Spatially Resolved Adsorption Structure and Diffusion Dynamics of Sn on (3×1)-O Nb(100)

Rachael G. Farber, Sarah A. Willson, Nathan S. Sitaraman‡, Tomas A. Arias‡, and Steven J. Sibener

Sibener Group
The James Franck Institute and Department of Chemistry
The University of Chicago

‡ Cornell University, Department of Physics, Ithaca, NY

Spatially Reso Structure and Diffusion Dyn 3×1)-O Nb(100)

Rachael G. Farber, Sarah an‡, Tomas A. Arias‡, and

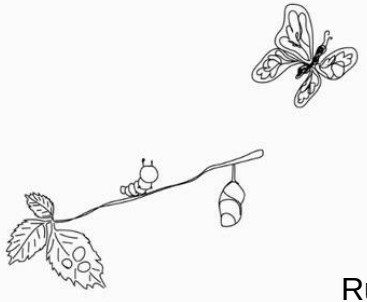
The James Franck Institute and Department of Chemistry
The University of Chicago

‡ Cornell University, Department of Physics, Ithaca, NY

The Sun and Her Flowers

you do not just wake up and become the butterfly

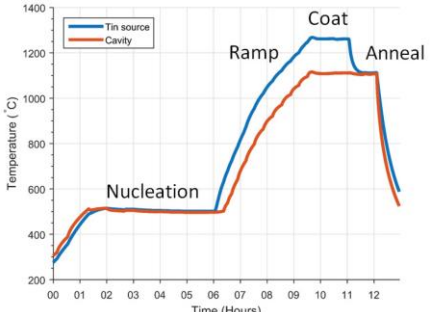
- *growth is a process*

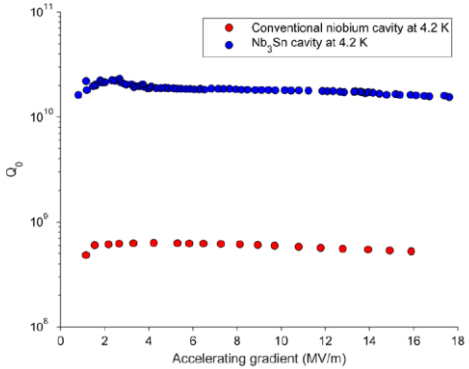


Rupi Kaur

Vapor Diffusion Procedures for Nb_3Sn SRF Cavities and Resultant Cavity Performance

- Vapor diffusion is a prominent technique for Nb_3Sn film growth
- Current Nb_3Sn SRF cavities quench ~ 17 MV/m
  - Far below the theoretical maximum of 96 MV/m
- **Defects in the Nb_3Sn film lower cavity performance**
  1. Nb oxide thickness
  2. Underlying substrate crystallography
  3. Sn nucleation and diffusion behavior





A thorough understanding of the structural and chemical features influencing Nb_3Sn growth must be realized

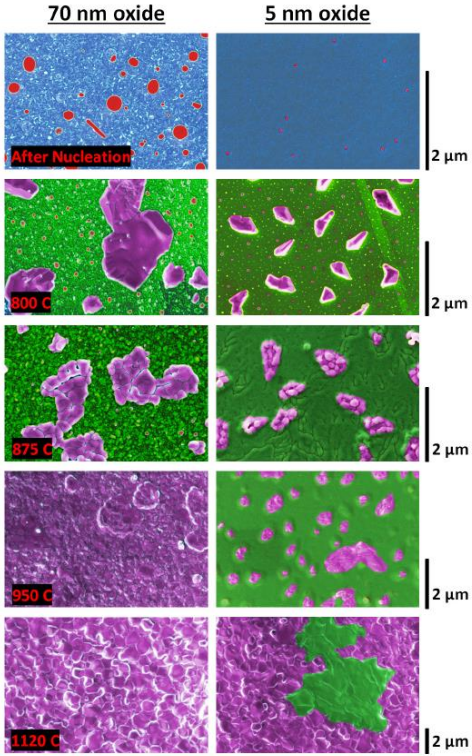
U. Pudasaini, G. Eremeev, C. E. Reece, G. Ciovati, I. Parajuli, N. Sayeed, M. J. Kelley. *SRF2019*, Dresden, Germany, 65-70 (2019)

R. D. Porter, T. Arias, P. Cueva, D. L. Hall, M. Liepe, J. T. Maniscalco, D. A. Mueller, N. Sitaraman. *LINAC'18*, Beijing, China, 462-465 (2018)

The Underlying Nb Substrate Influences Nb_3Sn Growth and Film Quality

- There is not a thorough understanding of the Nb_3Sn growth mechanism on Nb substrates
- Nb substrate properties are known to effect Nb_3Sn film quality
  - Underlying substrate crystallography
  - **Native oxide thickness**
- A thicker native oxide layer results in more homogeneous Sn coverage, enhanced RF shielding, and enhanced cavity performance

An atomic-scale, mechanistic investigation into the relationship between Nb oxide and Nb_3Sn formation is necessary to inform predictive Nb_3Sn growth models

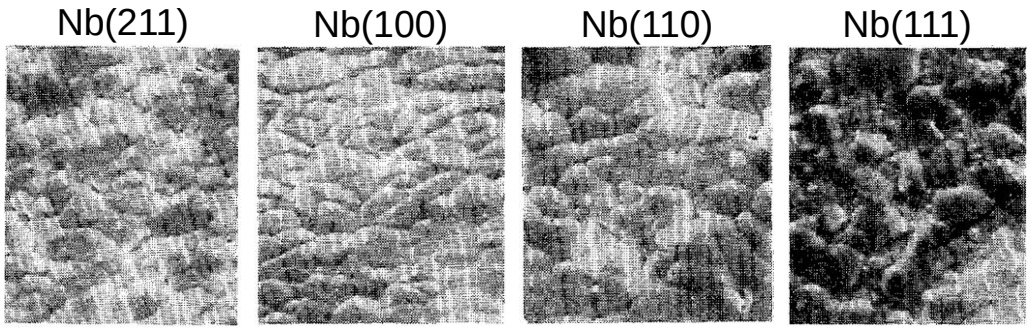


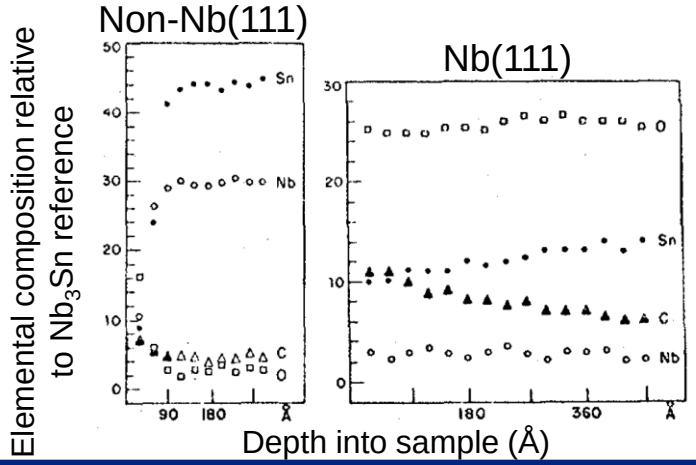
R. D. Porter, T. Arias, P. Cueva, D. L. Hall, M. Liepe, J. T. Maniscalco, D. A. Mueller, N. Sitaraman. *LINAC'18*, Beijing, China, 462-465 (2018)

