U. of Chicago - Fermilab - ANL Collaboration on SRF Nb Research, Nov 27 2007

Fundamental Studies of the Interfacial Chemical Kinetics and Morphological Evolution of Niobium During Oxidation

Steven J. Sibener, Univ. of Chicago
The James Franck Institute and Department of Chemistry
& Lance Cooley (FNAL)

Methods for Examining Niobium and Alloy Surfaces:

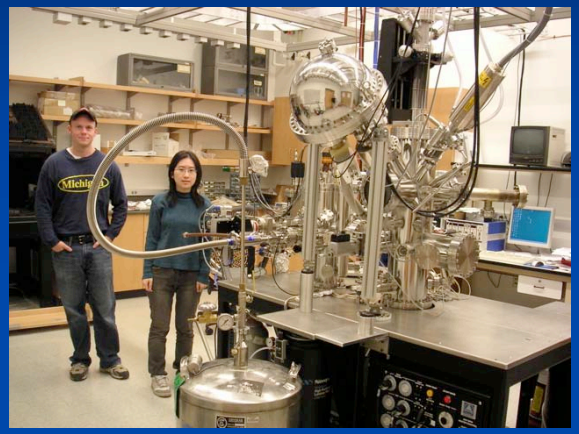
- **Structural Evolution:** UHV-STM and Air/Electrochemical AFM
- **Chemical Evolution:** *In Situ* Molecular Beam Surface Scattering with *in situ* Vibrational & Electronic Spectroscopy and XPS
- **Controlled Chemical Environment During Reactions:** O, O_2, H_2O, H_2
- **Synergistic Effects:** Interfacial oxidation with electrons, photons, local electric fields, trace water, ….
- **Field Emission:** Map local work function on clean/oxidized surfaces
- **Single Crystals and Technical Materials:** Nb, Nb Alloys

Key Questions:

- What is the nature of the clean Nb interface?
- What are the stages of interfacial oxidation including mechanism, kinetics and stability?
- Influence of other species on the oxide, e.g., H_2O, H_2 ?
- Single crystalline interfaces (100, 110, 111) vs. polycrystals including influence of grain boundaries?
- Communication of the interfacial oxide w/ the bulk?
- *Effect of baking/cooldown procedures on the interface?*
- How do different polishing procedures influence the interfacial chemistry? Can we design an optimal chemical/mechanical polishing procedure?
- Correlation of the above with superconductivity?

Unique Surface Instrumentation in the Sibener Group for Scattering, Imaging, & Interfacial Spectroscopy

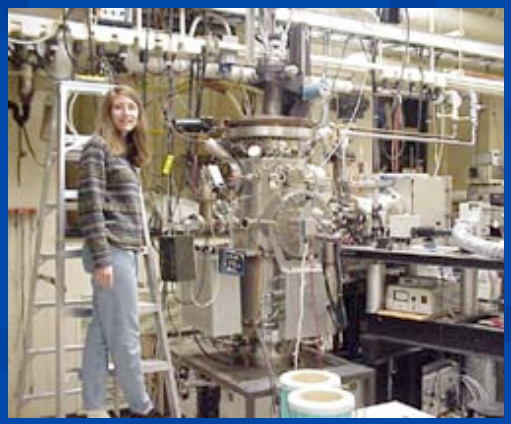
LHe Cooled UHV Scanning Tunneling Microscope with XPS, Auger, ISS



Inelastic He Atom Scattering for Determining Surface Forces of Clean/Oxidized Surfaces

Reactive Gas-Surface Oxidation with $O(^1D)$ and $O(^3P)$

Beam Scattering with *In Situ* Vibrational & Electronic Spec



Illustrative Examples of Interface Oxidation Studies from the Sibener Group: Ni, Rh, Graphite

Related Studies Can Be Done on Nb and Alloys

1. Profound Differences During Metallic Oxidation with O vs. O_2 : Extent of Oxidation for Rh(111)

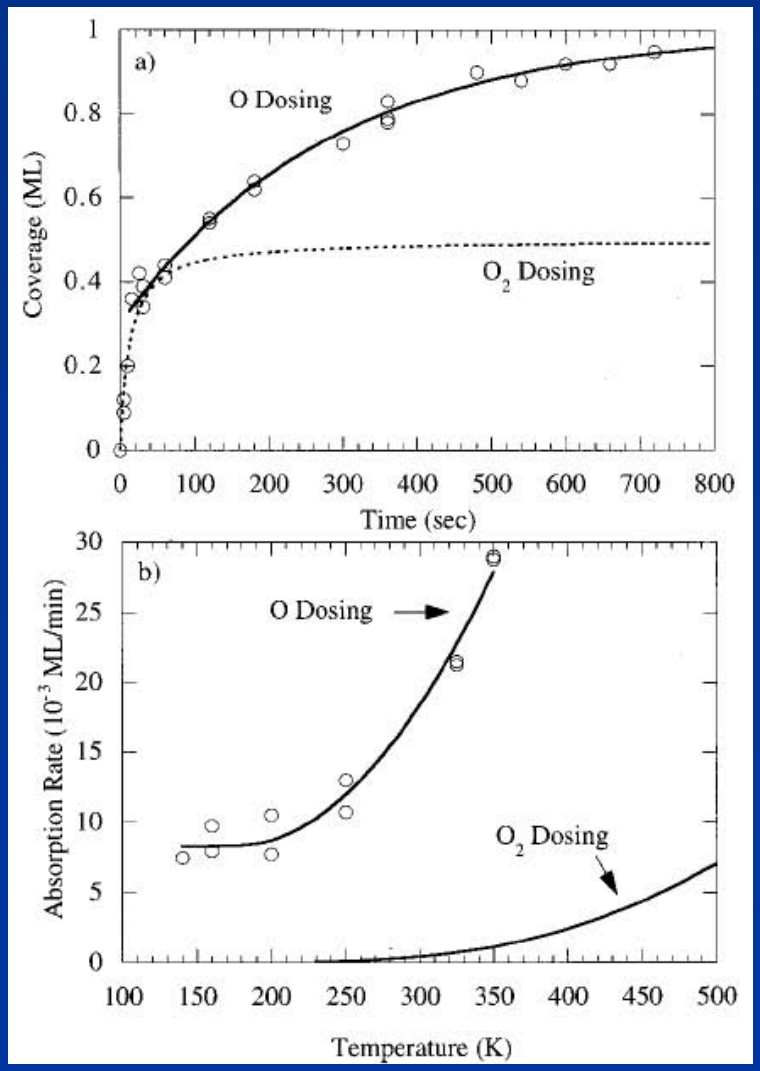
2. Profound Differences During Metallic Oxidation with O vs. O_2 : Kinetics of Oxidation for Ni(111)

3. Electron Effects Can Profoundly Influence Oxidation Chemistry & Kinetics of Metals: Ni(111)

4. Real-Time STM Imaging Reveals Morphological Evolution of Stepped Ni(977) During Oxidation

5. Defects Govern Graphite Interfacial Oxidation

Atomic vs. Molecular Oxygen/Rh(111): Differences in Metallic Oxidation and Overlayer Structure



