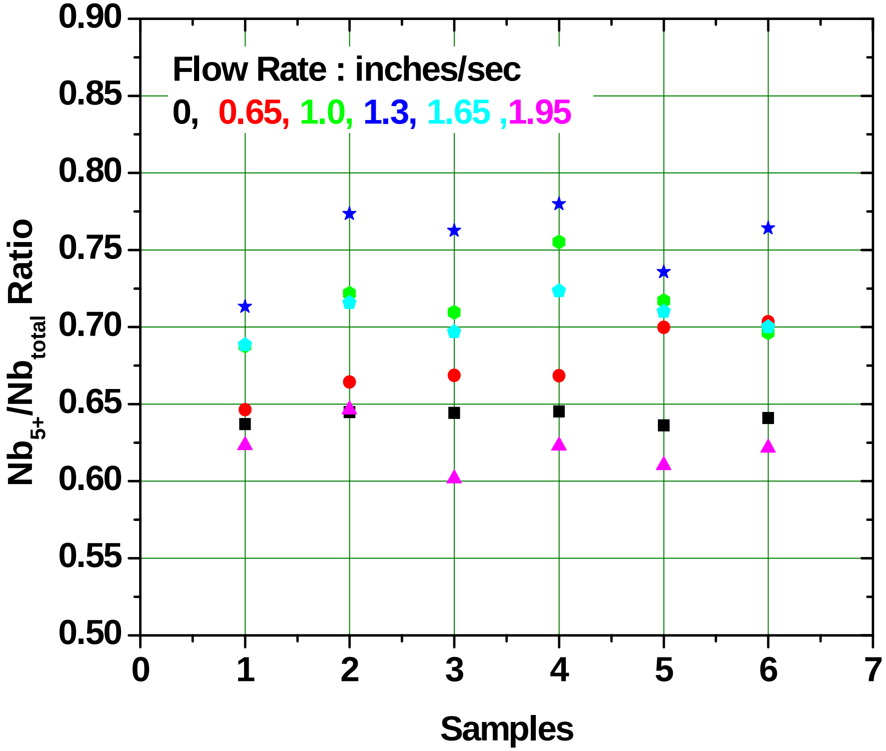
Flow Rate Dependence of Surface Topography

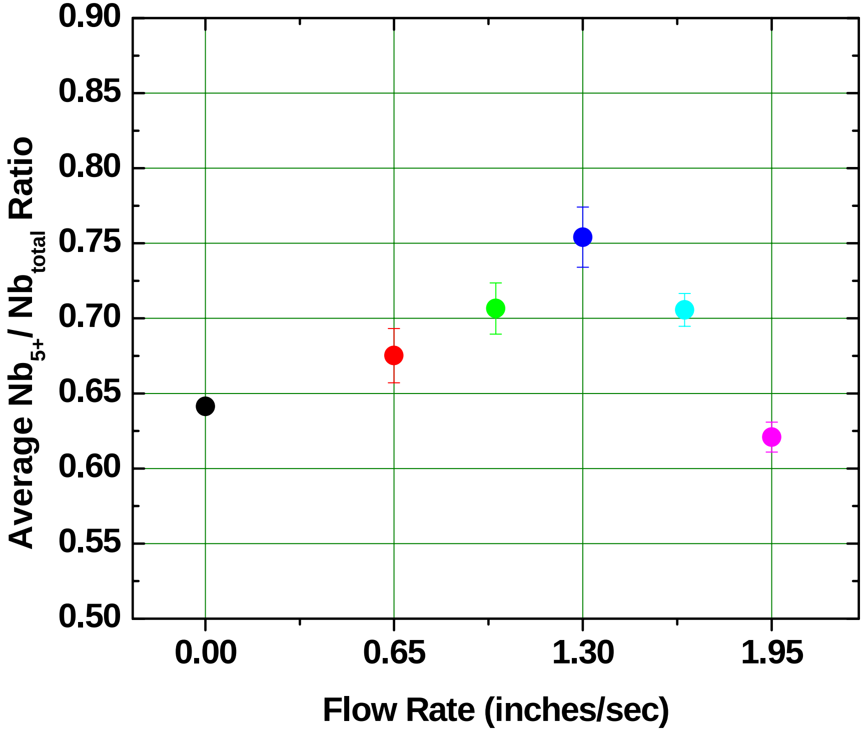




No significant effect of BCP flow rate on surface roughness .

Flow Rate Dependence of Surface Chemistry

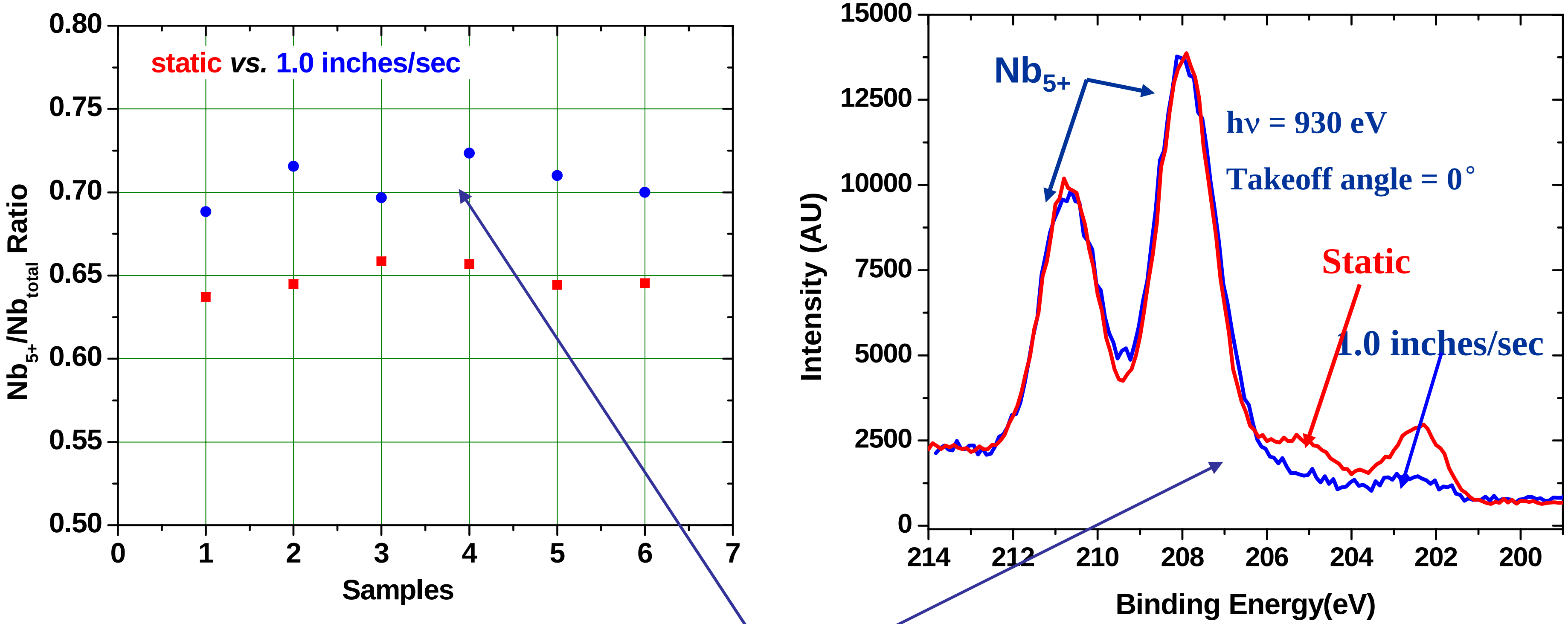




Effect of flow rate on niobium surface chemistry is significant

Flow Rate Dependence of Surface Chemistry

XPS measurement -relative Nb_2O_5 Thickness



Nb_2O_5 is thicker on the high-flow sample

H. Tian, C. Reece , M. Kelley, et. al. Applied Surface Science, Vol. 253(3), 2006, p.1236-1242

Summary and Future Work

The effect of BCP on polycrystalline niobium surface have been systematically examined for the first time.

The micron-scale roughness does not change with treatment conditions. But the thickness of Nb_2O_5 increases with a range of realistic solution flow rate.

Future work:

A microscopic understanding of Nb BCP mechanism is important for optimizing the preparation of high gradient niobium cavity.

Outline: EP

1. **Motivation-Understanding for Improving Performance.**

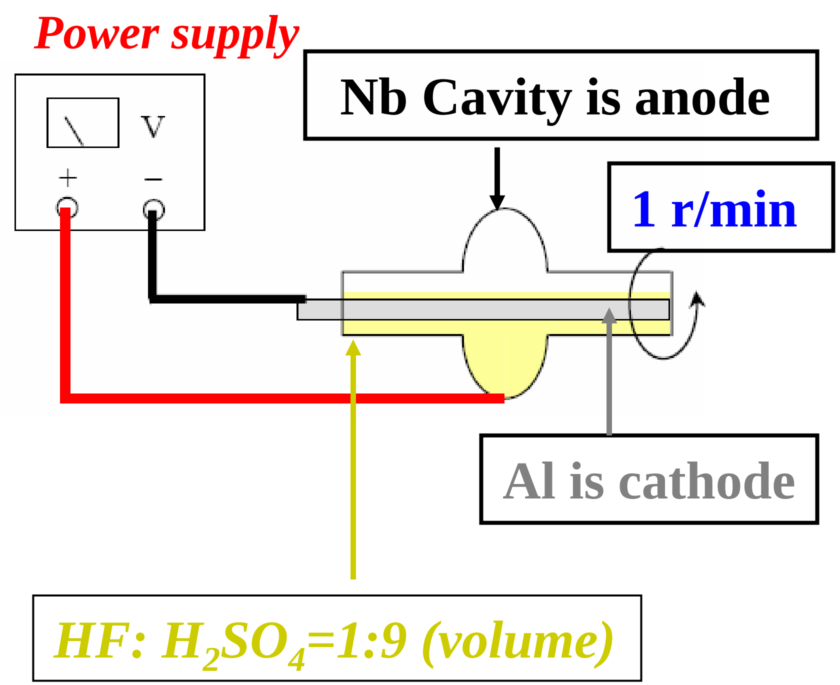
2. **Characterization of Niobium Surface Topography.**

3. **X-ray Photoelectron Spectroscopy (XPS) Studies of Niobium Surface Oxide.**

4. **Surface Study of Niobium Buffered Chemical Polished (BCP) Under Conditions for SRF Cavity Production.**