The Underlying Nb Substrate Crystallography Influences Nb_3Sn Growth Behavior

- Nb_3Sn growth as a function of Nb surface termination
  - Cylindrical (rod) Nb(110) single crystal
  - Nb(110), Nb(100), Nb(211), and Nb(100)
- **The Nb(111) sample had undesired Nb_3Sn film properties**
  - Contaminant incorporation
  - Irregular grain size and roughness

Crystallographic orientation of the underlying Nb substrate influences contaminant incorporation and Nb_3Sn film quality

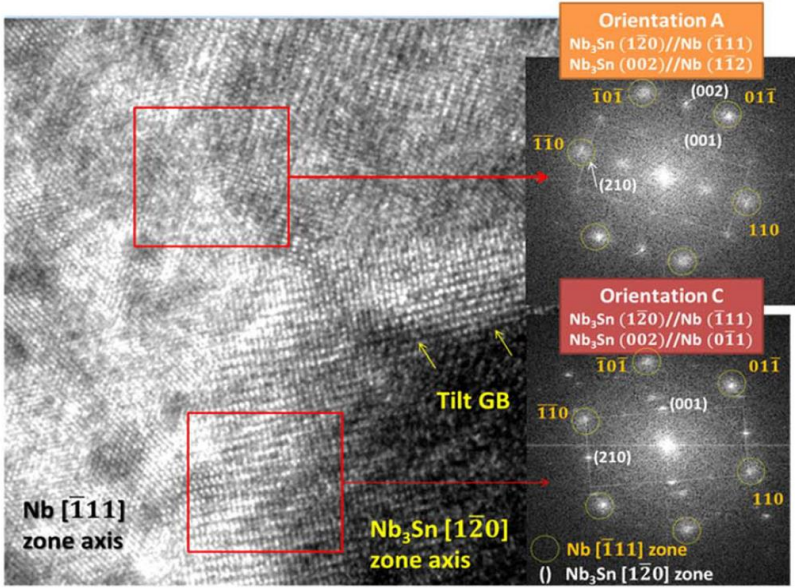




V. Diadiuk, J. Bostock, M. L. A. MacVicar, *IEEE Trans. Magn.*, **15**, 610-612 (1979)

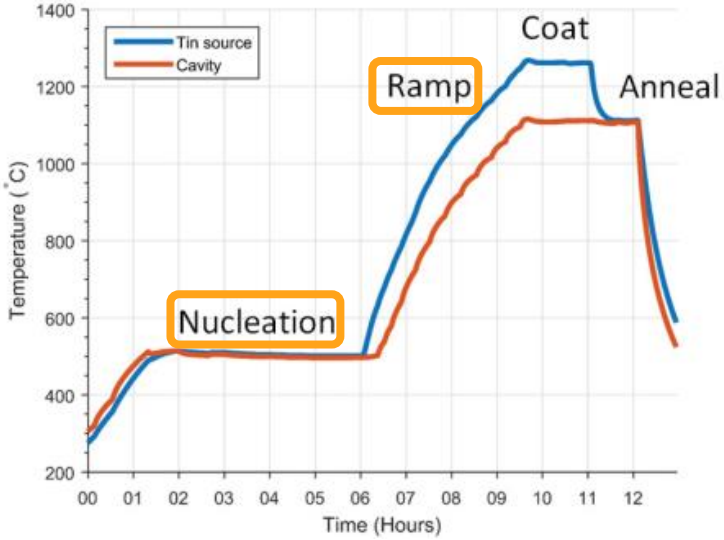
Analysis of Nb_3Sn/Nb SRF Cavity Coupons and Surface Mediated Nb_3Sn Growth Behavior

- Continuing efforts to understand the growth mechanisms of Nb_3Sn
  - Strong relationship between Sn heterogeneity and irregular grain size to the Nb surface orientation
  - Influence of Nb_2O_5 on Sn nucleation and diffusion
- Minimize imperfections and defects in Nb_3Sn film
- There is still not a comprehensive understanding of the surface mediated processes guiding Nb_3Sn growth



J. Lee, S. Posen, Z. Mao, Y. Trenikhina, K. He, D. L. Hall, M. Liepe, D. N. Seidman, *Supercond. Sci. Technol.*, **32**, 024001 (2019)

Leveraging Ultra High Vacuum Surface Science Techniques to Elucidate Nb_3Sn Growth Mechanisms

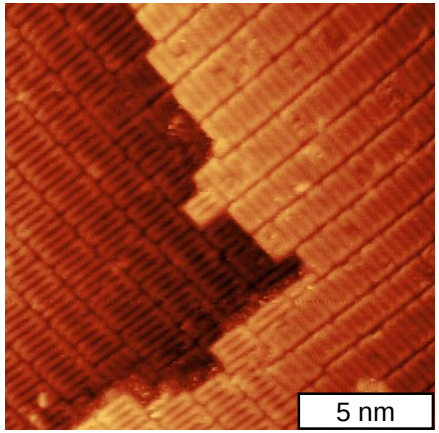


1. How does the native (3×1)-O surface oxide participate in Sn adsorption?
2. How does sample temperature impact Sn diffusion behavior?
3. Do atomic scale surface defects (step edges) influence Sn adsorption or diffusion behavior?