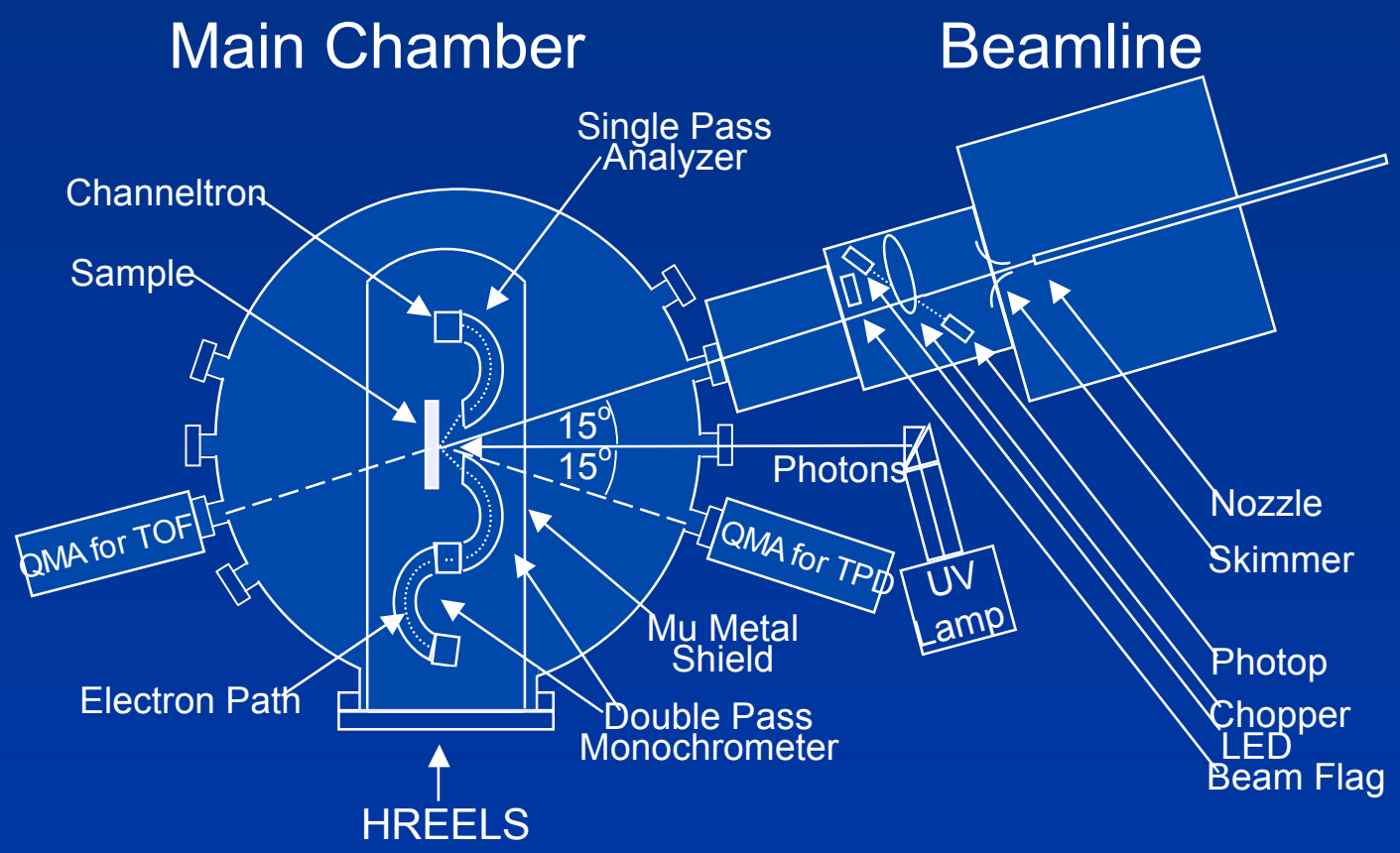
Surface Structure Differs with O vs. O_2 Exposure:

100% (1x1)-O/Rh(111) with O vs. 50% (2x1)-O with O_2

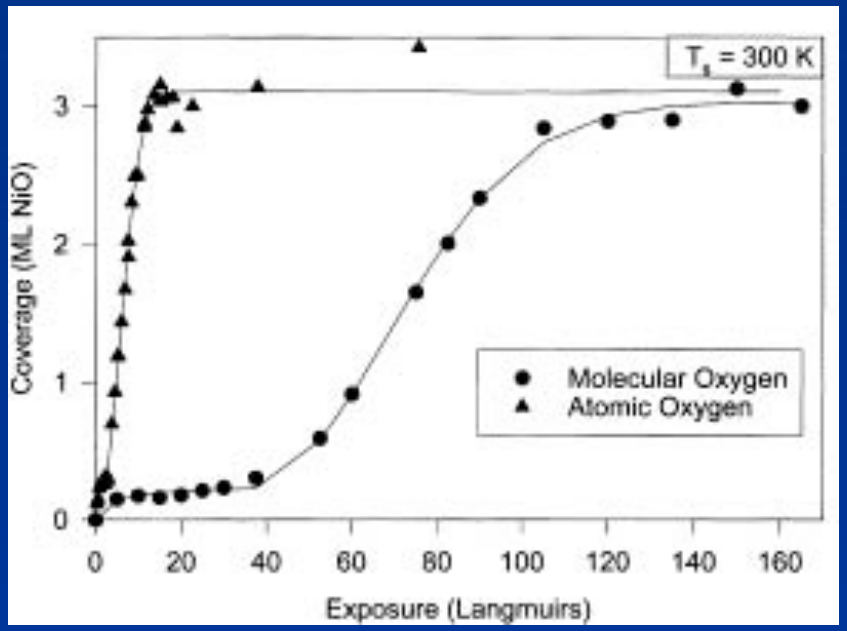
Kinetics & Extent of Oxygen Uptake Strongly Different for O vs. O2 Exposure; Especially at Low and Moderate Temperatures

Combined Supersonic Beam/HREELS Facility: Synergistic Effects: Electrons, Photons, & Ions