5. **Characterization of Niobium Electropolishing (EP).**

Electropolishing of Nb Cavity



Power supply

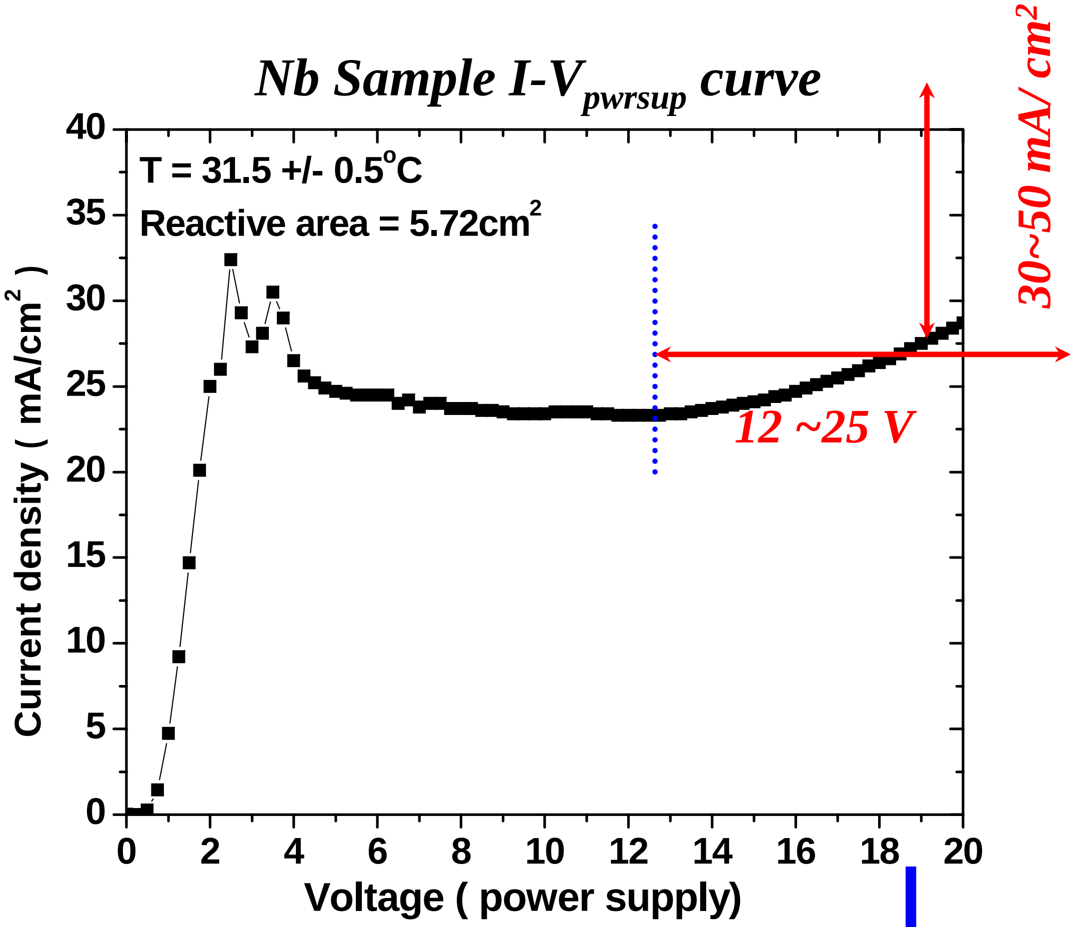
Nb Cavity is anode

1 r/min

Al is cathode

HF: H_2SO_4=1:9 (volume)

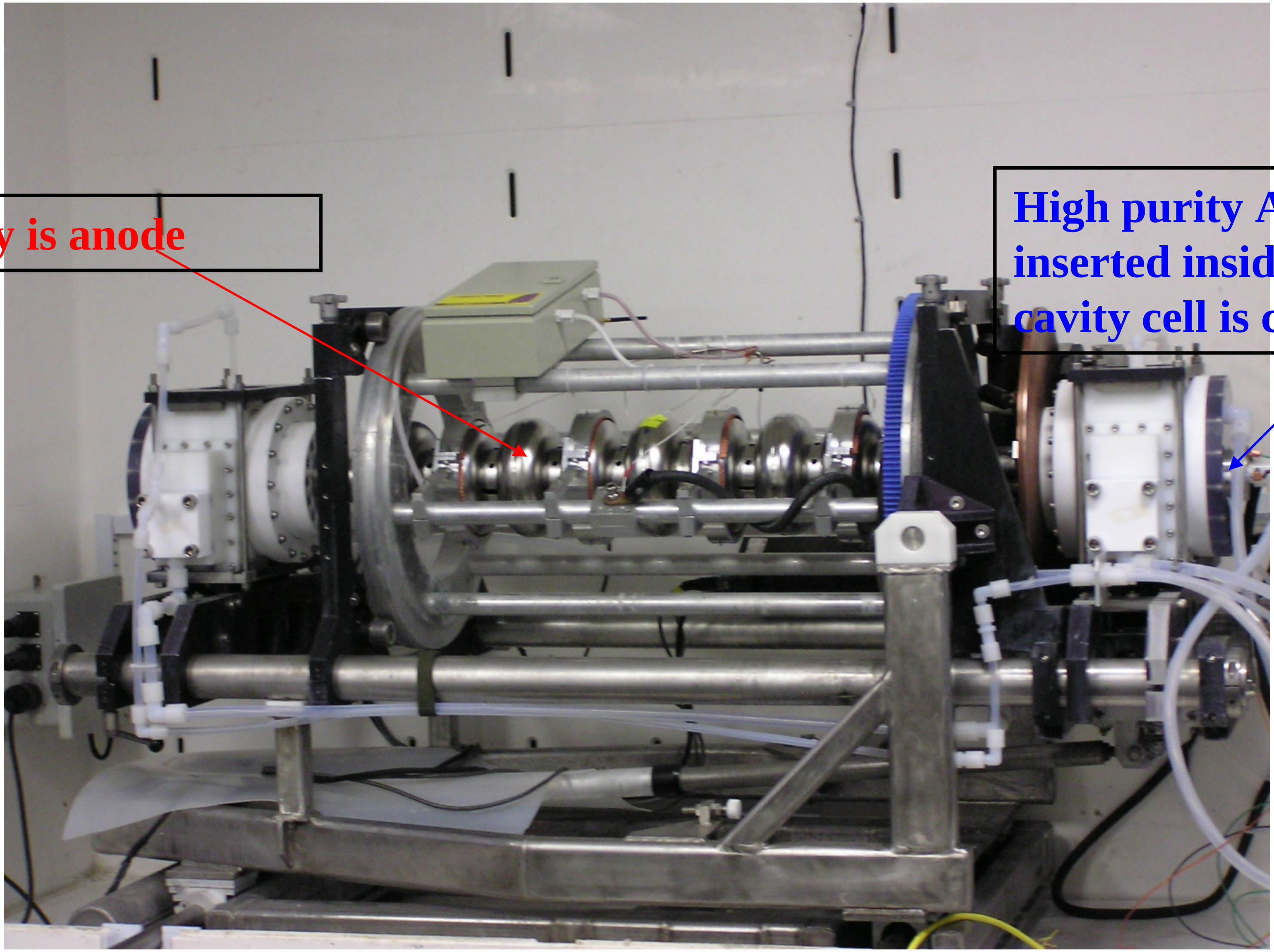
Nb Sample I-V_{pwrsup} curve



$$V_{pwsup} = V_{Nb} - V_{eletrolyte} - V_{Al}$$

Could not separate the impacts of anode (Nb), cathode (Al) and electrolyte individually . Impossible to clearly identify the local effect on Nb EP.

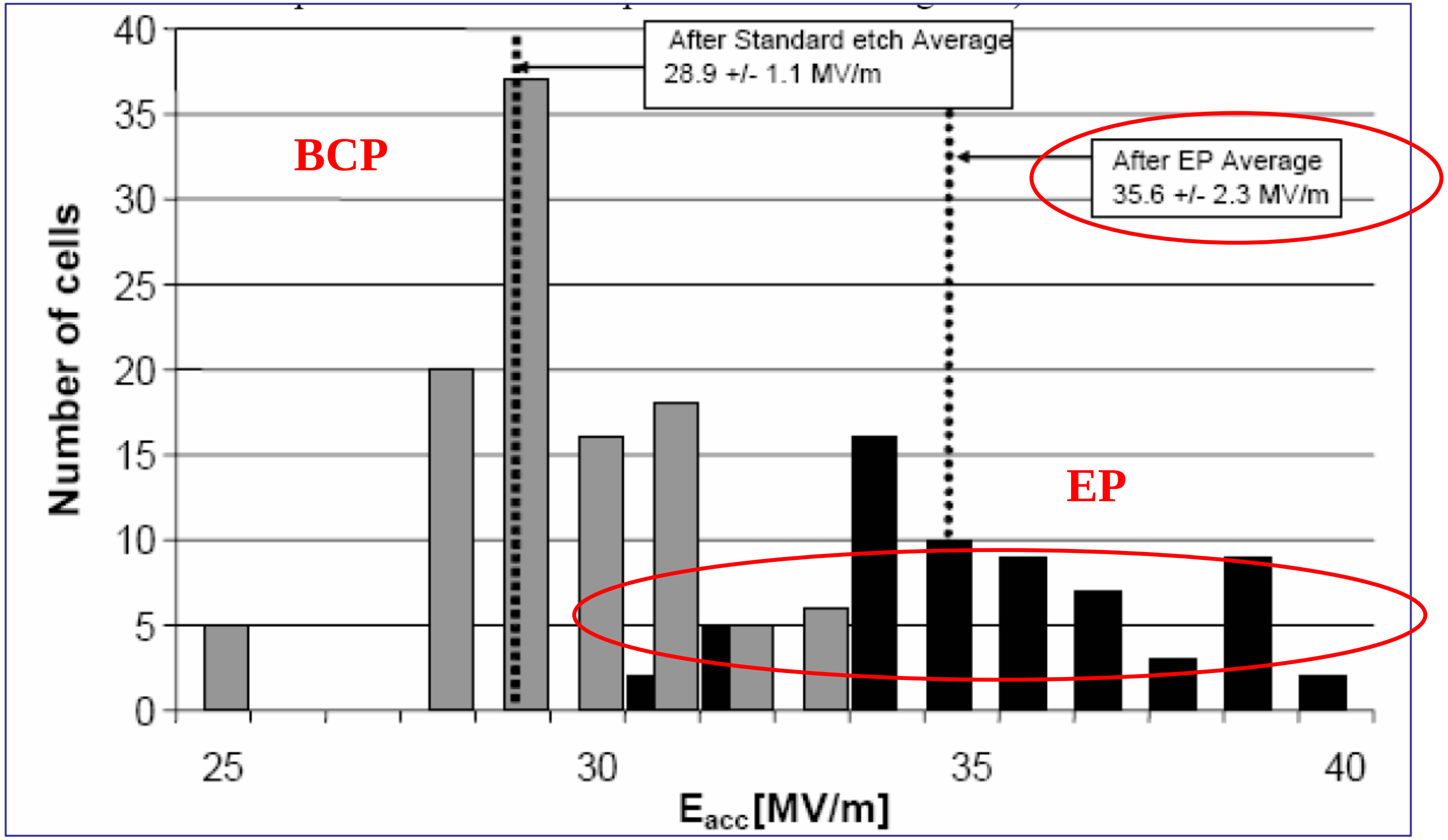
9-Cell Nb Cavity Electropolishing @ Jefferson Lab



Cavity is anode

High purity Al tube inserted inside of cavity cell is cathode

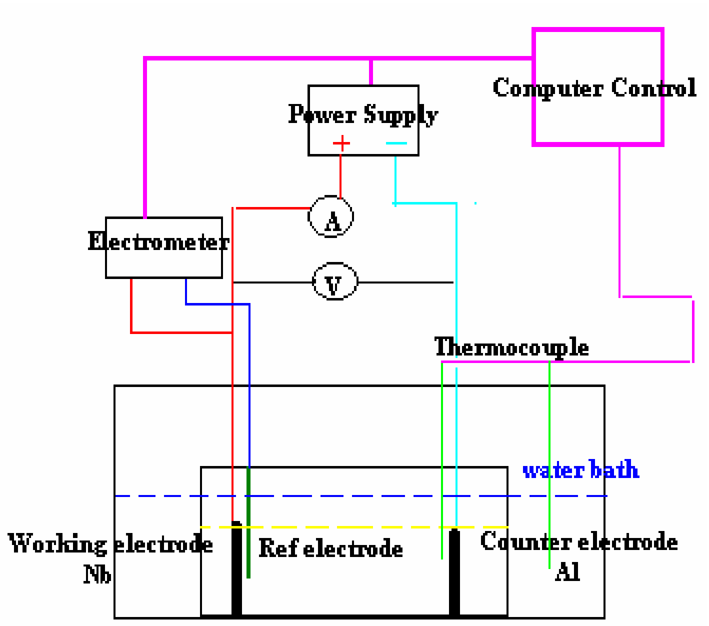
The Large Performance Variation of EP Nb SRF Cavities