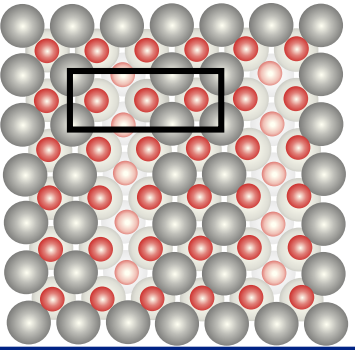
Using ultra-high vacuum (UHV) surface-sensitive techniques we aim to identify the interactions guiding Sn adsorption and diffusion on the (3 × 1)-O Nb(100) surface

R. D. Porter, T. Arias, P. Cueva, D. L. Hall, M. Liepe, J. T. Maniscalco, D. A. Mueller, N. Sitaraman. *LINAC'18*, Beijing, China, 462-465 (2018)

Nb(100) (3×1)-O as a Model System to Study Nb_3Sn Growth Mechanisms



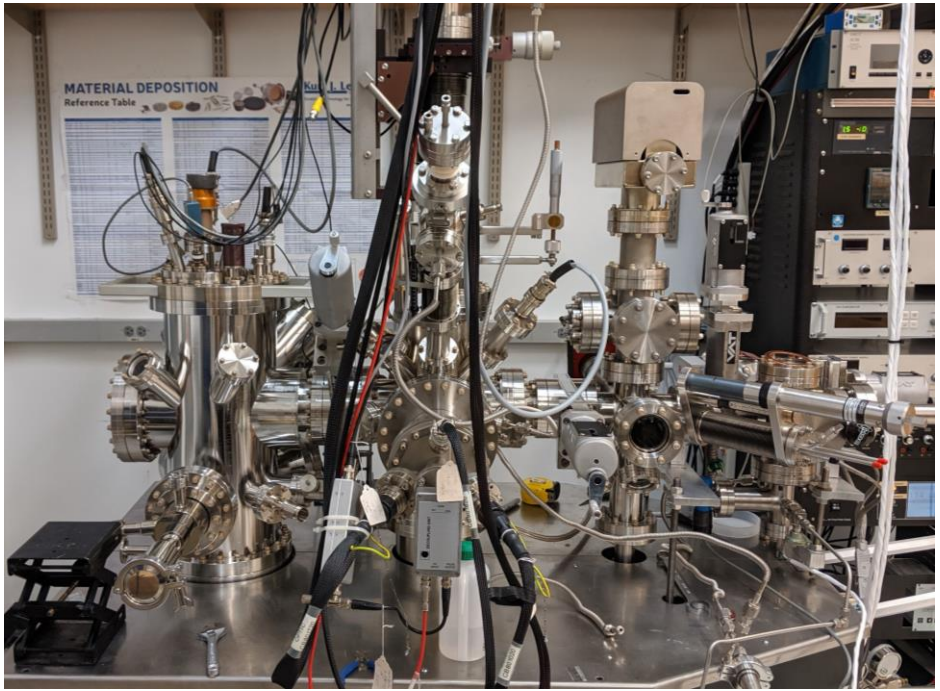
- **Use Nb(100) (3×1)-O as a model system** to compare to actual SRF cavity studies
  - It is understood that the (100) orientation forms favorable Nb_3Sn films
- Actual Nb SRF cavities have a native oxide (Nb_2O_5) layer present
- Nb(100) annealed at $T_{crystal}$ = 1800 K
  - **(3×1)-O ladders** (NbO) across the Nb(100) surface



Nb(100) serves as a model system due to the highly ordered (3×1)-O ladders that provide a structural reference for Sn adsorption and diffusion and structural stability at elevated temperatures

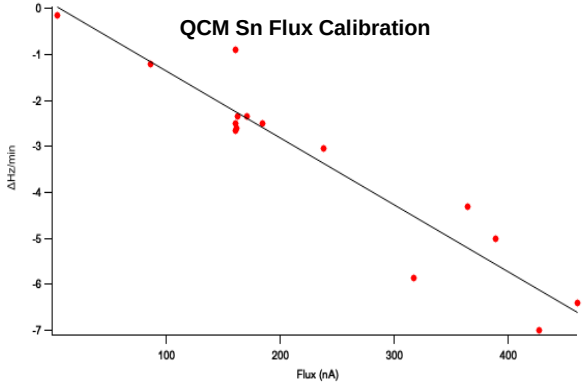
J. Lee, S. Posen, Z. Mao, Y. Trenikhina, K. He, D. L. Hall, M. Liepe, D. N. Seidman, *Supercond. Sci. Technol.*, **32**, 024001 (2019)
V. Diadiuk, J. Bostock, M. L. A. MacVicar, *IEEE Trans. Magn.*, **15**, 610-612 (1979)

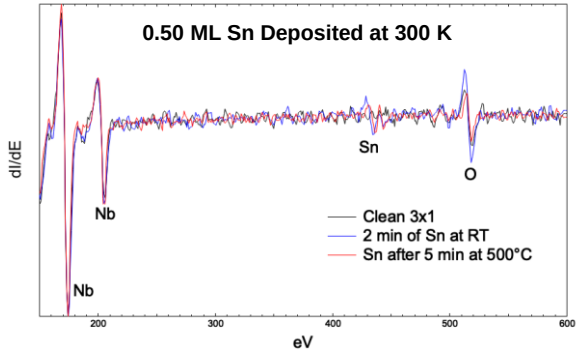
Ultra-High Vacuum Apparatus for *In Situ* Nb_3Sn Growth Experiments

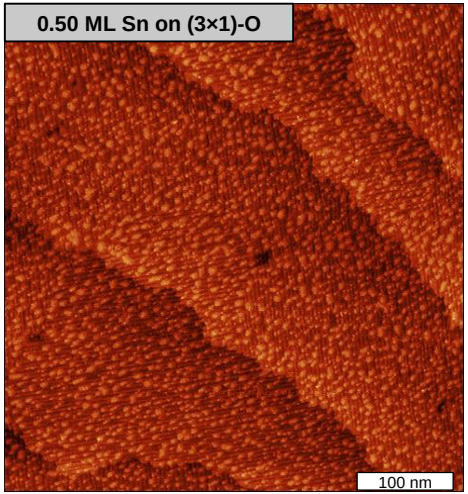


- *In situ* surface characterization using UHV surface science techniques
  - **Electron beam (e-beam) evaporation source**
    - Submonolayer Sn deposition
  - **Quartz crystal microbalance (QCM)**
    - Calibrate Sn deposition rates (sub-monolayer (ML))
  - Auger electron spectroscopy (AES)
    - Elemental analysis
  - Temperature programmed desorption (TPD)
    - Identify and quantify gas-phase species
  - X-ray photoelectron spectroscopy (XPS)
    - Elemental analysis
  - **Scanning tunneling microscopy (STM)**
    - Real space structural information
  - Scanning tunneling spectroscopy (STS)
    - Electronic characterization