Intense Supersonic Atomic Oxygen Beam Source



Comparison of Metallic Oxidation Kinetics for Atomic vs. Molecular Oxygen



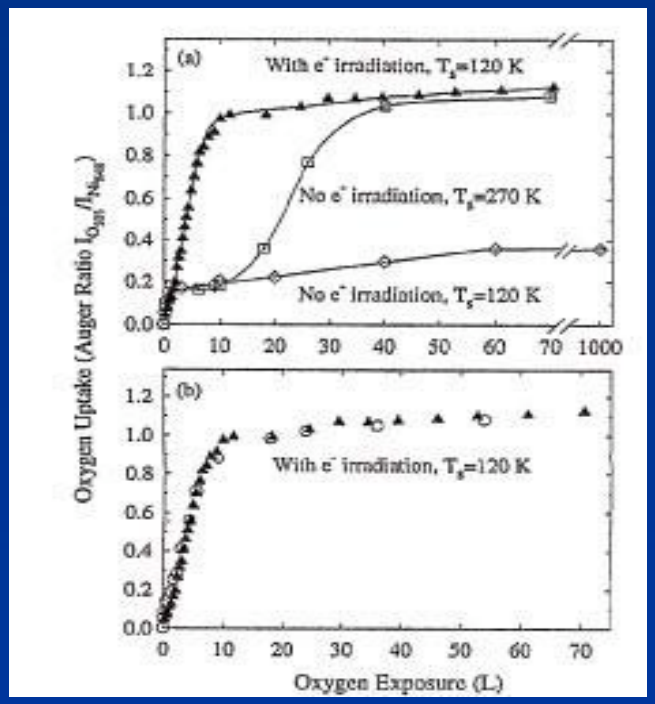
O vs. O_2 Oxidation of Ni(111)

* Enhanced Rate of Oxidation Observed for Atomic vs Molecular Oxygen
* Nucleation Step of Critical Mechanistic Importance
* Combined Use of Molecular Beams, STM, and Surface Spectroscopies

KEY FINDINGS/IMPLICATIONS

- Metallic Oxidation Kinetics Differ Between Atomic and Molecular Oxygen
- Atomic Oxygen Initiates Oxide Growth Rapidly
- Uptake Saturates at Same Level

Comparison of Metallic Oxidation Kinetics for Electron Irradiation vs. No Irradiation



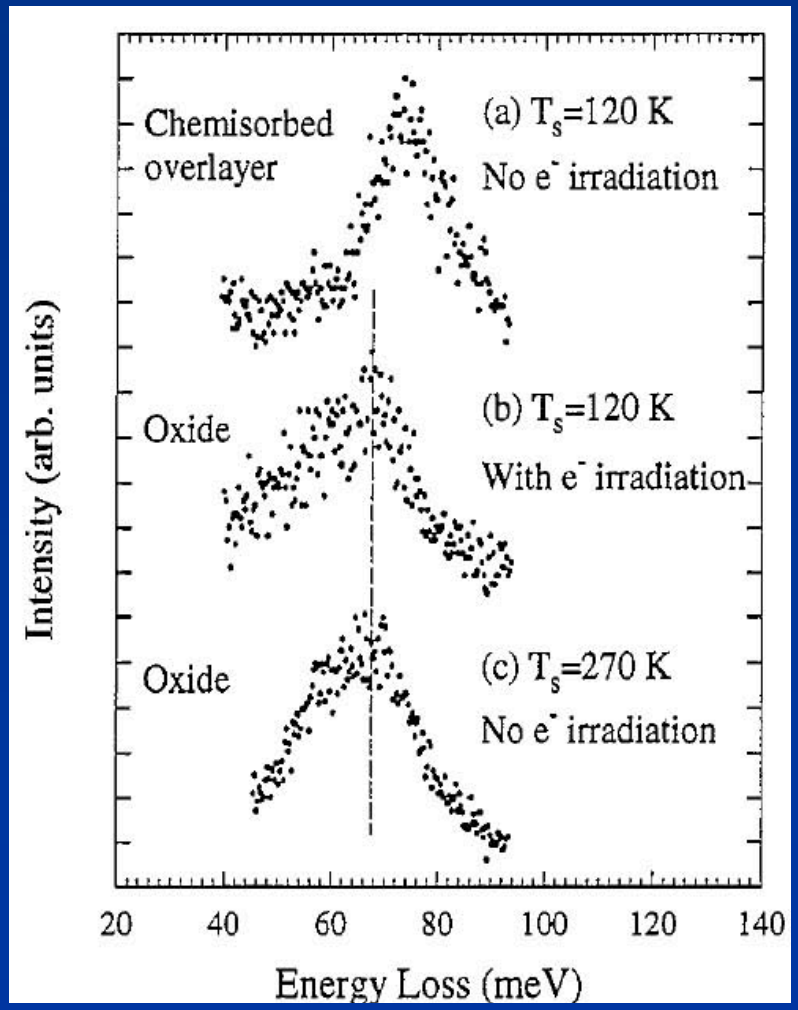
Oxidation of Ni(111)

Mechanism and Rate for Metallic Oxidation Influenced Strongly by Synergistic Effects Involving Electron Irradiation and Atomic Oxygen

KEY FINDINGS/IMPLICATIONS

- Metallic Oxidation Kinetics Change in Under Electron Irradiation
- Electron Irradiation Initiates Rapid Oxide Growth
- Synergistic Effects Involving Atomic Oxygen Present with both Simultaneous and Alternating Electron Exposure
- Nucleation Step Crucial
- Nucleation Mechanism Changes with Increasing O Kinetic Energy
- Mechanistic Differences Between Atomic vs. Molecular Oxygen

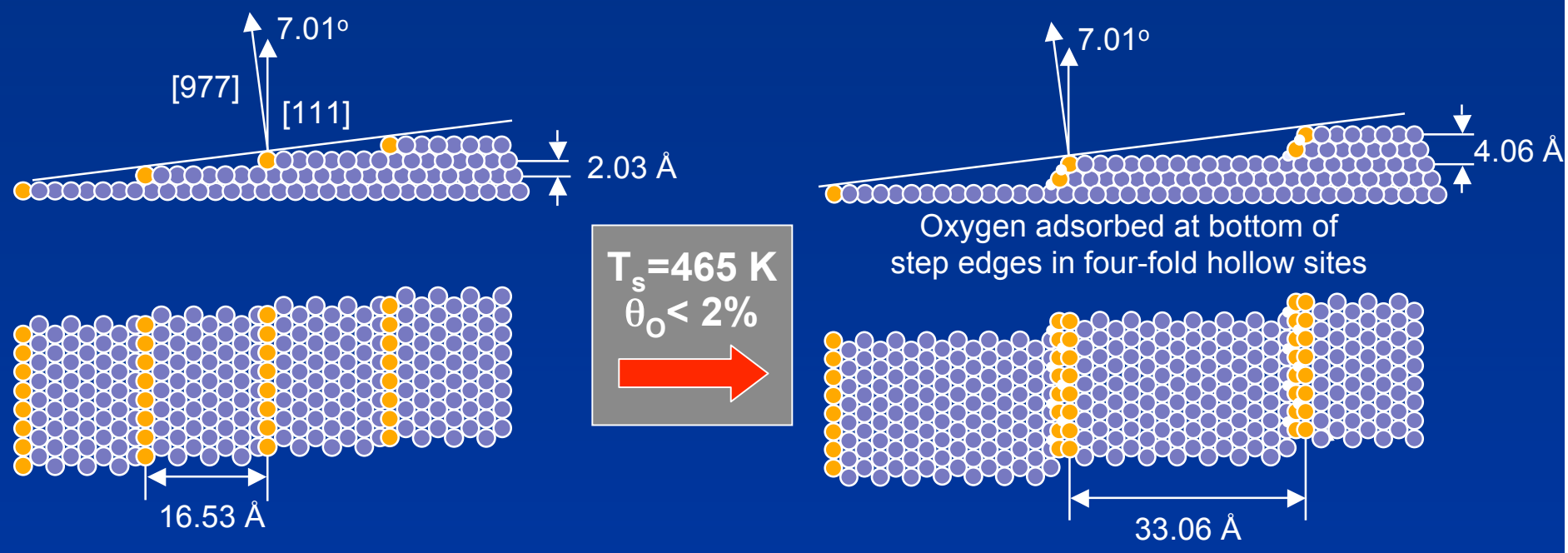
In Situ Vibrational Spectroscopy (HREELS) Gives Chemical View of Interface in Real-time During Oxidation Experiments