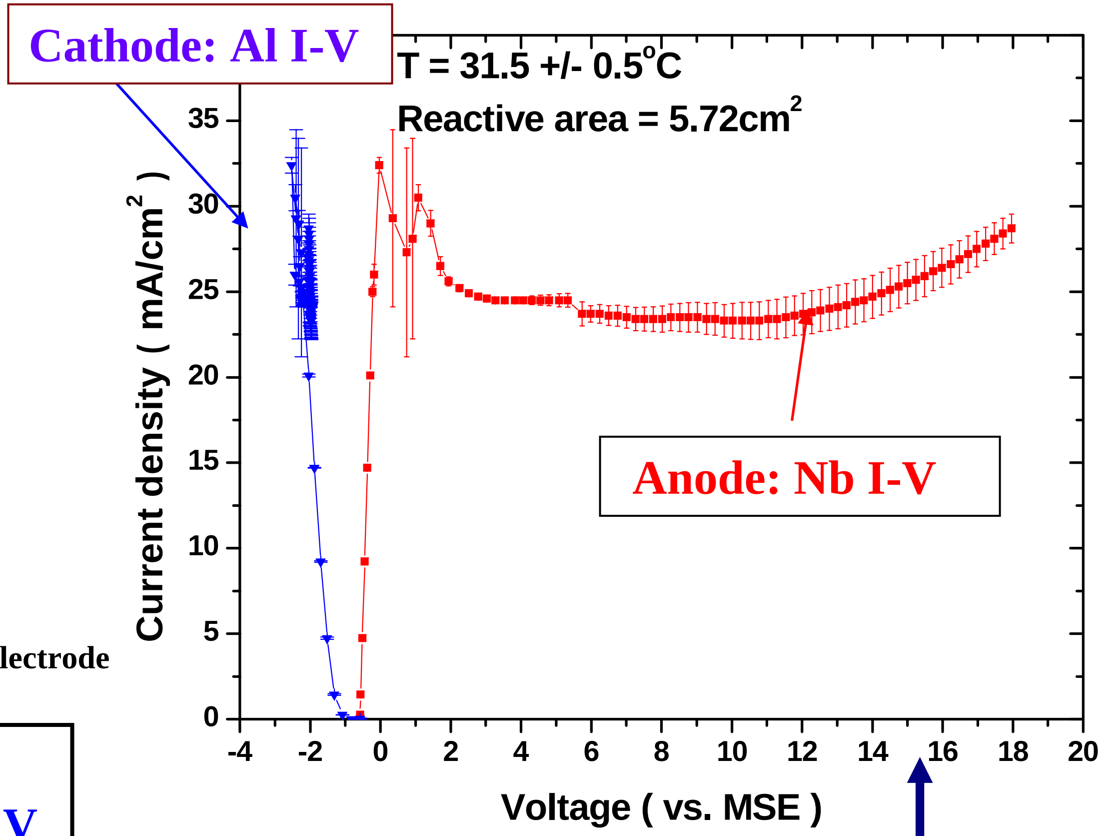
Nb cavity performance after BCP/EP. Courtesy of *www.linearcollider.org*

Microscopic understanding of the basic Nb EP mechanism is expected to provide an appropriate foundation with which to optimize the preparation of high-field niobium cavity surfaces.

"Three-Electrode-Setup" Improved Electrochemical Characterization of EP



MSE: saturated mercury mercurous sulfate electrode



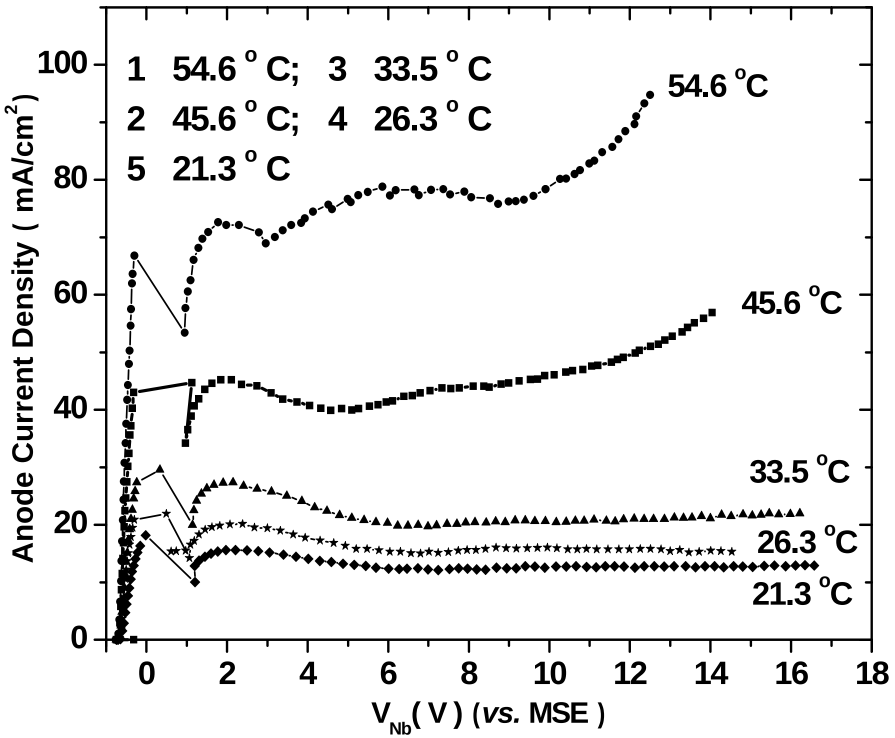
Example:

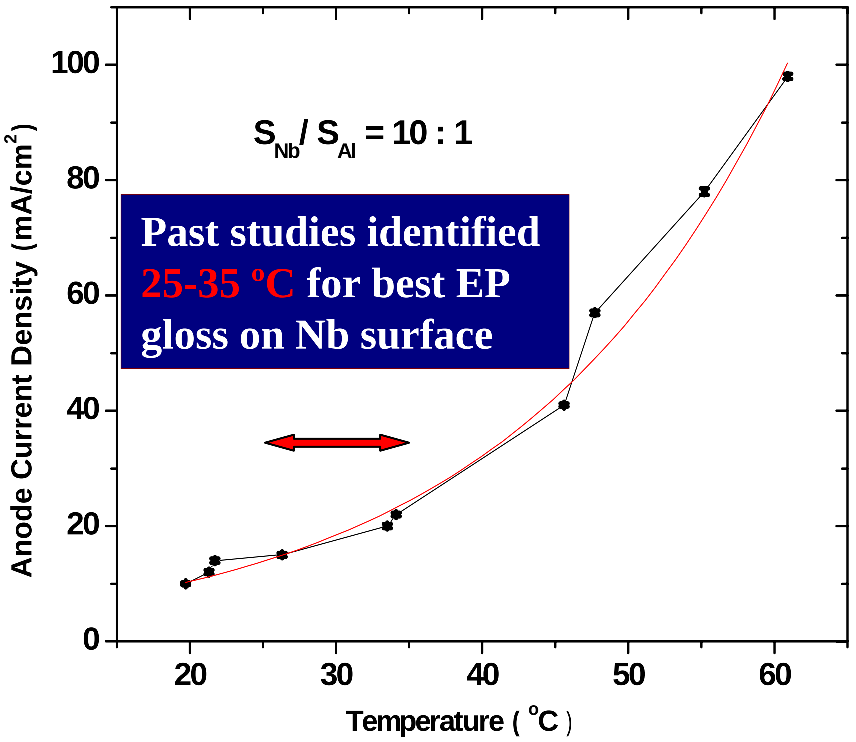
V_{PwrSup} = 15 V ; $V_{cathode}$: ~ 4 V
$V_{electrolyte}$: ~ 2 V; V_{anode}:~ 9V

"Three-electrode-setup "separates impacts of individual components in EP system.

Enables study of temperature, flow, and composition dependent effects (electrolyte) in detail.

Anode Current Density Strongly Depends on Local Temperature

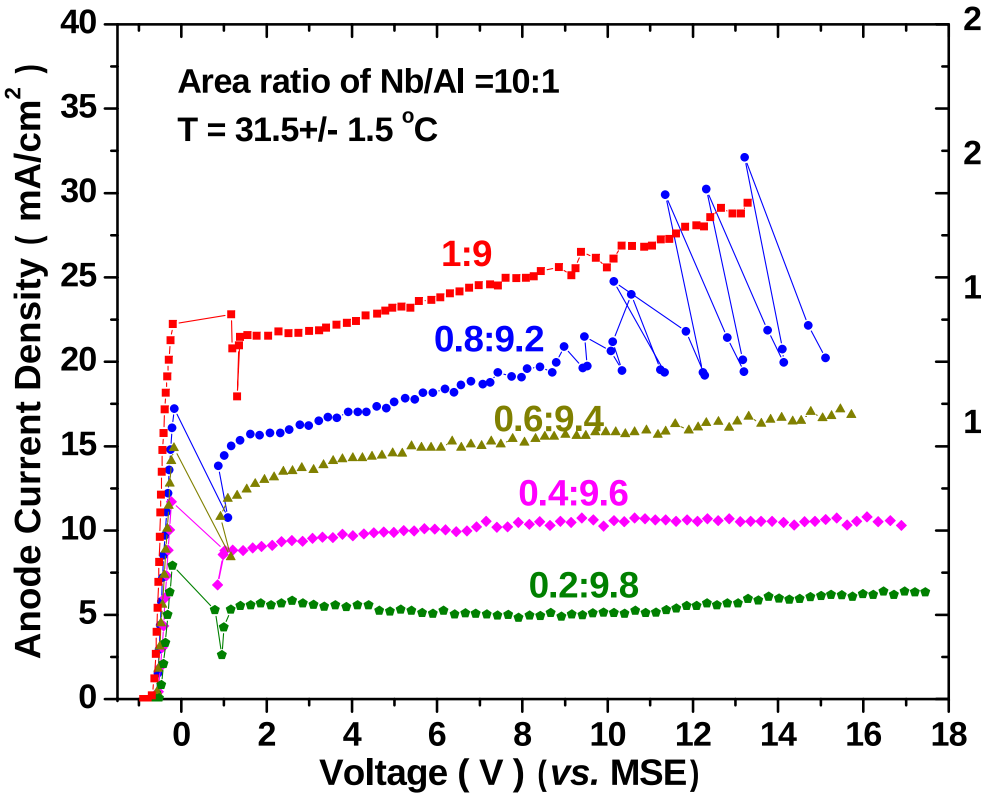




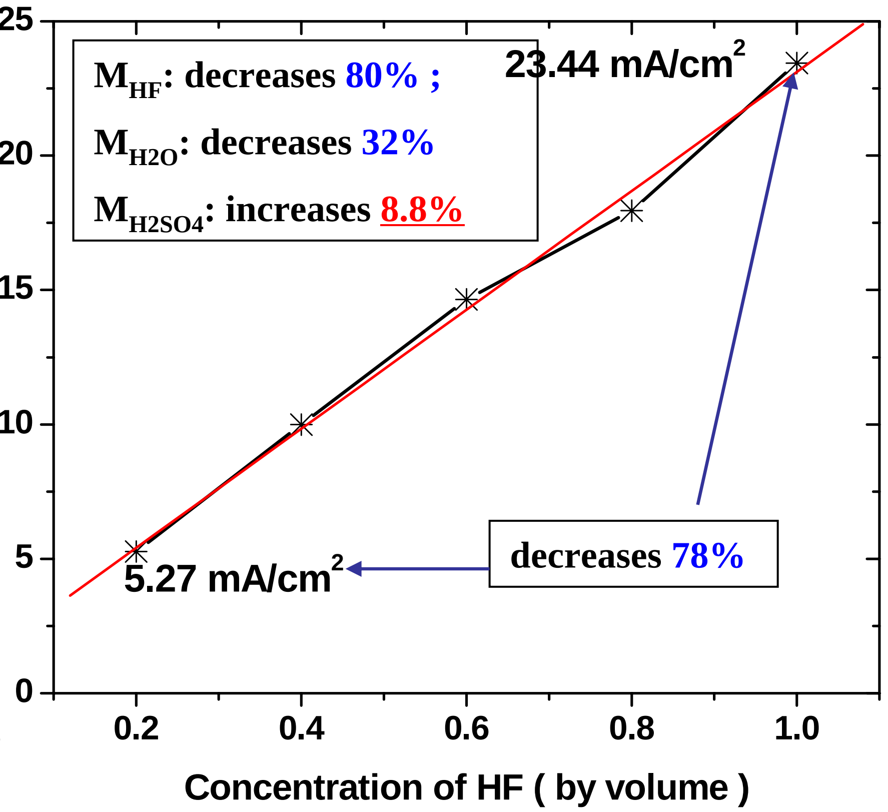
Past studies identified 25-35 °C for best EP gloss on Nb surface

For cavity EP, electrolyte also serves as the process coolant. Unstable temperatures is expected and particularly hot in no-flow condition and higher heat flux where flow rate is high. Non-uniform polishing is expected.