Sn Exposure Calibration and Analysis *via* QCM, AES, and STM



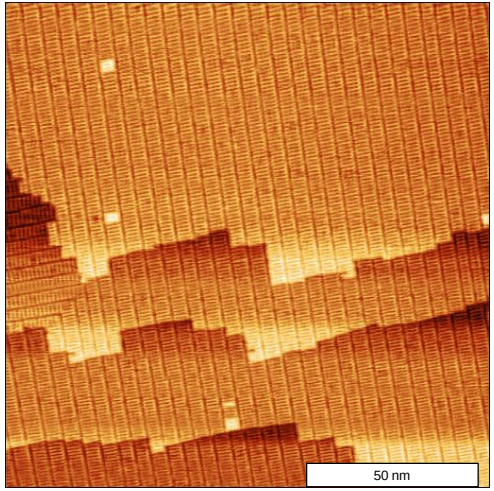




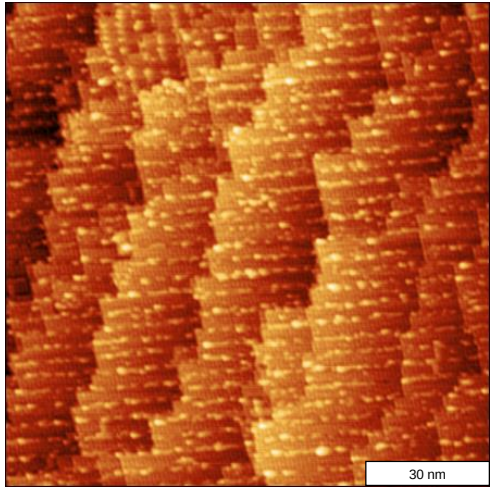
- QCM Calibration: ΔHz → ΔML
  - QCM: $5.51 \times 10^{14} \frac{Sn\ atoms}{Hz}$
  - ~ 0.112955 ML/Hz
- Tunable and reproduceable Sn deposition
- 0.5 ML Sn deposited at room temperature (300 K) shows <u>uniform surface adsorption</u>

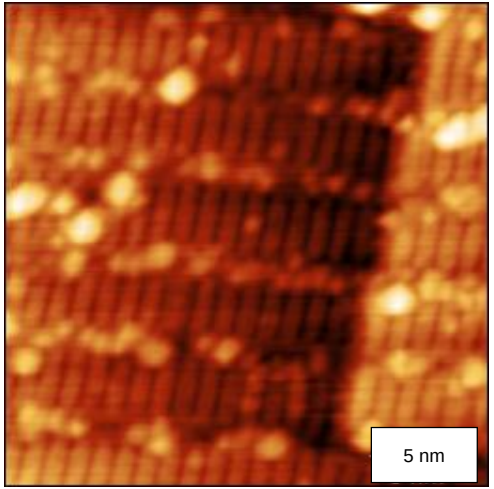
In order to determine preferred surface adsorption sites with atomic scale resolution a smaller Sn exposure is needed

Preferred Surface Adsorption Site for ~ 0.25 ML Sn Deposited at 300 K



0.25 ML Sn

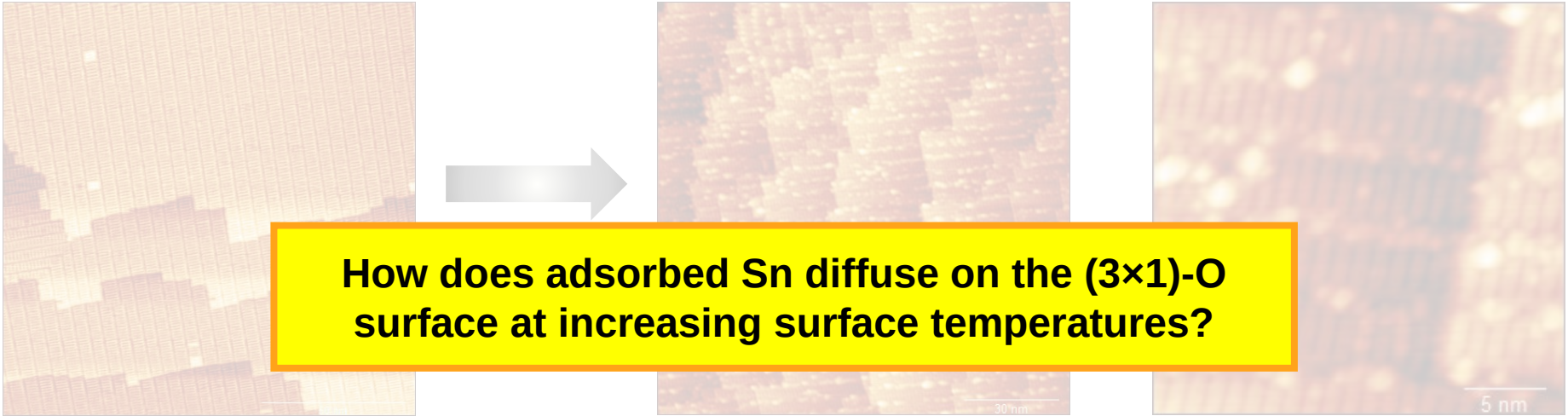




- Following Sn deposition at 300 K, Sn adatoms order **between** (3×1)-O ladder rows
- There is little adsorption along step edges or other surface defects

Sn adsorbs along (3×1)-O ladders. The oxide structure appears to influence Sn adsorption at 300 K more than larger surface defects.