Synergistic Effects of Electron Irradiation During Ni Oxidation

- At Low Temperatures Surface Passivates with Chemisorbed Oxygen Overlayer
- Synergistic Influence of Electrons Produce Surface and Bulk Oxide

Next Example: Trace Oxygen Adsorption Can Induce Single to Double Step Transformations for Ni(977)

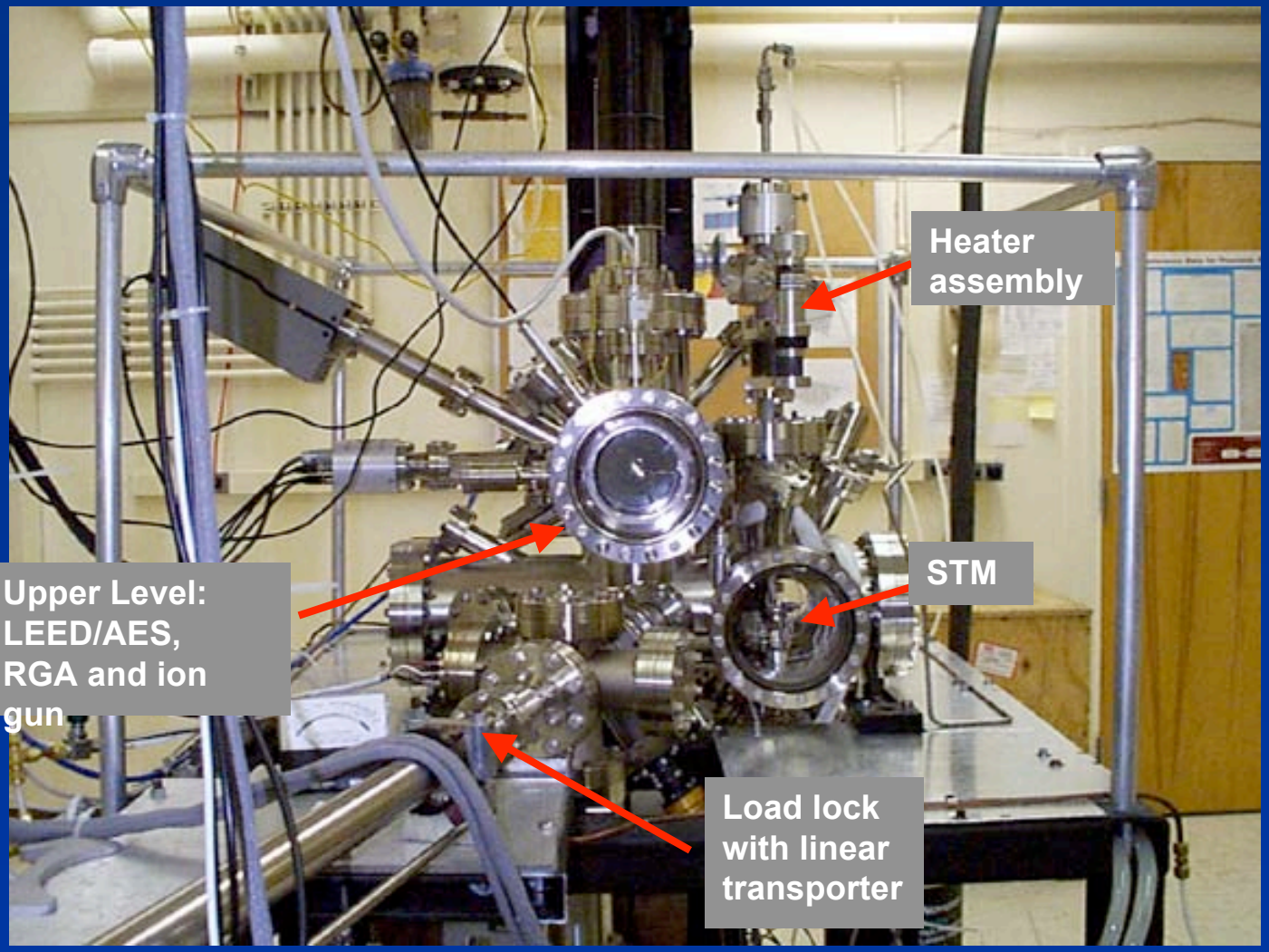


Single Steps

Double Steps

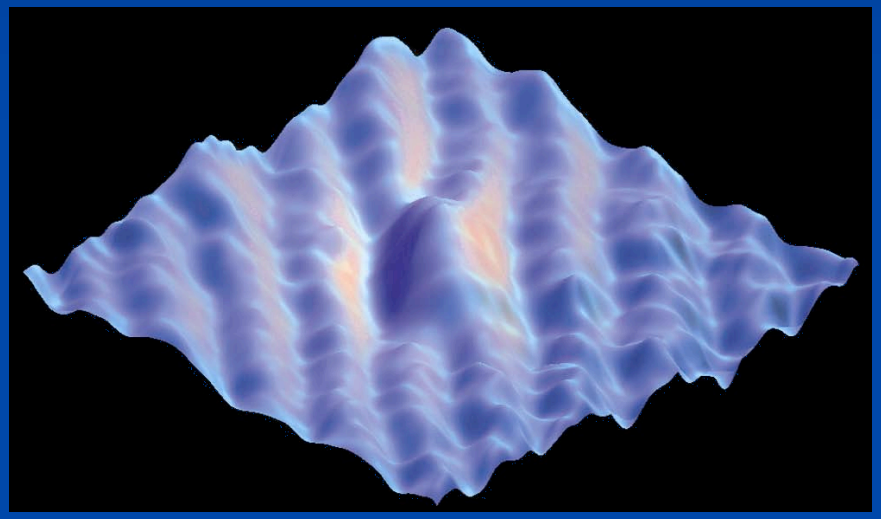
THE UNIVERSITY OF CHICAGO

Variable-Temp UHV Scanning Tunneling Microscope

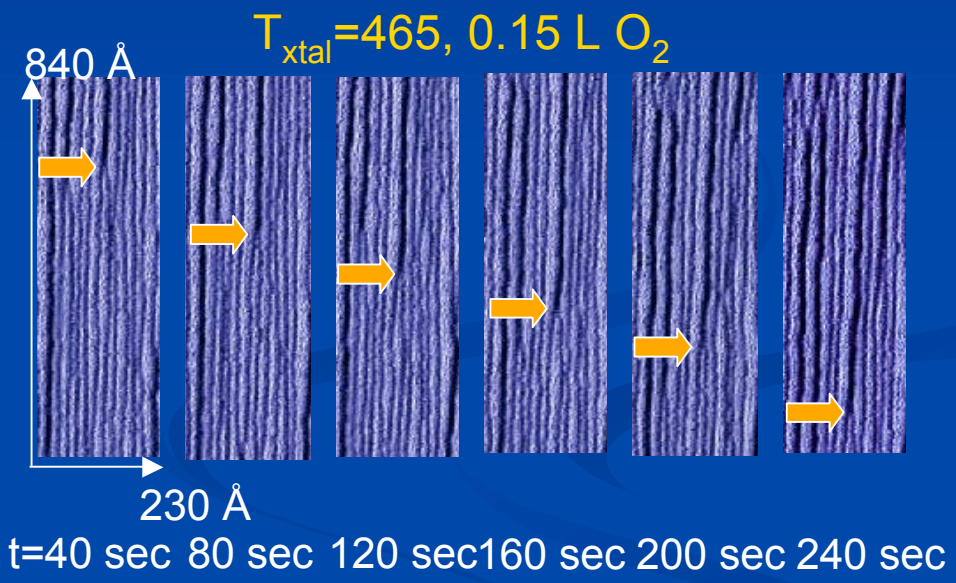


Interfacial Dynamics & Oxygen Driven Reconstruction of a Stepped Metallic Surface *Via* Time-Lapse Scanning Tunneling Microscopy