Anode Current Density Varies Linearly with HF Acid Volume Concentration


Area ratio of Nb/Al =10:1

T = 31.5+/- 1.5 °C


M_{HF}: decreases 80% ;

M_{H2O}: decreases 32%

M_{H2SO4}: increases 8.8%

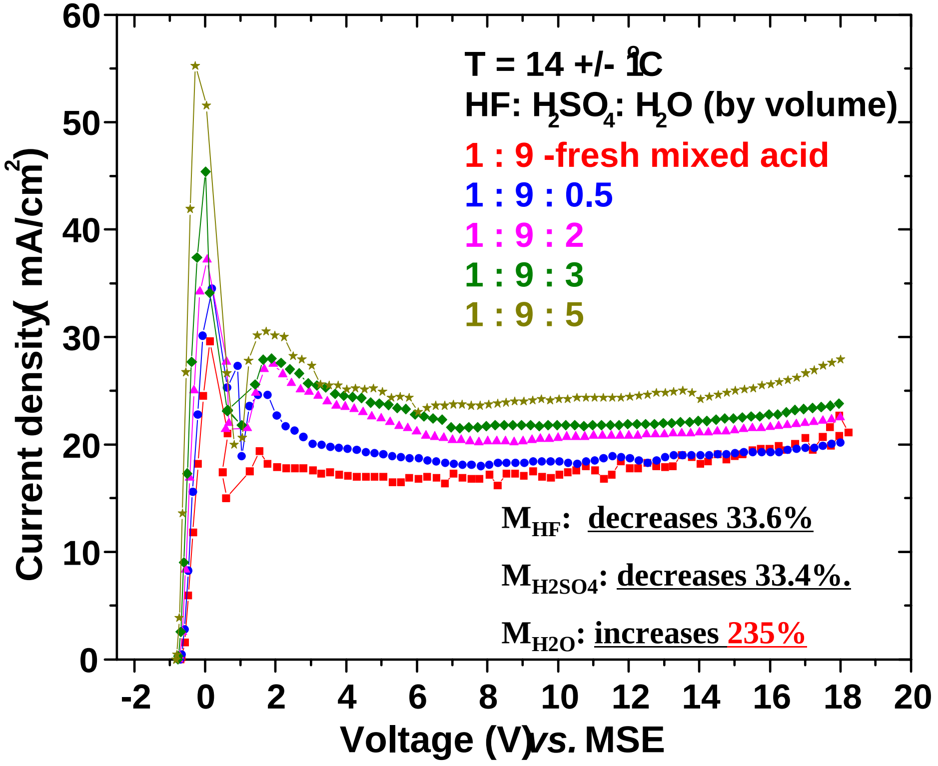
23.44 mA/cm^2

5.27 mA/cm^2

decreases 78%

HF acid loss may be expected due to evaporation and chemical reaction during process. The understanding of the detailed role of HF involved during the EP process requires further electrochemical studies.

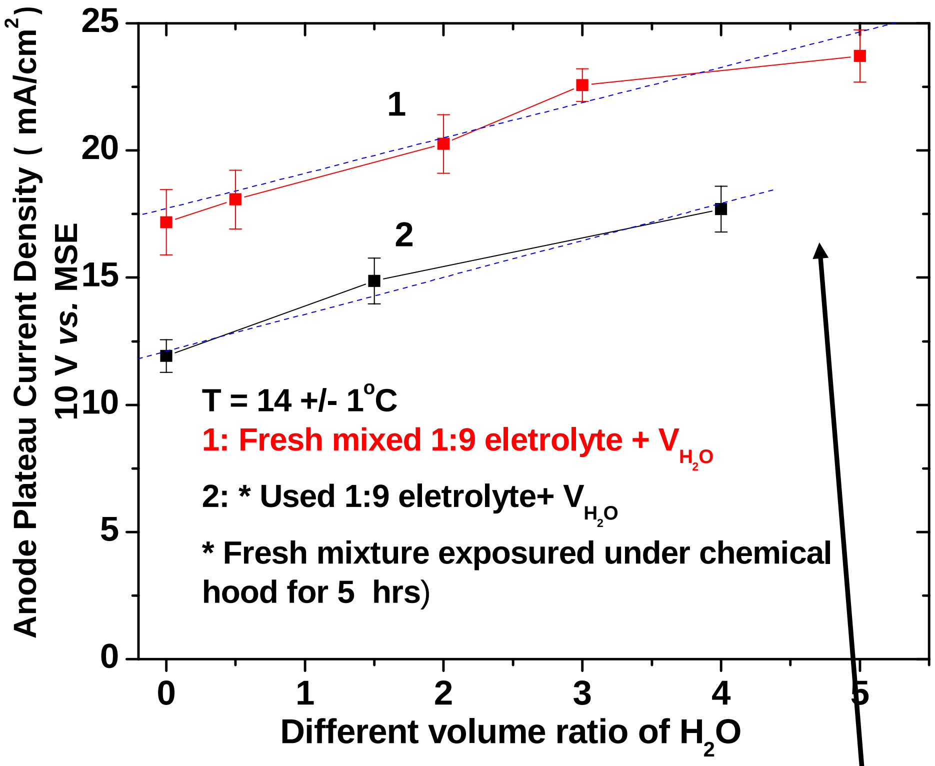
Additional Volume H_2O slightly Increases Anode Current Density



M_{HF}: decreases 33.6%

M_{H2SO4}: decreases 33.4%.

M_{H2O}: increases 235%



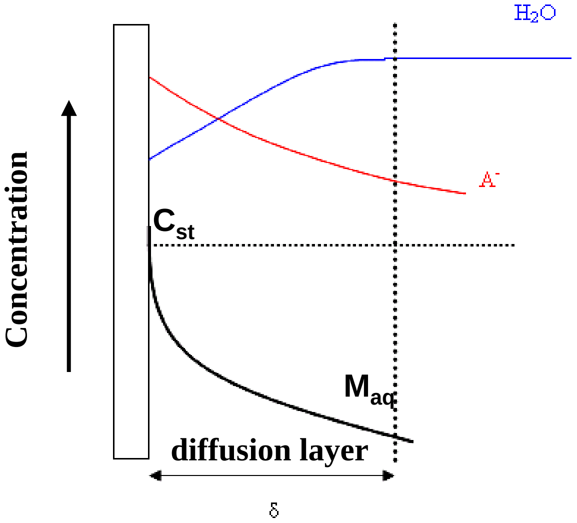
* Fresh mixture exposured under chemical hood for 5 hrs)

Anode current density slightly increases with additional volume of H_2O (38~42%); Compare curve 1 and curve 2(after 5 hrs exposure under chemical hood), current density decreases 30 % -HF evaporation

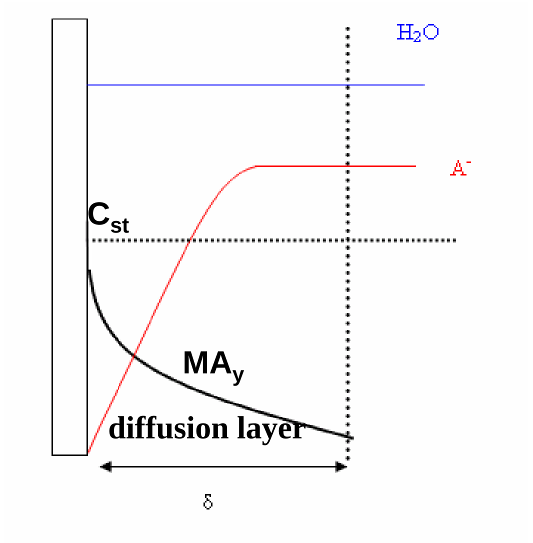
Current-Limited Plateau of Nb EP
Mass Transport Mechanism Has Been Unknown

Possible mass transport limiting species proposed -D. Landolt, Electrochemica Acta, Vol . 32(1)

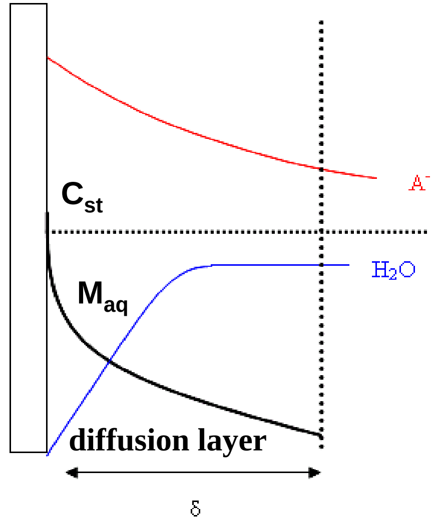
I) Metal Ions (M^{n+}_{aq})



II) Acceptor anion (A^-)



III) H_2O



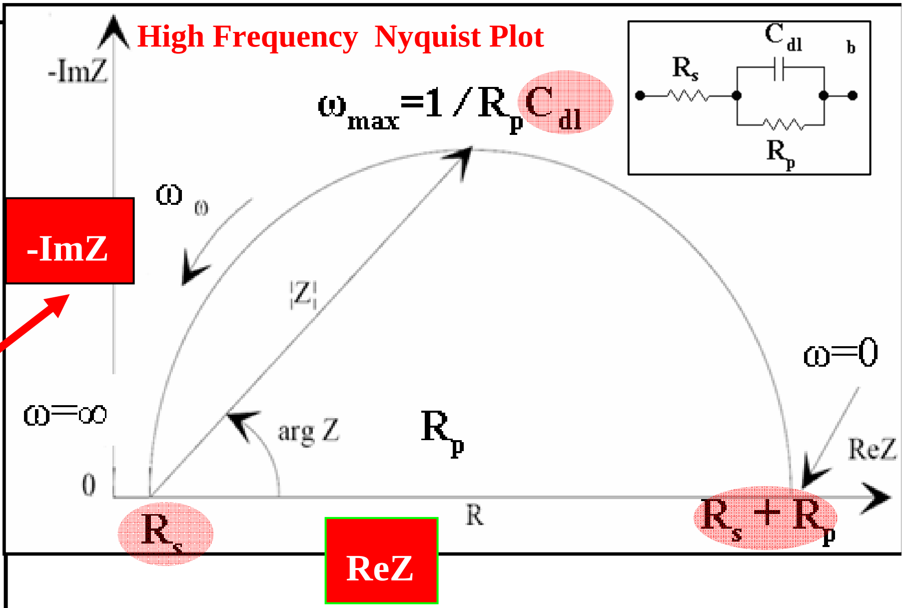
Micro-polishing (brightening) only occurs when the plateau is the result of diffusion-limitation alone. Understanding of mass transport mechanism requires further electrochemical study-EIS.

What is Electrochemical Impedance Spectroscopy?

- **Investigate the electrical dynamics of niobium-acid interaction during electropolishing.**

- **EIS: 10 mV variable-frequency ac superimposed on normal dc polarization voltage; record the impedance at the different frequency.**

$$Z = \frac{R_p}{1+\omega^2 C_{dl}{}^2 R_p{}^2} + R_s - j\frac{\omega C_{dl} R_p{}^2}{1+\omega^2 C_{dl}{}^2 R_p{}^2}$$

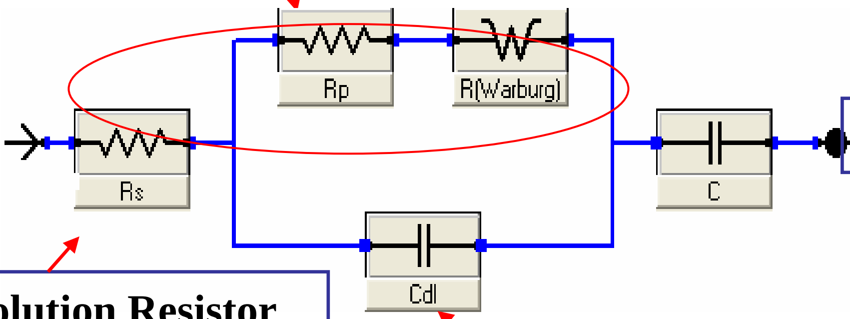


Nyquist Plot

R_p: Polarization Resistor

$R_{warburg}$: Diffusion Resistor

Nb



Ref. Elec.