Preferred Surface Adsorption Site for ~ 0.25 ML Sn Deposited at 300 K

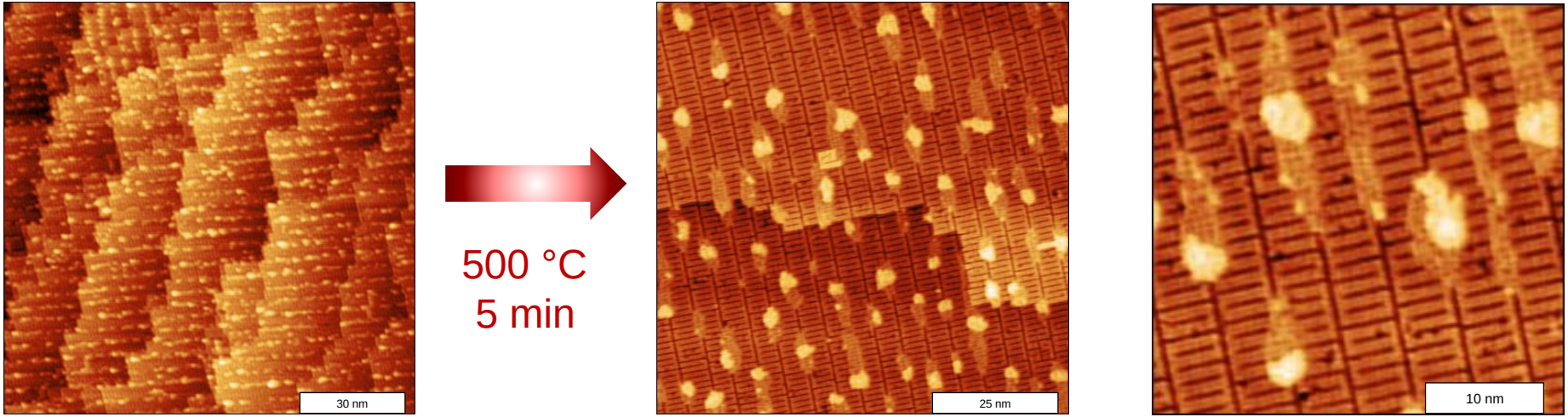


How does adsorbed Sn diffuse on the (3×1)-O surface at increasing surface temperatures?

- Following Sn deposition at 300 K, Sn adatoms order between (3×1)-O ladder rows
- There is little to no adsorption along step edges or other surface defects

Sn adsorbs along (3×1)-O ladders. The oxide structure appears to influence Sn adsorption at 300 K more than larger surface defects.

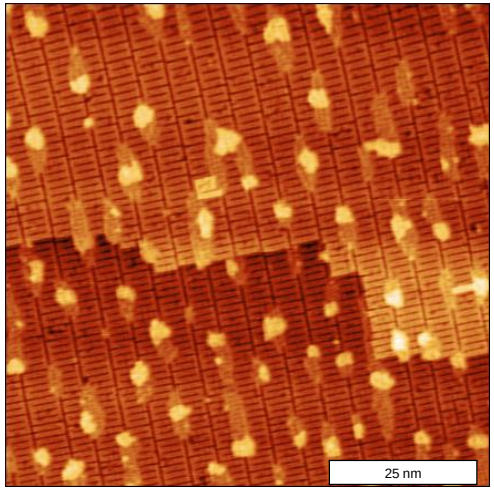
Structural Evolution of Sn on (3×1)-O/Nb(100) Following Anneal at 500 °C



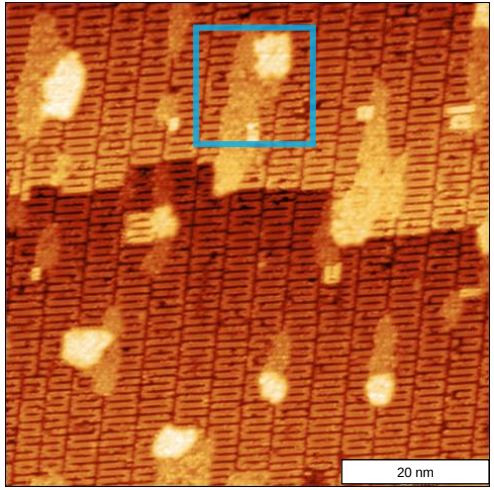
- Sn diffusion along (3×1)-O ladders
- Heterogeneous Sn structures
- Larger surface defects are not the primary site for Sn aggregation

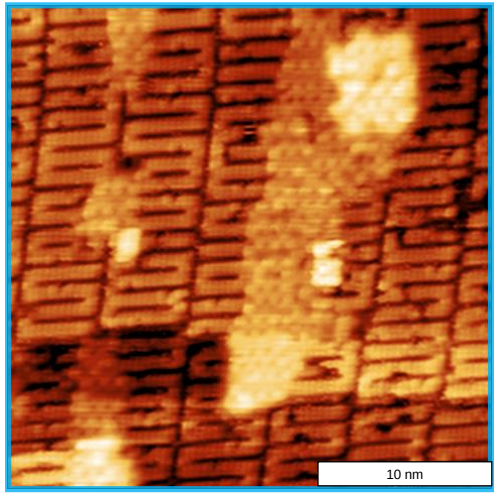
There appears to be a barrier for Sn diffusion <u>across</u> the NbO ladders at Sn nucleation temperatures

Structural Evolution of Sn on (3×1)-O/Nb(100) Following Anneal at 600 °C



600 °C
5 min

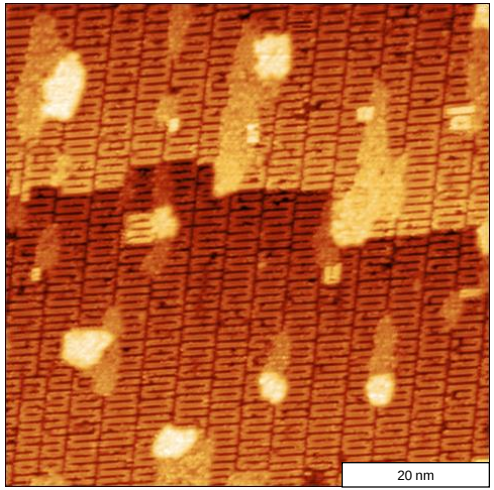




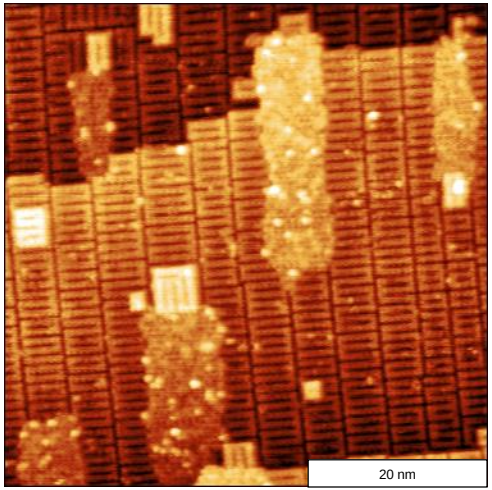
- The primary diffusion pathway appears to be between the (3×1)-O ladders with some growth across ladders
- Beginning to see migration towards larger scale defects (step edges)