STM Image of Zippering Event



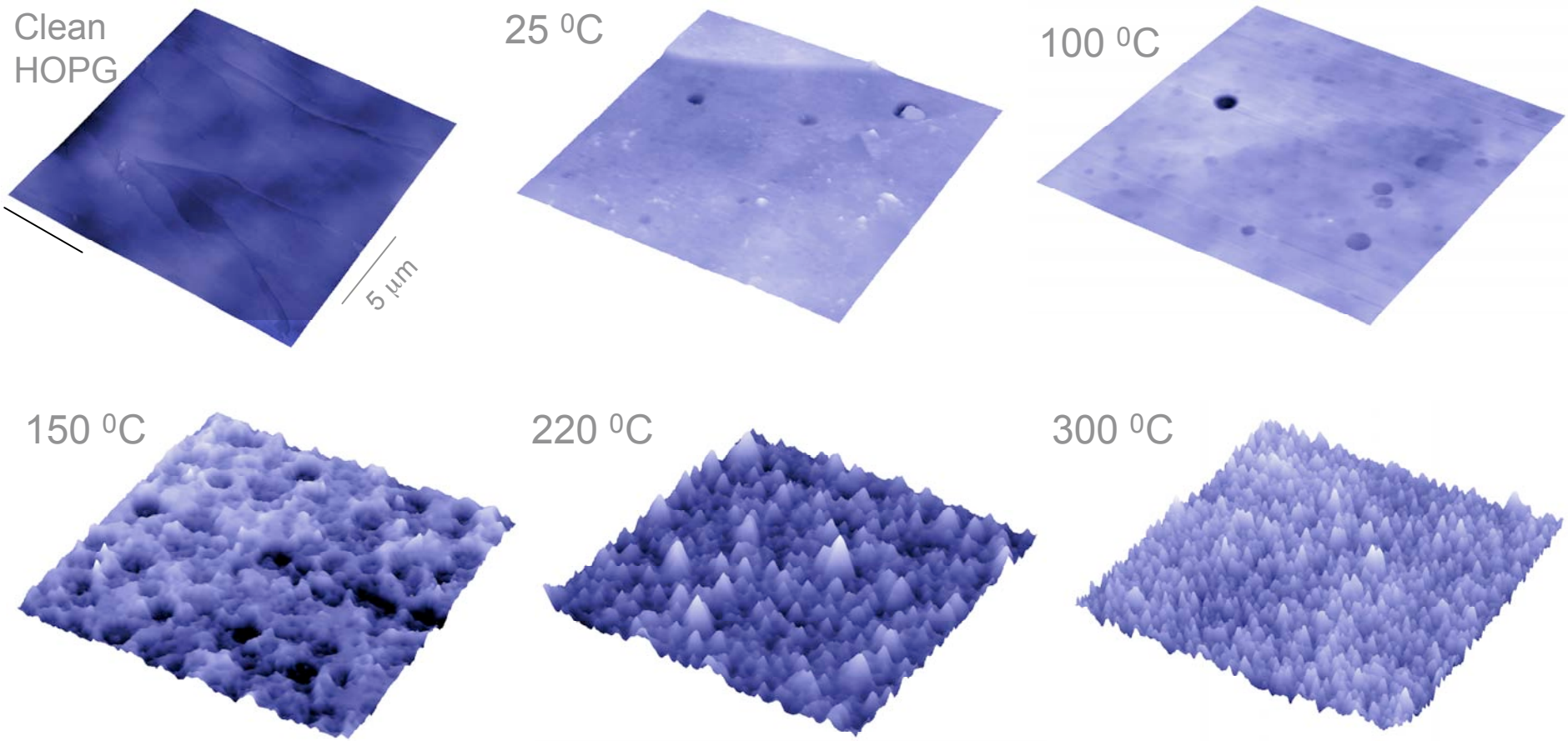
Zippering Event During Oxidation



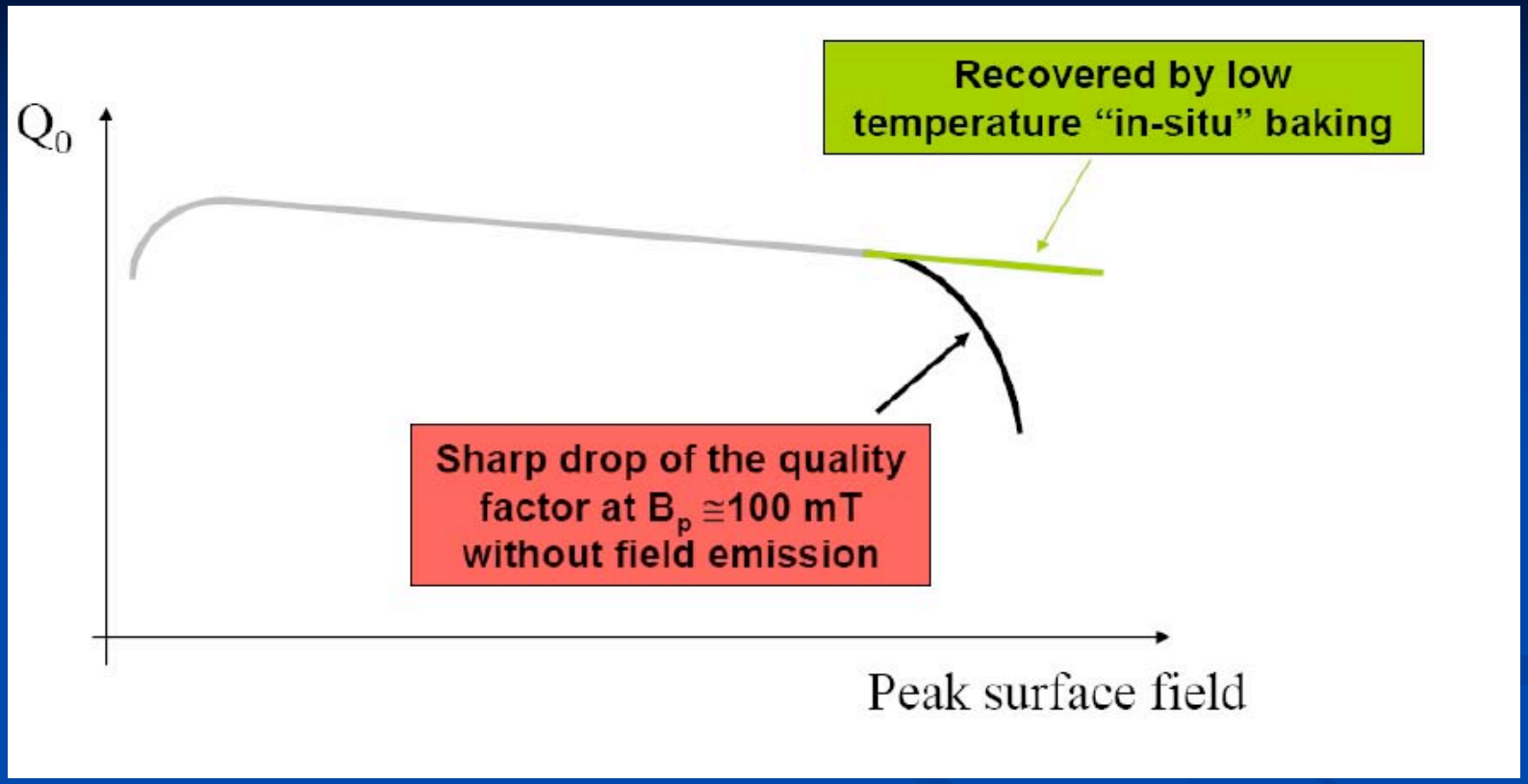
T.P. Pearl and S.J. Sibener

J. Phys. Chem. *B105*, 6300-6306 (2001)
J. Chem. Phys. *115*, 1916-1927 (2001)
Surf. Sci. Lett. *496*, L29-L34 (2002)

Surface Morphology Evolution of HOPG after Exposure to 5 eV O(^{3}P) as a Function of Surface Temperature