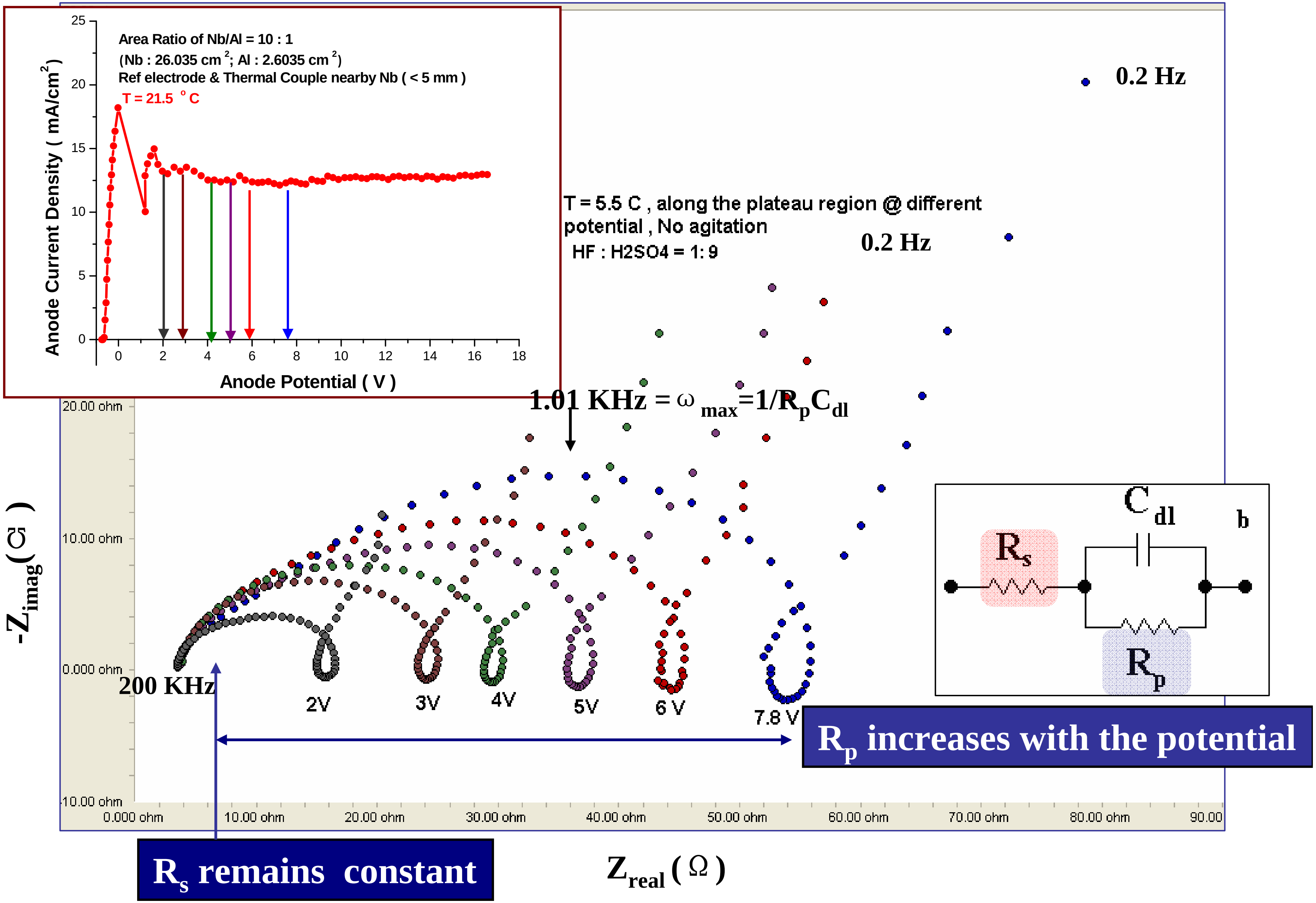
R_s: Solution Resistor

C_{dl} :Capacitor of Electrode Surface

EIS

Possible equivalent circuit of Nb-acid interface during EP

EIS Study of Constant Current Density



T = 5.5 C , along the plateau region @ different potential , No agitation

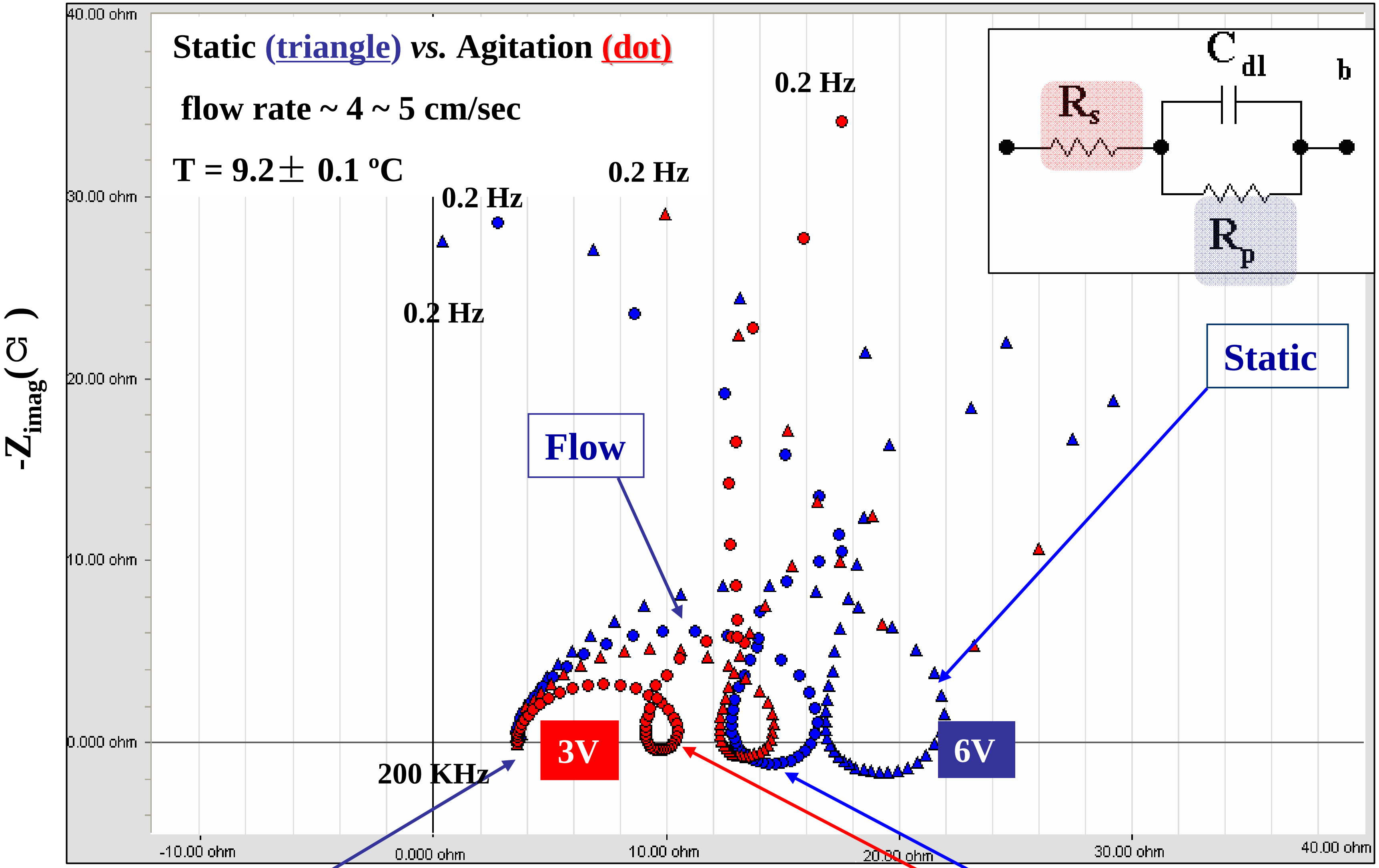
HF : H2SO4 = 1: 9

$1.01\ \text{KHz} = \omega_{max} = 1/R_pC_{dl}$

R_p increases with the potential

R_s remains constant

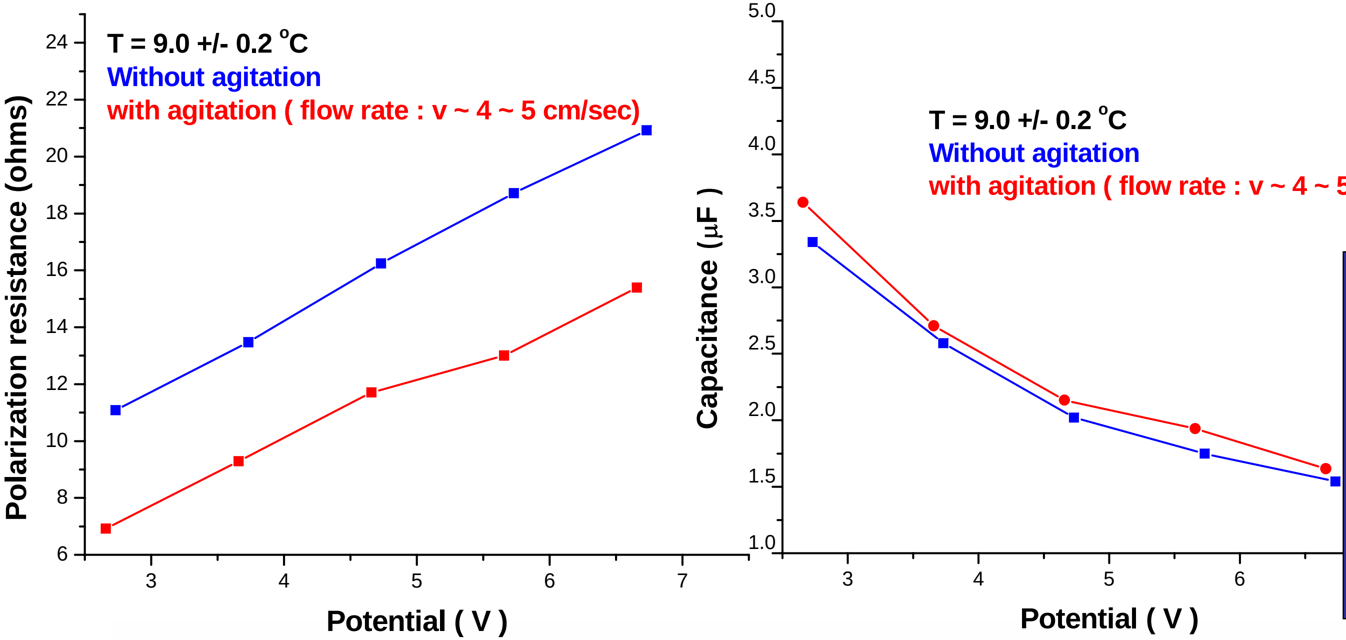
EIS Study of Different Flow Rates



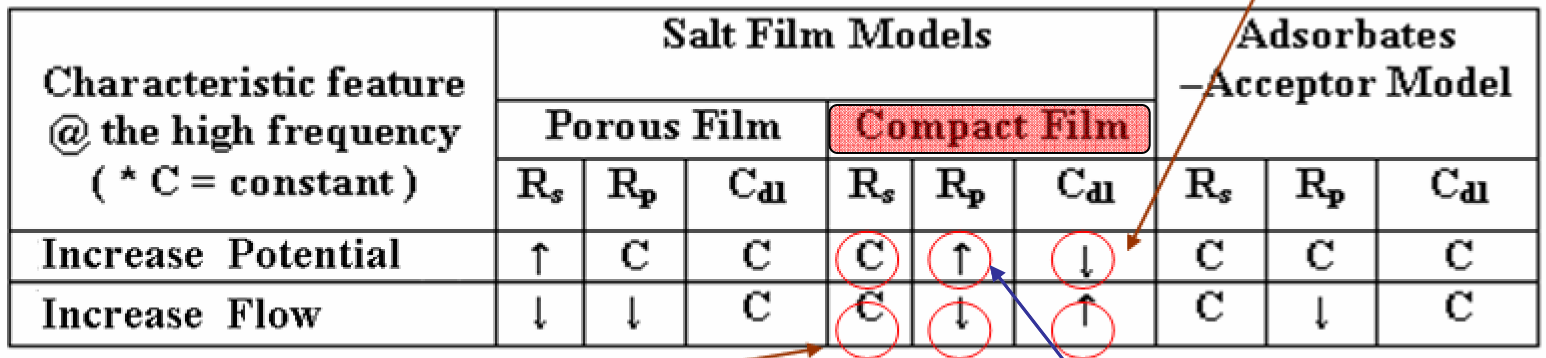
R_s @ at different flow condition remains as constant

R_p decreases with increasing flow

What We have Learned from EIS Studies?