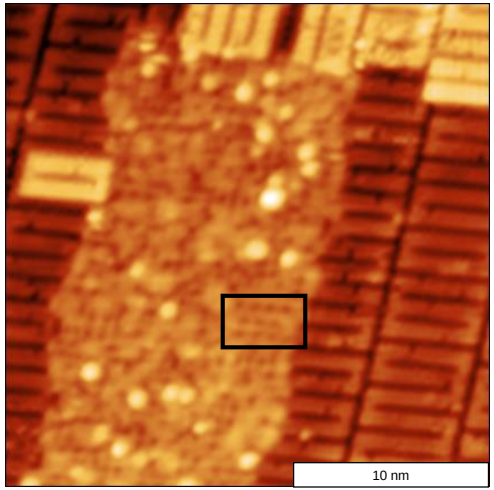
Sn ML structures are growing in width and there is some Sn migration towards step edges

Structural Evolution of Sn on (3×1)-O/Nb(100) Following Anneal at 700 °C



700 °C
5 min

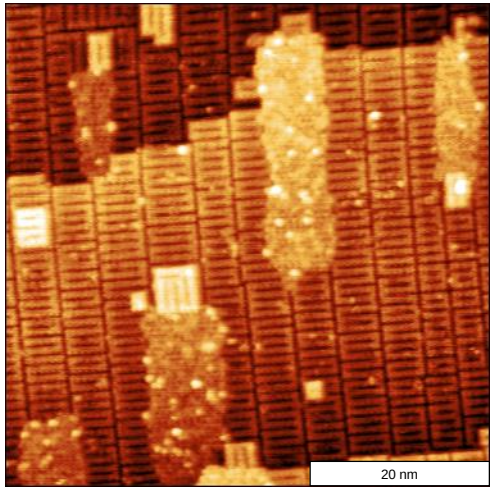




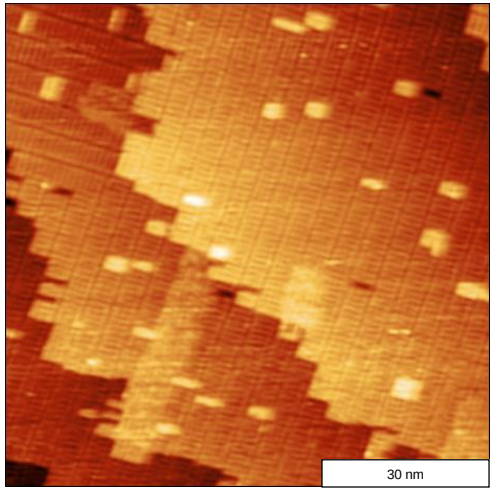
- Sn/(3×1)-O interactions are still dominant over larger surface defects
  - Step edges are not saturated
- Sn ML structures are anchored by terrace step edges

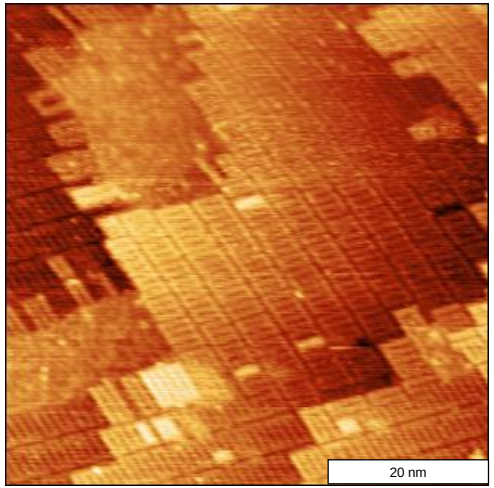
Sn ML width is contained within NbO ladder structure, but Sn is now interacting with terrace step edges

Structural Evolution of Sn on (3×1)-O/Nb(100) Following Anneal at 800 °C



800 °C
5 min

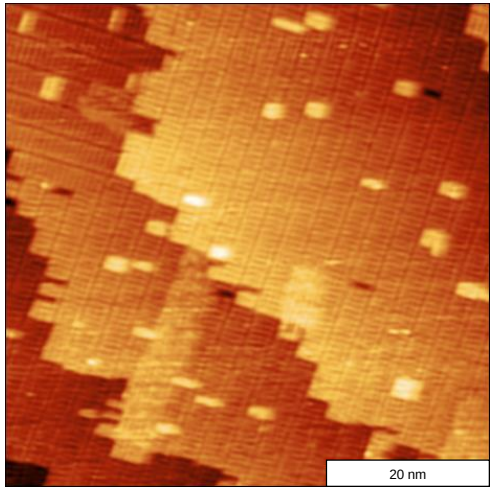




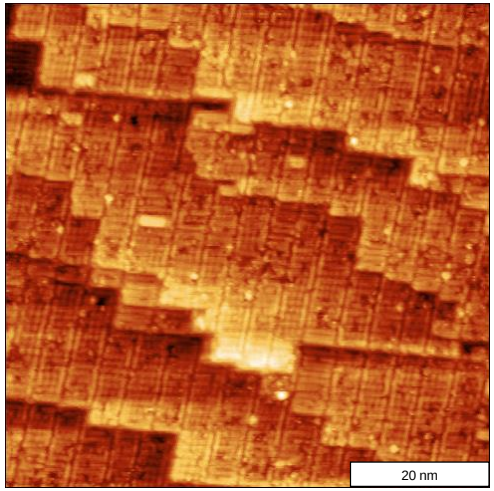
- Sn adlayer spanning entire terrace from step edge to step edge
- Step edge reconstruction associated with Sn diffusion
  - **Sn oxidation?**
  - **NbO reconstruction?**

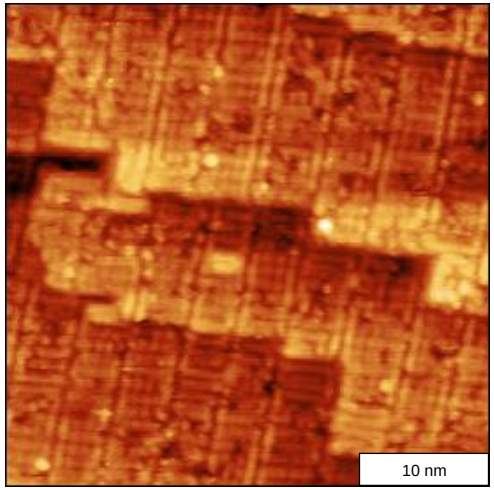
Evidence of structural evolution of (3×1)-O surface with continued Sn diffusion