Q-Drop of Solid Nb Cavities (Detlef Reschke, DESY; SRF 2007)



What is a bake??? Open Air, Humidity, Pure Nitrogen, Vacuum, UHV???

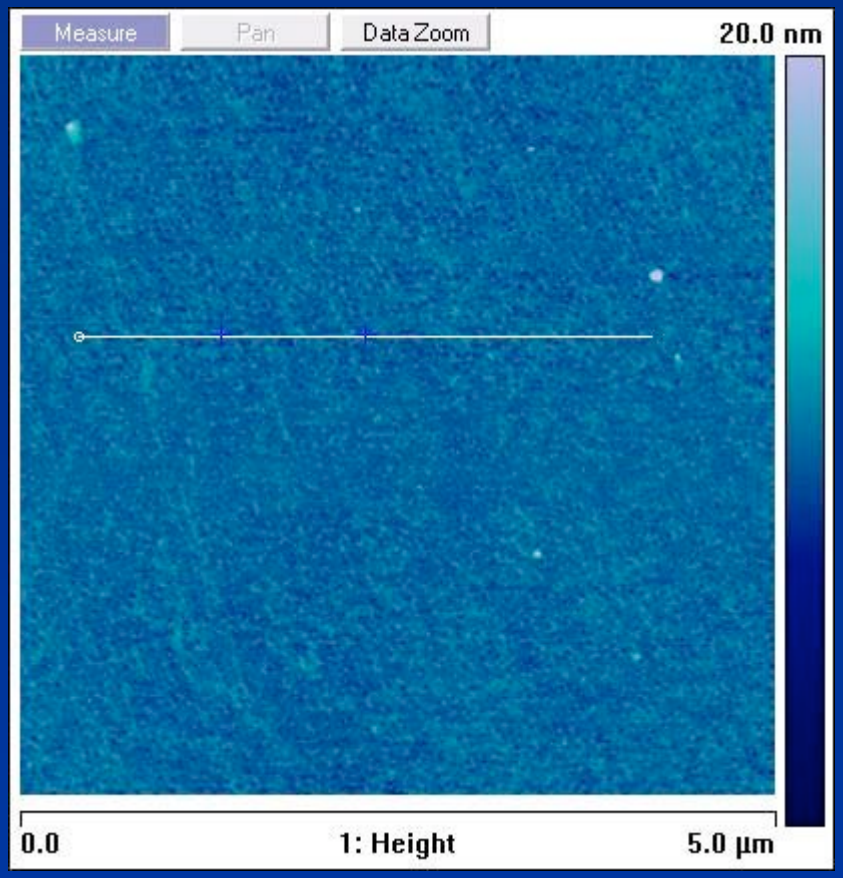
Temperature of bake??? 110-125 C 1-2 days; 135 - 150 C 3 - 12 hours

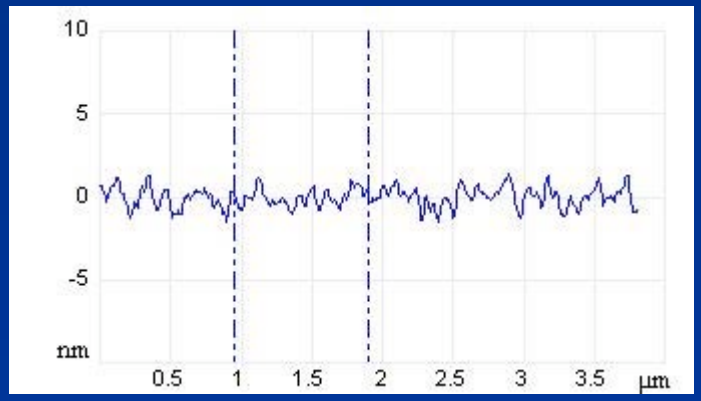
Cooldown rate??? It matters!

What occurs at the atomic level wrt O, H, Nb, & Interfacial Structure???