C_{dl} ↓ at different potential regions & C_{dl} ↑ at different flow conditions are consistent with the “compact salt film” model.

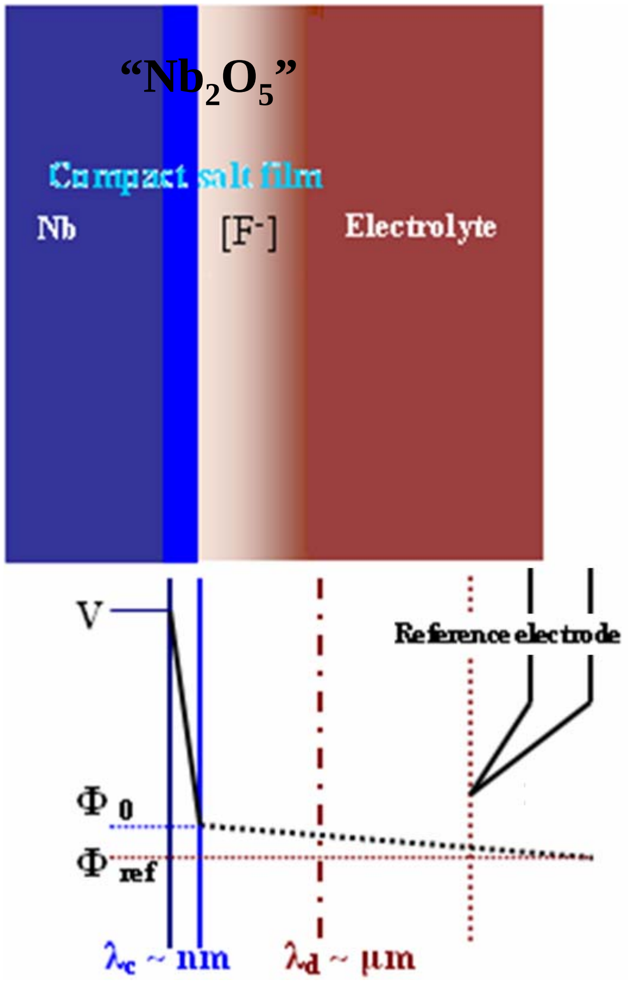


Characteristic feature @ the high frequency (* C = constant)	Salt Film Models						Adsorbates –Acceptor Model		
	Porous Film			Compact Film					
	R_s	R_p	C_{dl}	R_s	R_p	C_{dl}	R_s	R_p	C_{dl}
Increase Potential	↑	C	C	C	↑	↓	C	C	C
Increase Flow	↓	↓	C	C	↓	↑	C	↓	C

Constant R_s at different potential regions and flow condition rules out the “porous salt film” model.

R_p ↑ at different potential regions is inconsistent with the “adsorbates acceptor” model.

EIS Indicates “Compact Salt Film” Model



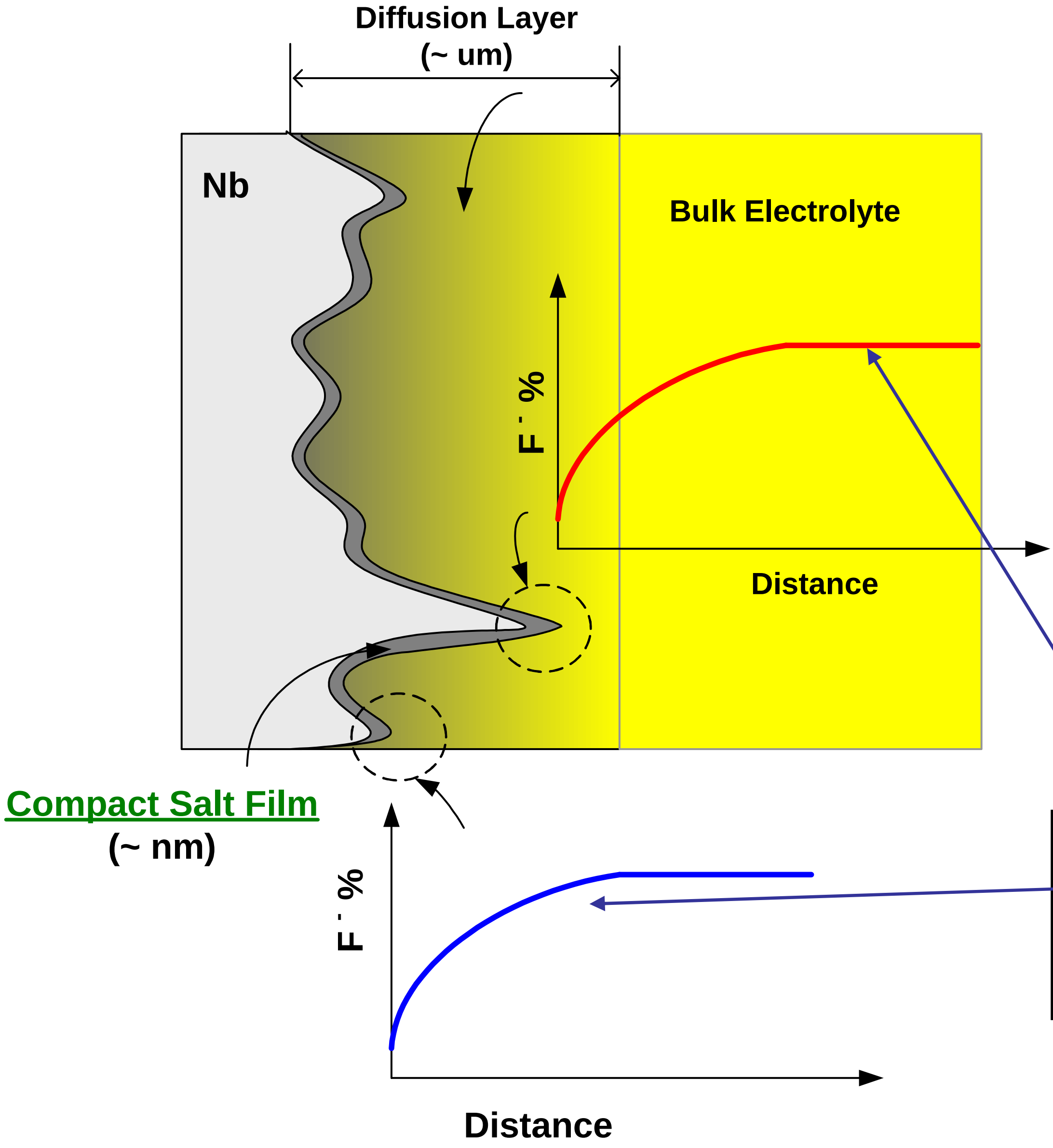
compact film

diffusion layer

- ➢ **Sulfuric acid tends to anodize the Nb under polarization potential producing the "compact salt film”- “Nb_2O_5”.**
- ➢ **HF acid tends to dissolve the Nb oxide under kinetic control with the "at the surface" concentration of F^-.**
- ➢ **F^- concentration “at the surface” is limited by how fast it diffuses through the electrolyte (~diffusion layer).**
- ➢ ***The local gradient in F^- concentration produces the desired polishing action.***

H. Tian, S. Cocoran, C. Reece, M. Kelley, Journal of the Electrochemical Society (submitted)

The Diffusion-Limited Access of F^- To the Salt Film Produces Best Polishing



Local temperature, flow & electrolyte composition affect the local F^- gradient

Summary and Future Work

➢**The first use of "three-electrode-setup" reveals that Nb EP strongly depends on the local electrolyte temperature and HF/H_2SO_4 volume ratio.**

➢**High frequency impedance data provide strong evidence for the presence of a compact salt film (Nb_2O_5) in the current-limited plateau region.**

➢**The results suggest that the diffusion-limited access of the F^- anion to the salt film surface limits the local reaction rate, creates the plateau and yields the micropolishing.**

Future work:

➢**Monitor polishing effect with different concentration HF acid, different flow rate, different temperature electrolyte and different process voltage ➡ specify optimum processing protocol.**

➢**Simulation & develop feedback to monitor cavity process.**

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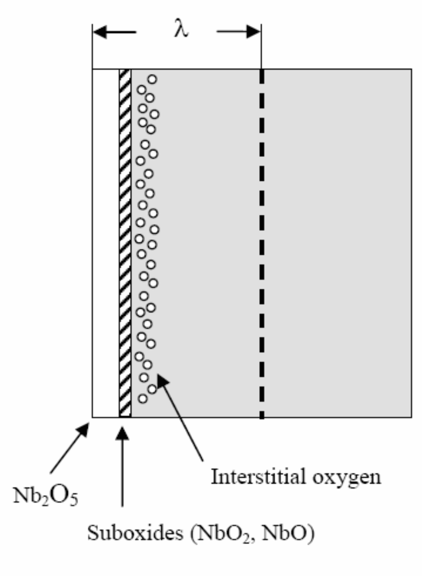
Guilhem Ribeill

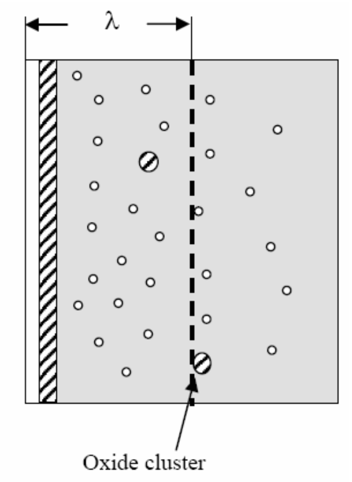
My families and friends for your constant support and pray!