Structural Evolution of Sn on (3×1)-O/Nb(100) Following Anneal at 900 °C



900 °C
5 min

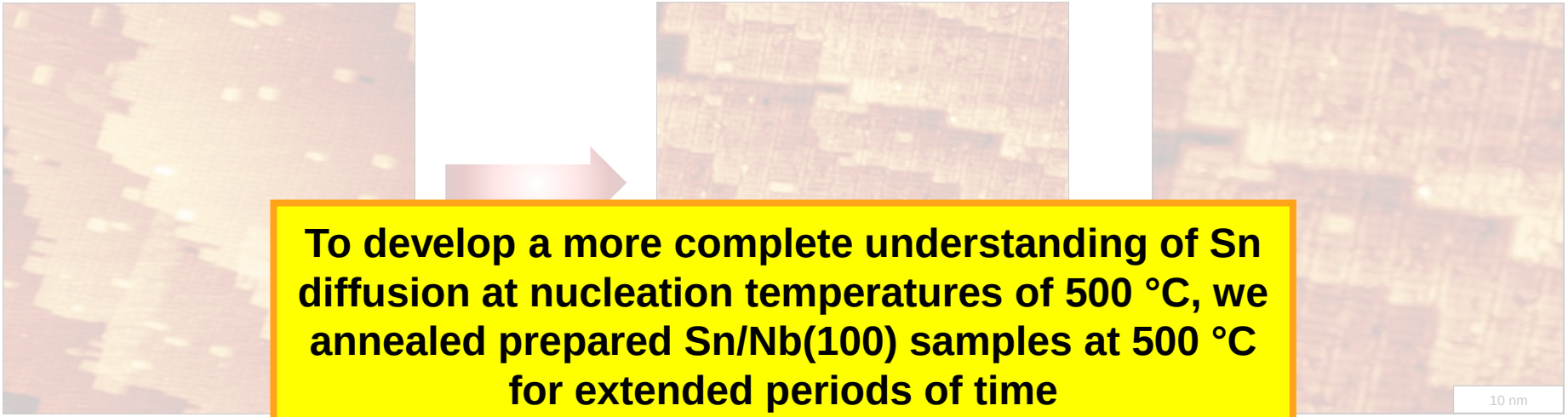




- Sn desorbed from (3×1)-O/Nb(100) surface
- Underlying (3×1)-O surface oxide has visible defects
  - Step edges no longer show evidence of reconstruction

All Sn has desorbed from the (3×1)-O/Nb(100) surface. This is a consequence of low Sn coverages under UHV conditions

Structural Evolution of Sn on (3×1)-O/Nb(100) Following Anneal at 900 °C

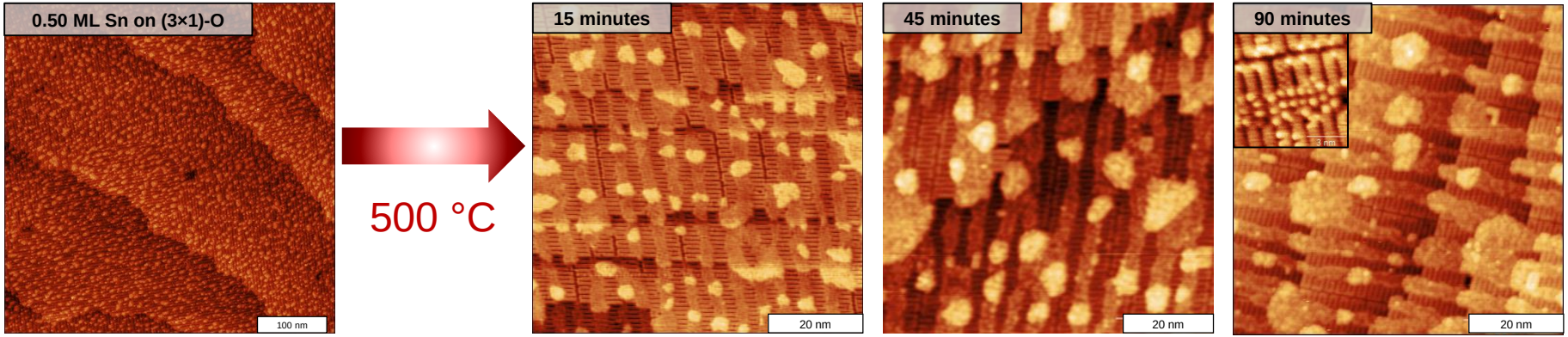


To develop a more complete understanding of Sn diffusion at nucleation temperatures of 500 °C, we annealed prepared Sn/Nb(100) samples at 500 °C for extended periods of time

- Sn desorbed from (3×1)-O/Nb(100) surface
- Underlying (3×1)-O surface oxide has visible defects
  - Step edges no longer show evidence of evolution

All Sn has desorbed from the (3×1)-O/Nb(100) surface. This is a consequence of low Sn coverages under UHV conditions

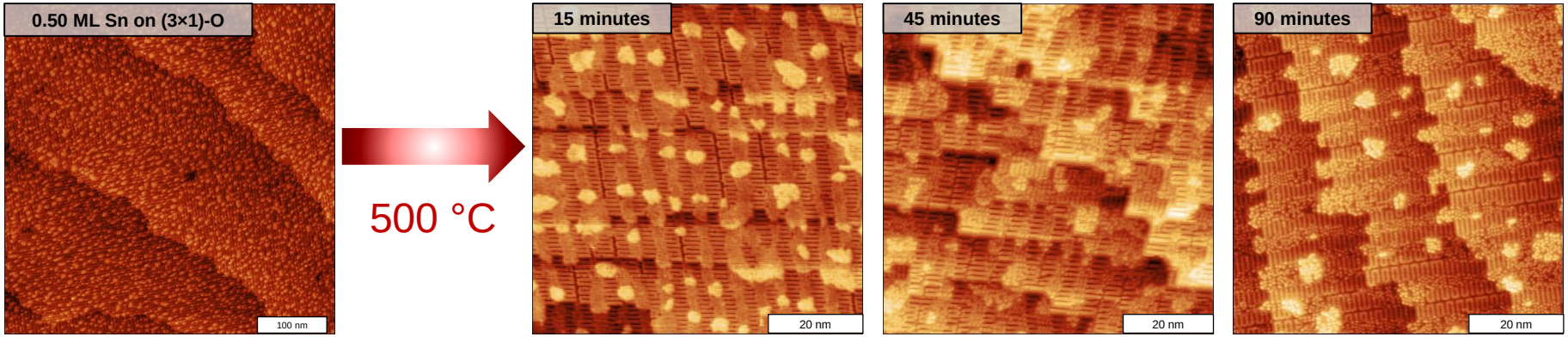
Structural Evolution of 0.5 ML Sn on (3×1)-O/Nb(100) Following Anneal at 500 °C



- There is minimal evolution to the Sn adlayer with prolonged annealing at 500 °C
- High resolution STM imaging shows complex Sn ML structure
- Sn also seen to adsorb to (3×1)-O ladder edges