5-micron view of Niobium Polished at Cabot Microelectronics

Atomic Force Microscopy Image of As-Received Sample

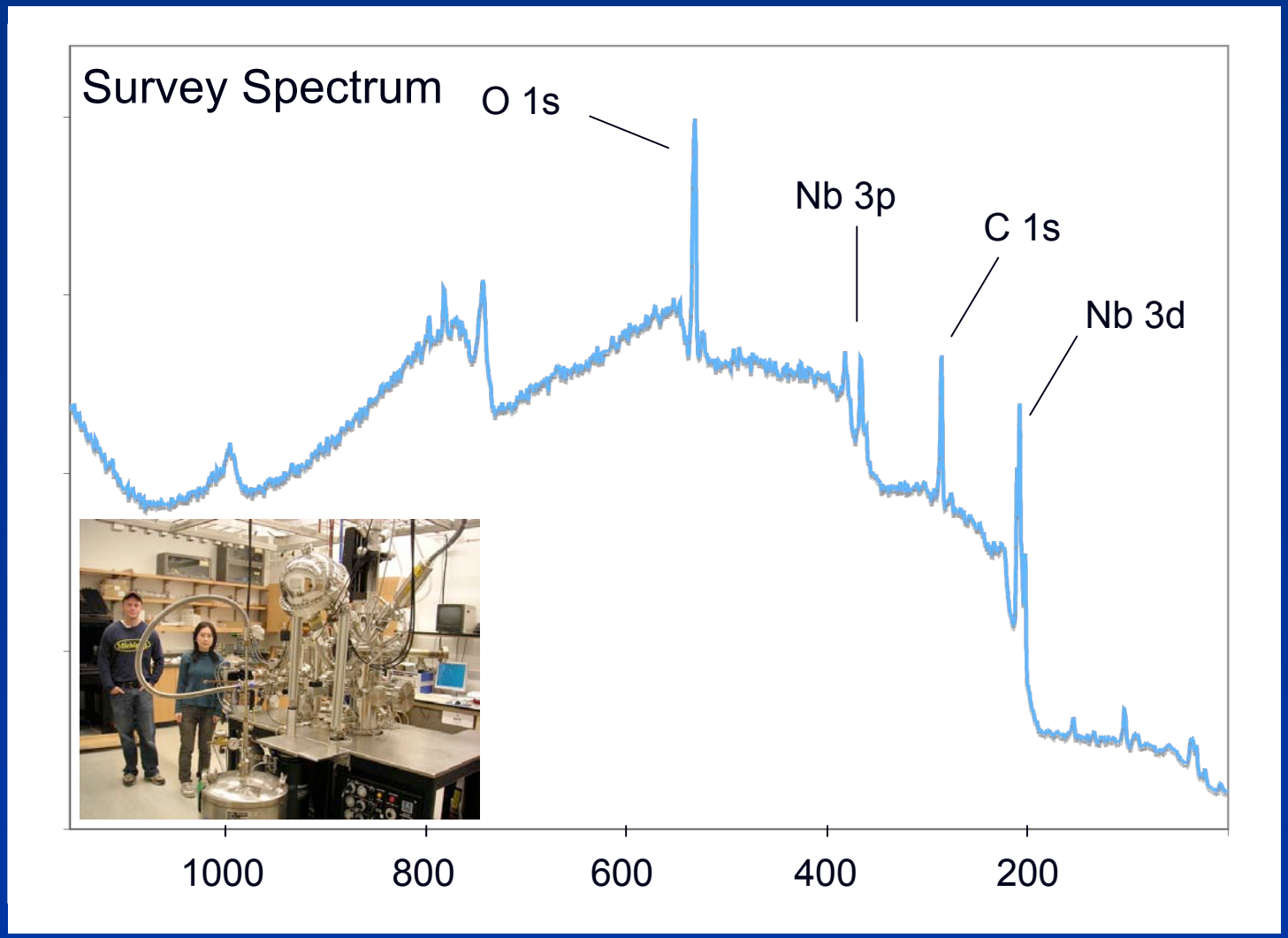




Average roughness is <0.5 nm

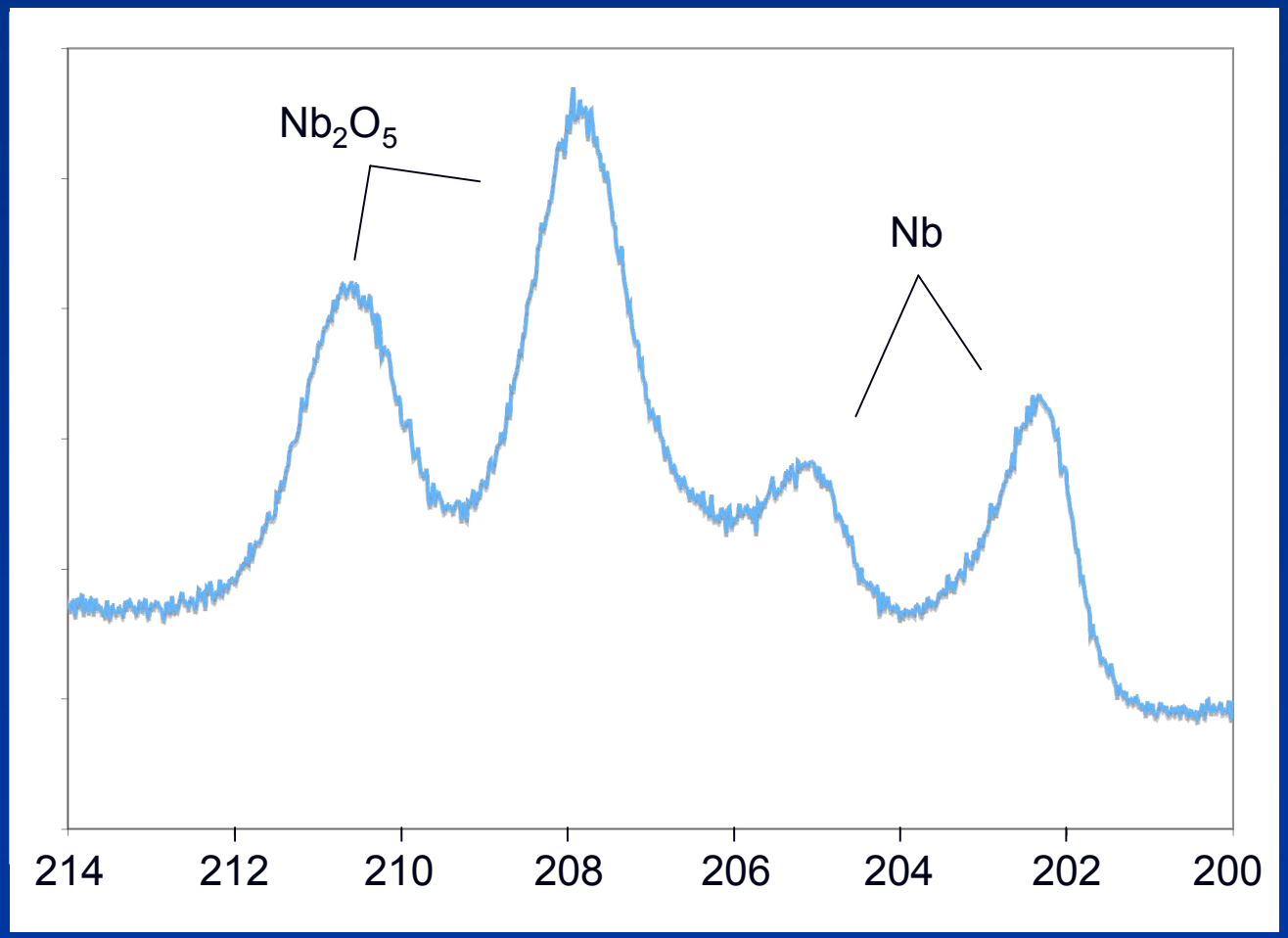
Imaging: Nataliya Yufa, Graduate Student at UChicago