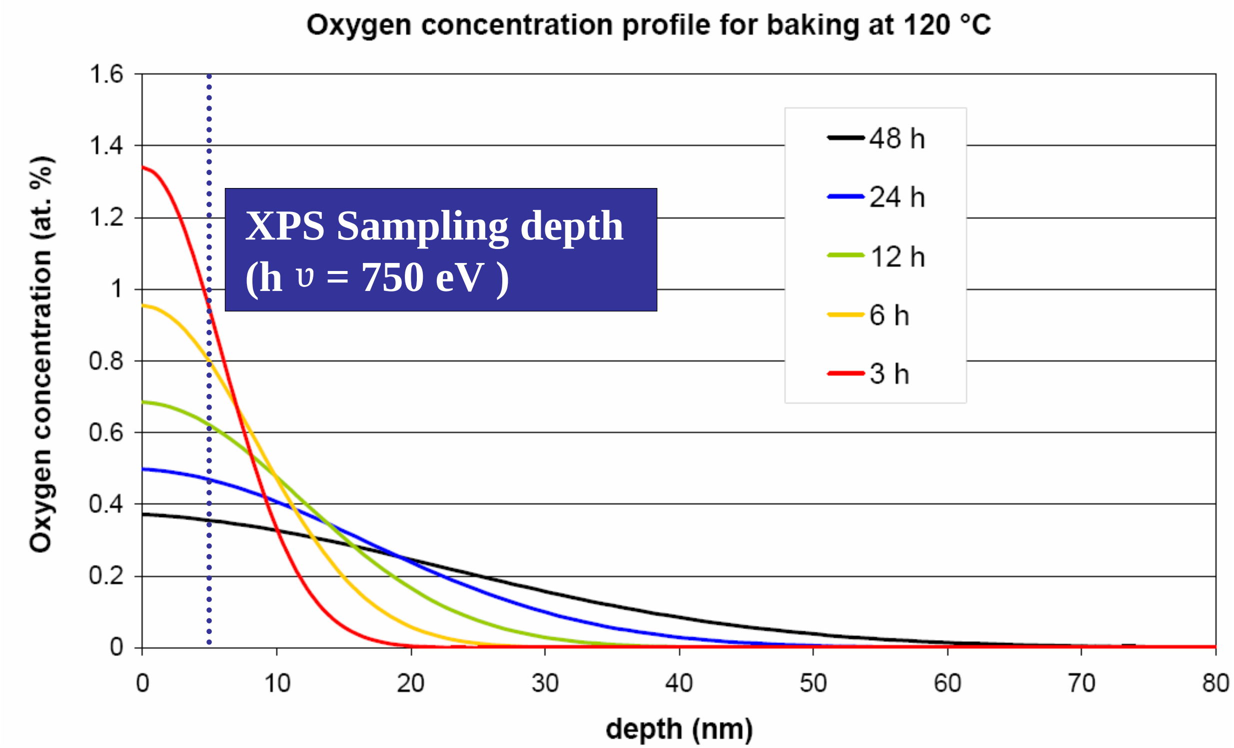
“Oxygen Diffusion” Under Different Baking Duration

Before Baking



After Baking





XPS Sampling depth (h υ = 750 eV)

Courtesy of G. Ciovati , internal talk , Jefferson lab

$$\frac{\partial c(x,t)}{\partial t} = D(T)\frac{\partial^2 c(x,t)}{\partial x^2}$$

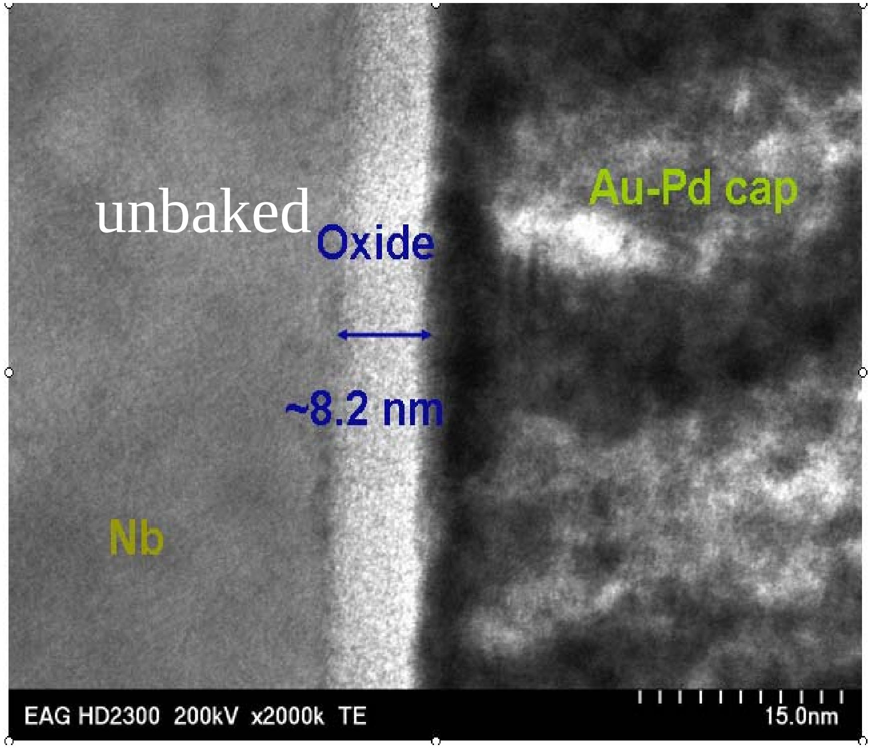
$$c(x,t) = u(x,t) + v(x,t)$$

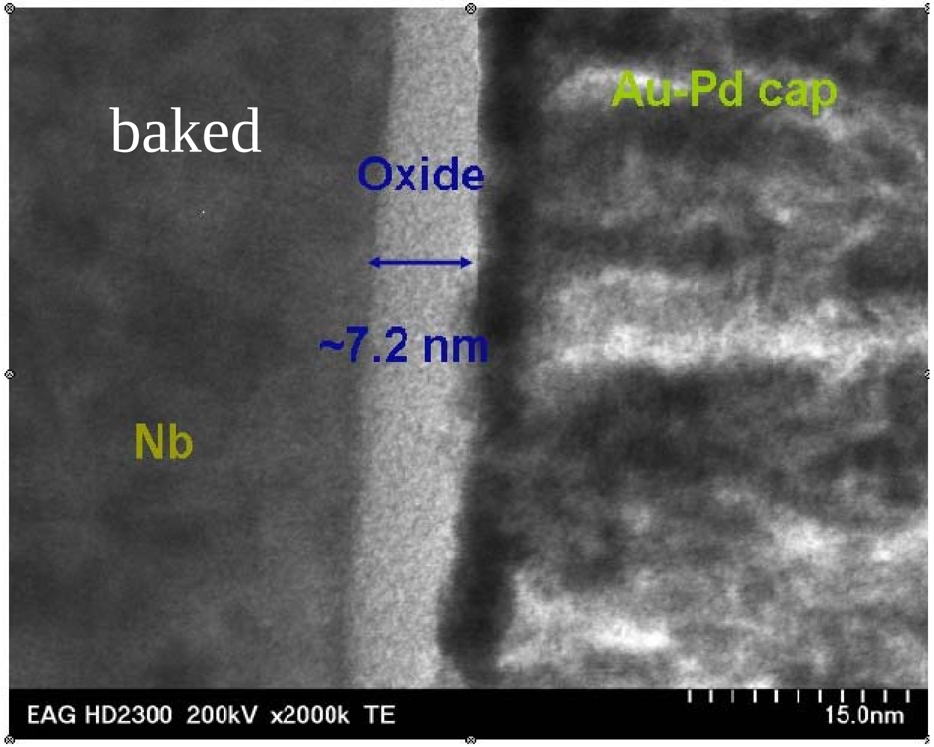
Nb$_2$O$_5$ reduction ?

interstitial oxygen (10%) ?

Oxides Structure (Unbaked/Baked)

preliminary TEM results

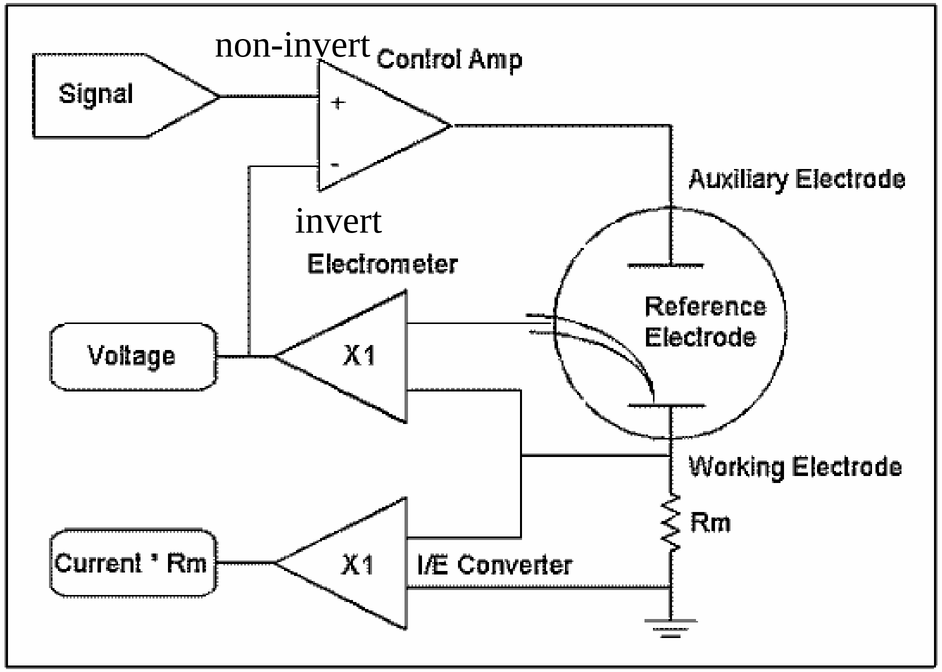




No clear structure change can be observed (suboxide, interstitial oxygen- cluster)

Potentiostat Primer

A simplified schematic of Potentiostat



Control amplifier- the cell voltage is controlled to be identical to the signal source voltage.

The electrometer circuit measures the voltage difference between RE & WE It has zero input current and an infinite input impedance.

The Current-to-Voltage (I/E) converter in the simplified schematic measures the cell current.

A working electrode - where the potential is controlled & the current is measured, serves as a surface on which the electrochemical reaction takes place.

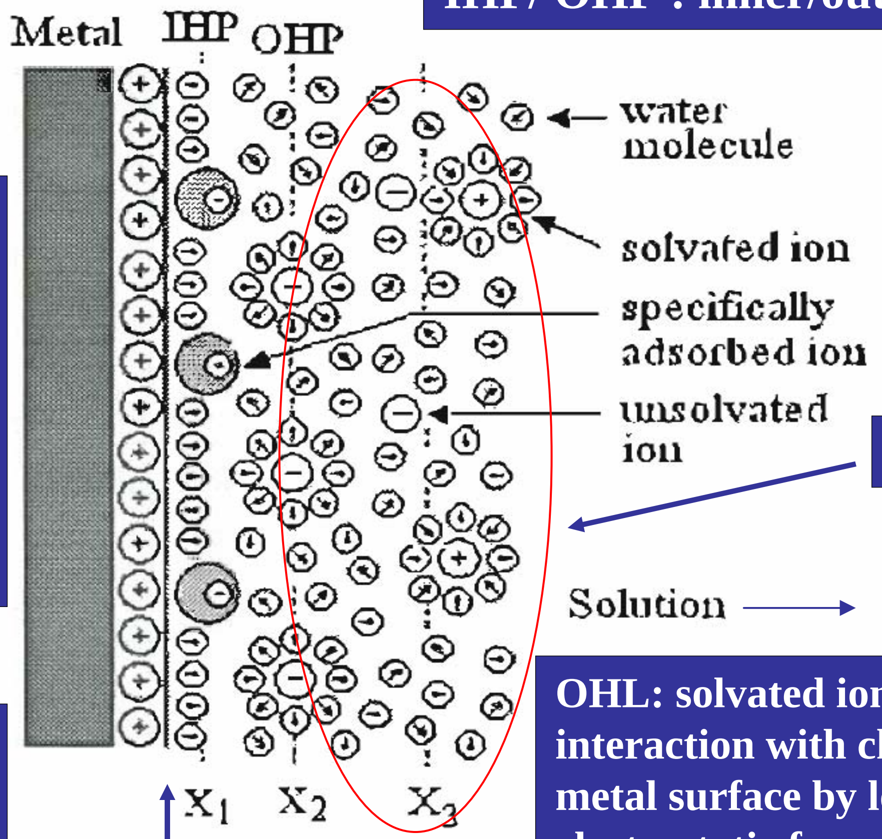
The reference electrode : used in measuring the working electrode potential and have a constant electrochemical potential as long as no current flows through it.

An Auxiliary electrode (counter electrode) : a conductor that completes the cell circuit.

The Electrode-Electrolyte Double Layer

IHP/ OHP : inner/outer Helmholtz plate

Nb



Ionization: 1) metal ion move through electrolyte with applied potential. 2) electron recombine with positive ion 3) water dipoles and negative ions drag metal ions into electrolyte.