There is minimal structural evolution following prolonged annealing at 500 °C

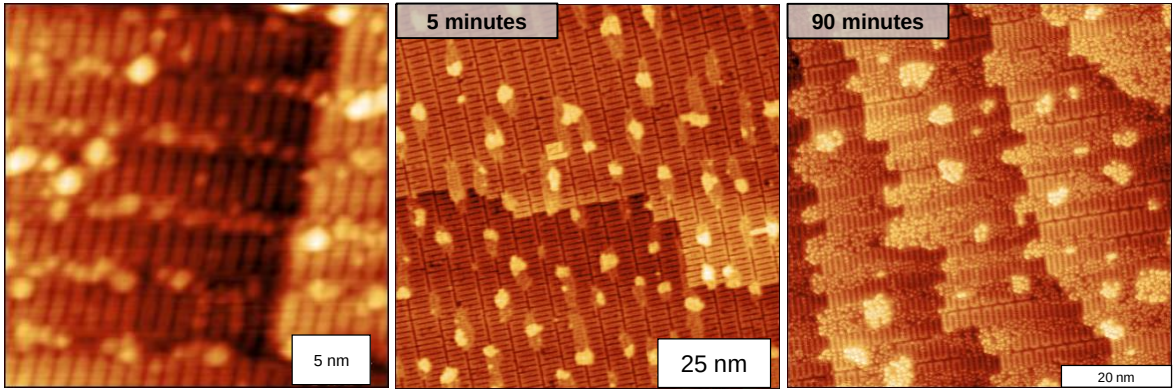
Structural Evolution of 0.5 ML Sn on (3×1)-O/Nb(100) Following Anneal at 500 °C



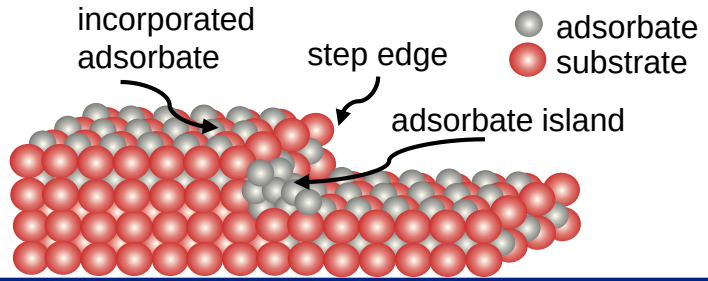
- There is minimal evolution to the Sn adlayer with prolonged annealing at 500 °C
- High resolution STM imaging shows complex Sn ML structure
- Sn also seen to adsorb to (3×1)-O ladder edges

There is minimal structural evolution following prolonged annealing at 500 °C

Summary and Ongoing Work: Sn Adsorption and Diffusion Behavior on Oxidized Nb(100)

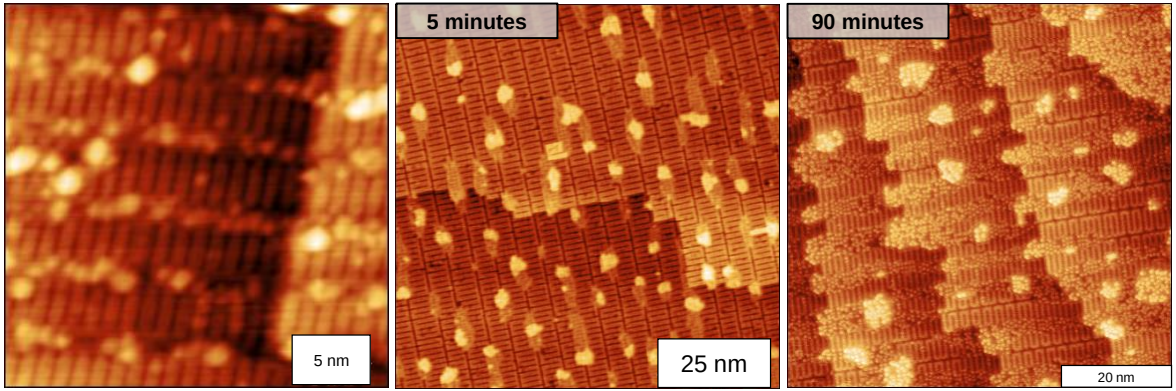


- Initial results investigating Sn/(3×1)-O/Nb(100)
  - Visualization of Sn adsorption and diffusion behavior
  - Sn adlayer structure does not significantly change with increased annealing at 500 °C

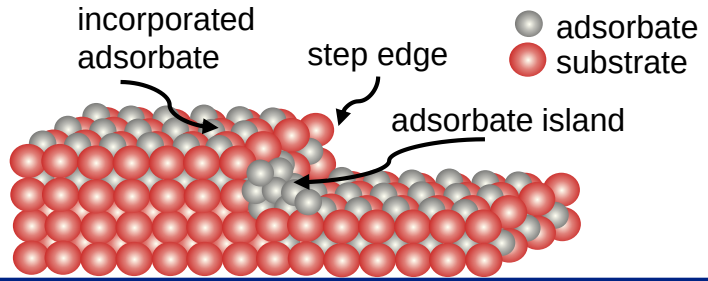


Using UHV surface science techniques, we have visualized Sn adsorption and diffusion behavior on oxidized Nb(100) at relevant Nb_3Sn growth temperatures

Summary and Ongoing Work: Sn Adsorption and Diffusion Behavior on Oxidized Nb(100)



- Ongoing work is focused on:
  - **STS:** electronic characteristics of Sn adlayers
  - **XPS:** oxidation of Sn and Nb as a function of Sn coverage and annealing temperatures
  - Collaboration with Arias group for theoretical support



Using UHV surface science techniques, we have visualized Sn adsorption and diffusion behavior on oxidized Nb(100) at relevant Nb_3Sn growth temperatures

Acknowledgments

- Center for Bright Beams
  - U.S. National Science Foundation under award PHY-1549132, the Center for Bright Beams
- Cornell University - Collaborators
  - Tomas Arias and graduate student Nathan Sitaraman

The Sibener Group

- Steve Sibener
- Sarah Willson
  - 3rd year PhD candidate

Thank you for your attention! Questions?

- Center for Bright Beams
  - U.S. National Science Foundation under award PHY-1549132, the Center for Bright Beams
- Cornell University - Collaborators
  - Tomas Arias and graduate student Nathan Sitaraman

The Sibener Group

- Steve Sibener
- Sarah Willson
  - 3rd year PhD candidate