UChicago Nb XPS Spectrum of FNAL Sample Polishing Done at Cabot Microelectronics



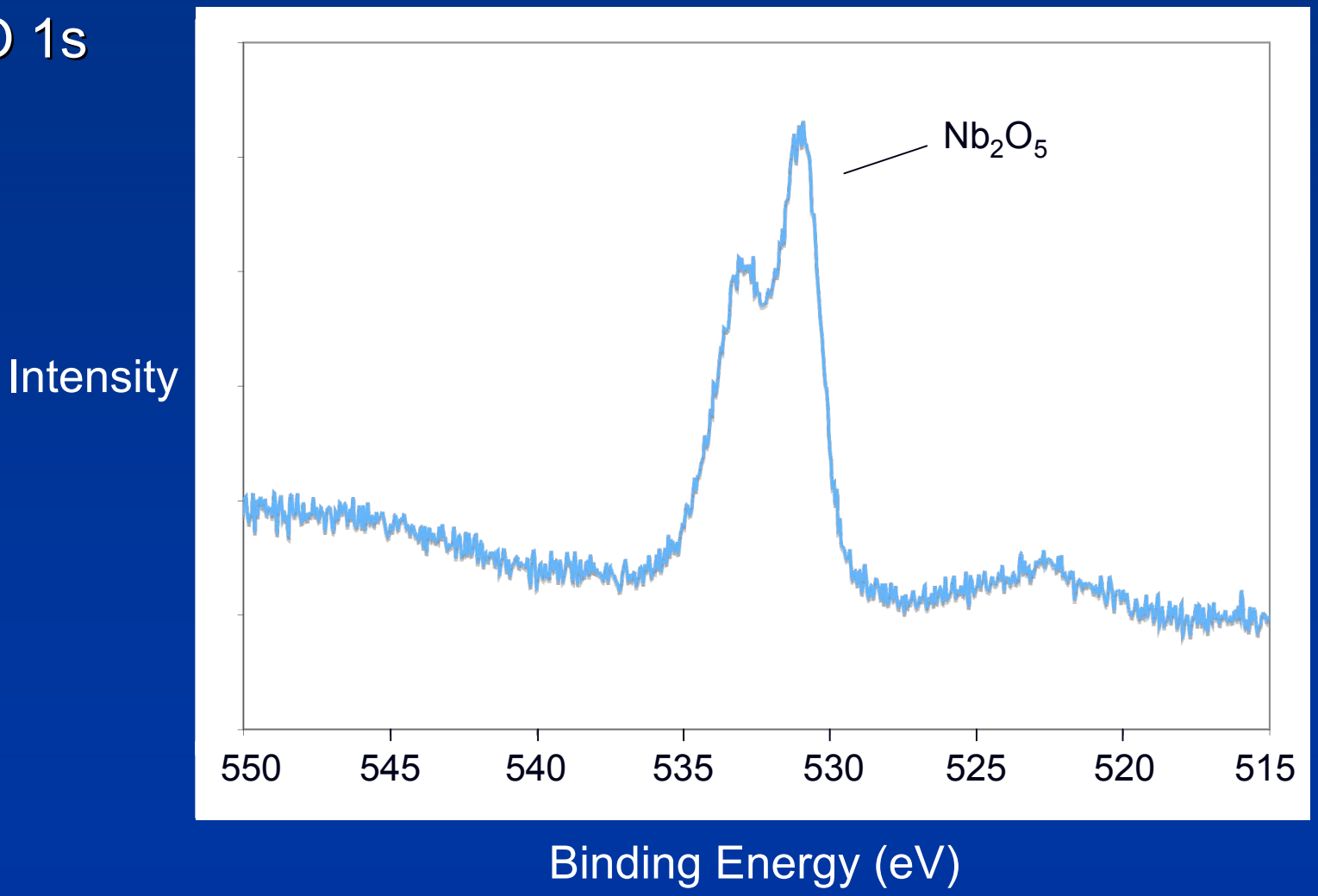
XPS of Nb Sample - High Res View of Nb 3d

- Nb 3d



XPS of Nb Sample - High Res View of O 1s

- O 1s



Quantitative Chemical Assessment of the "As-Polished" Nb Surface

(i.e., without UHV cleaning procedures)

- Quantification of Surface and Selvedge Nb and O
  - From the survey spectrum, the sample surface region is:
    - 20.1% Nb, 41.4% O, 37.5% C and 1% Co
  - From the high-resolution spectrum of the Nb 3d peak we find:
    - 63.6% is from Nb_2O_5 and 36.4% from Nb
  - From the high-resolution spectrum of the O 1s peak, we find:
    - 71.6% is from Nb_2O_5 and 28.4% from other sources, most likely water

Nb 20.1% → 7.3% (Nb); 12.8% (Nb_2O_5)

O 41.4% → 29.6% (Nb_2O_5); 11.8% (other)

O : Nb = 2.3

This value is less than 2.5, probably due to existence of other NbO_x ($x \leq 2$)

UHV-XPS: Miki Nakayama, Graduate Student at UChicago

U. of Chicago - Fermilab - ANL Collaboration on SRF Nb Research, Nov 27 2007

Fundamental Studies of the Interfacial Chemical Kinetics and Morphological Evolution of Niobium During Oxidation

Steven J. Sibener, Univ. of Chicago
The James Franck Institute and Department of Chemistry
& Lance Cooley, FNAL

Expts for Examining Nb & Related Oxides Getting Underway

- Single Crystals & Technical Materials: Nb, ALD Coatings (ANL)
- Chemical Evolution and Communication with Selvedge/Bulk
- Structural Evolution
- *Baking and Cooldown After Annealing - What is Going On?*
- Chemical Environment During Reactions: O, O_2, H_2O, H_2
- Synergistic Effects: electrons, photons, local electric fields
- Field Emission and Local Work Function