IHL: water dipoles and some negative ions

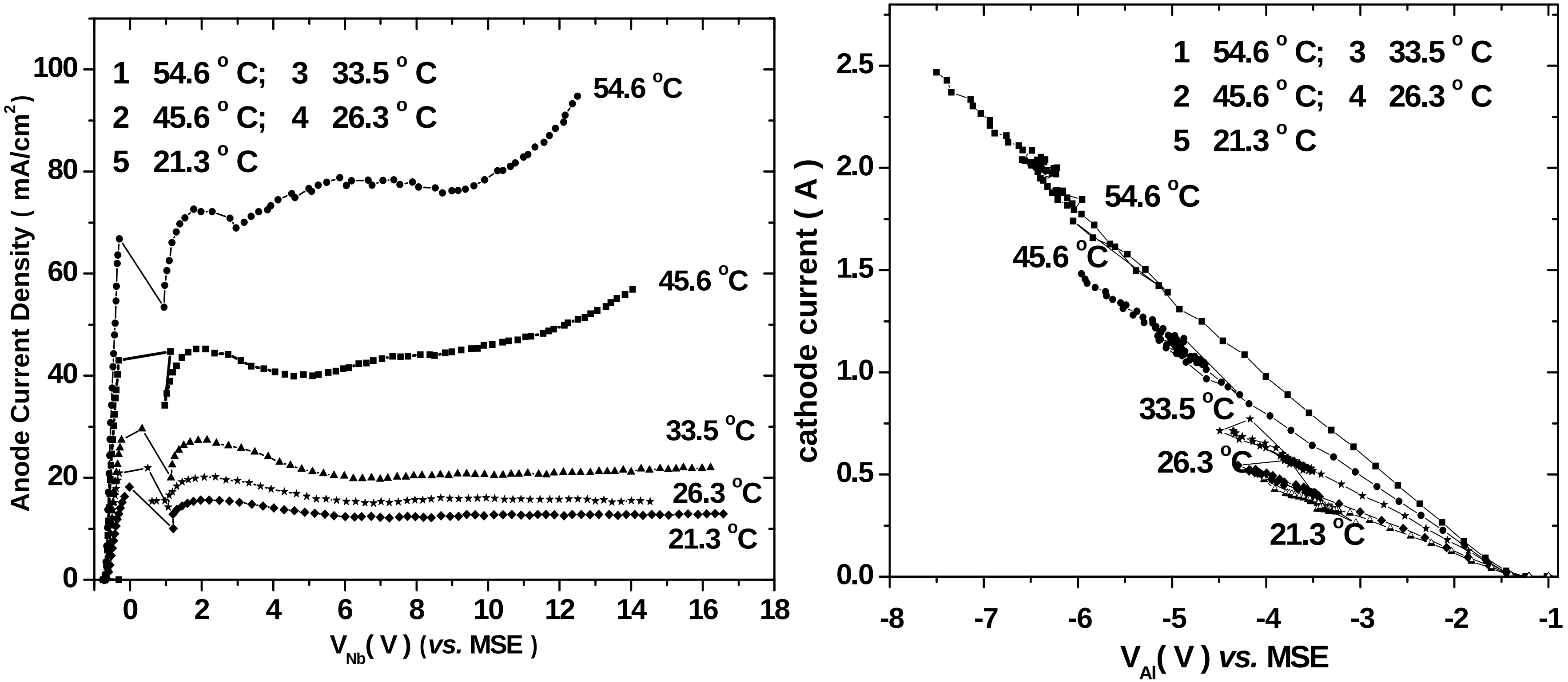
Diffuse layer

$HF+H_2SO_4+H_2O$

OHL: solvated ion, the interaction with charged metal surface by long range electrostatic force

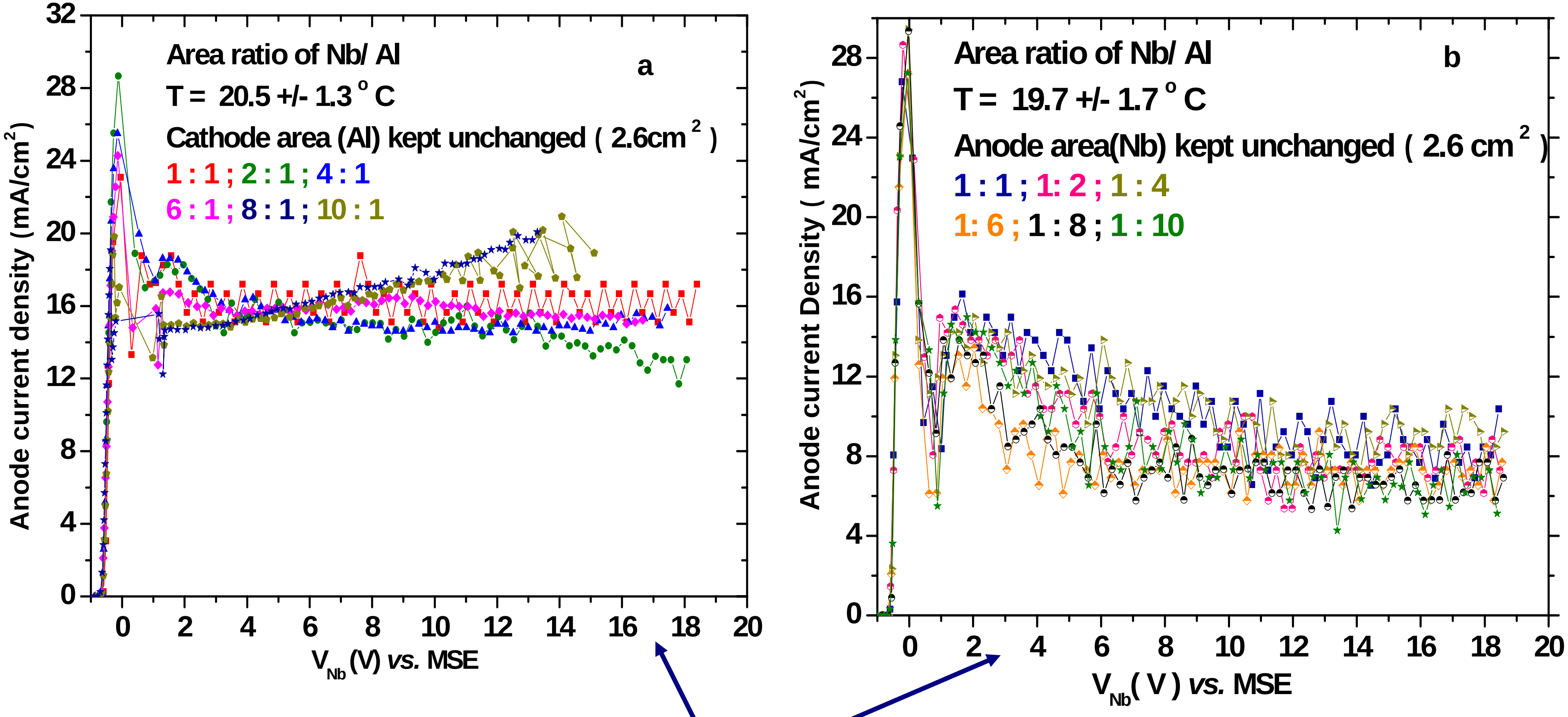
The electron-electrolyte interface behave like a capacitor .

Effect of Electrolyte Temperature



The strong dependence of the measured anode current density on the local electrolyte temperature is observed; power dissipated at the cathode increases with electrolyte temperatures.

Anode Current Density Does Not Depend on the Relative Area of Anode and Cathode



Anode current density remain constant

The Mass Transport Mechanisms

Nernst-Planck equation (1-dimension)

$$J_i(x) = -D_i \frac{\partial C_i(x)}{\partial x} - \frac{z_i F}{RT} D_i C_i \frac{\partial \phi(x)}{\partial x} + C_i \upsilon(x)$$

Diffusion, movement of species (ions, molecules) driven by a gradient of chemical potential (i.e. a concentration gradient)

Migration, movement of ions driven by a gradient of electrical potential

Convection, natural convection driven by density gradient; forced convection (stirring, vibration)

RDE ←

$i_L = 0.62nFAD^{2/3} \nu^{-1/6} \omega^{1/2} (C^0 - C^*)$

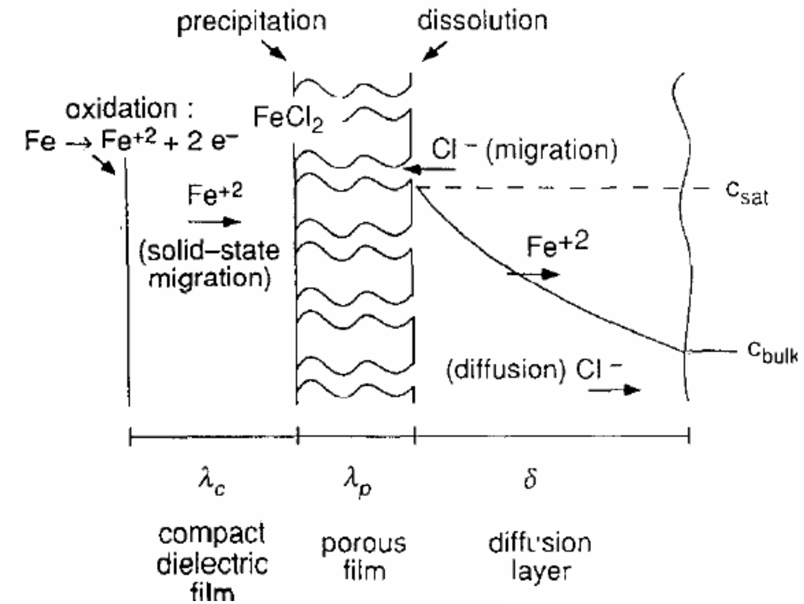
$i_L \rightarrow \omega^{1/2} \rightarrow D$

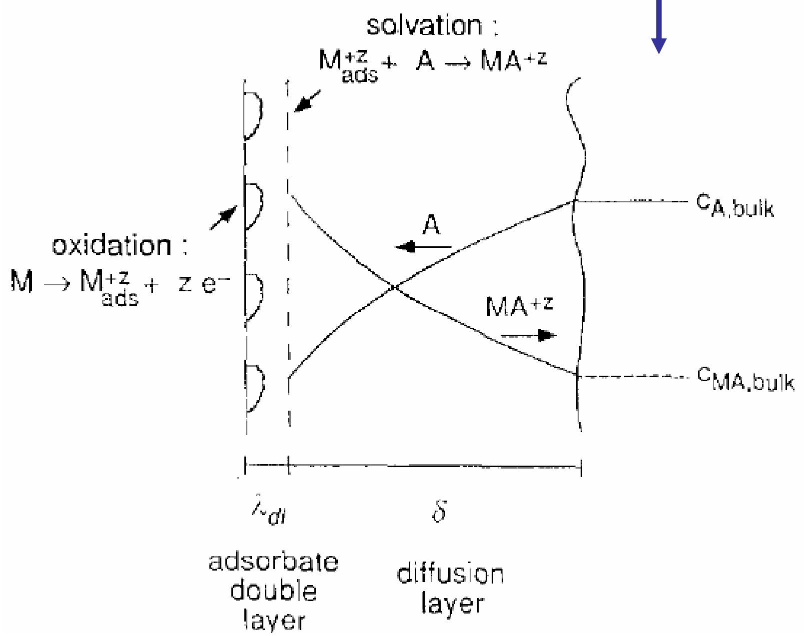
Possible Mass Transport Mechanisms

The rate of transport of cations across the diffusion layer into the bulk electrolyte limits the anodic dissolution rate

Pores of precipitates are filled with electrolyte, anions and cations transport current by migration. ~ μ m

The limited current -diffusion of acceptor species through diffusion layer





Precipitates fix C_{M+} =$C_{saturation}$

Courtesy of M. Matlosz,Electrochimica Acta. Issue 4, Vol. 40, 1995, pp. 393

Duplex (compact + porous) salt film mechanism : involves rate limiting diffusion of cations of the dissolving metal from anode into the bulk.

Adsorbate acceptor mechanism : involves rate limiting diffusion acceptor anions (such as H_2O) which are consumed at the anode by formation of complexes (MA^{+z}) or hydrated metal ions.