Role of surface oxide and anodization in Nb_3Sn nucleation

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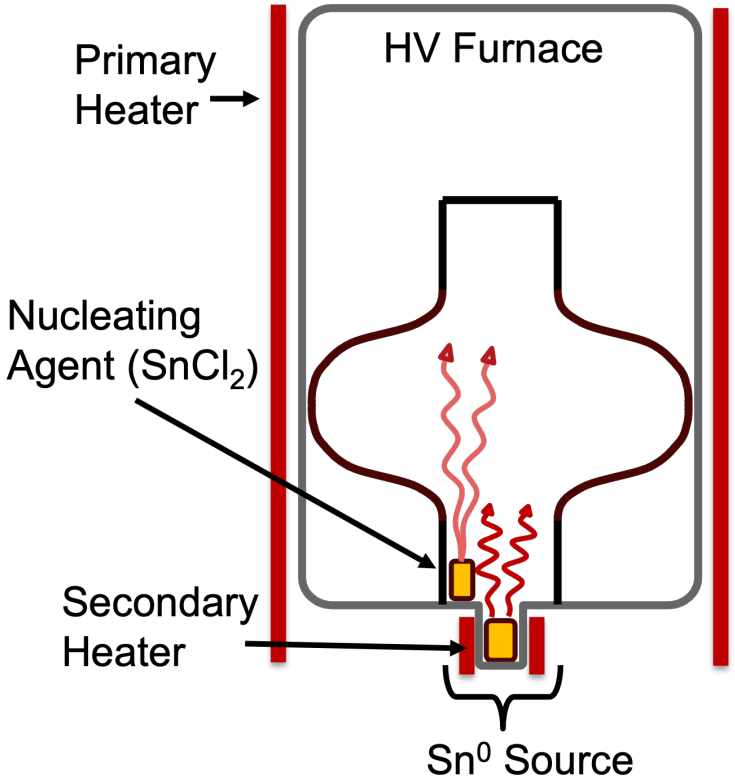
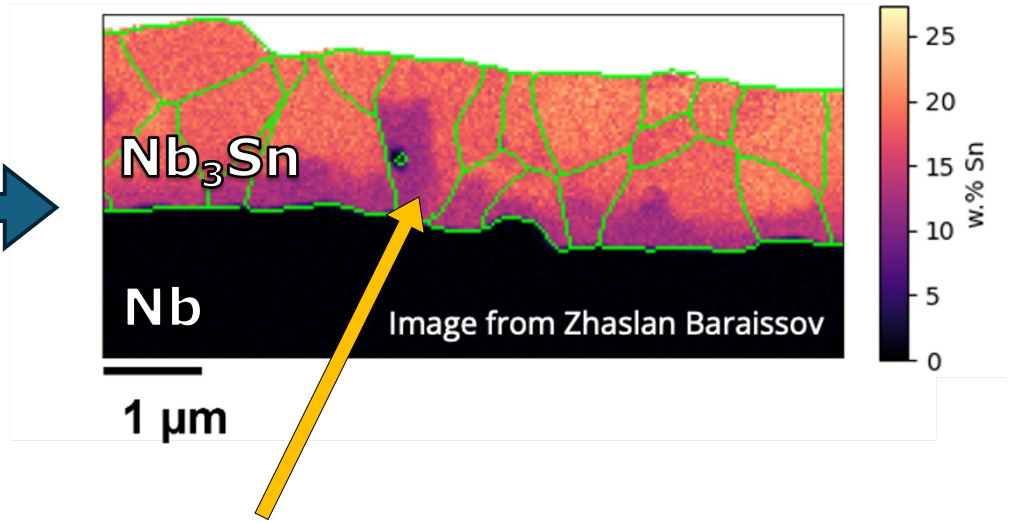
Research funded by Center for Bright Beams, NSF award PHY-1549132. Work also supported by U.S. DOE Office of High Energy Physics under grant No. DE-SC0008431. This work made use of the Cornell Center for Materials Research shared instrumentation facility.

How Nb_3Sn is made and where it falls short

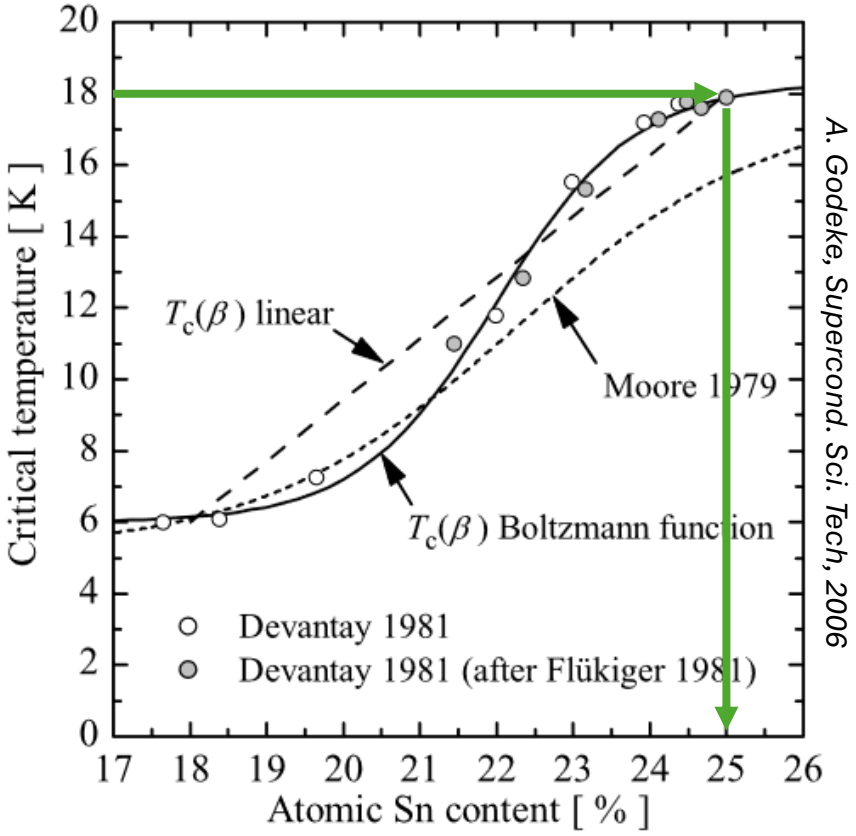




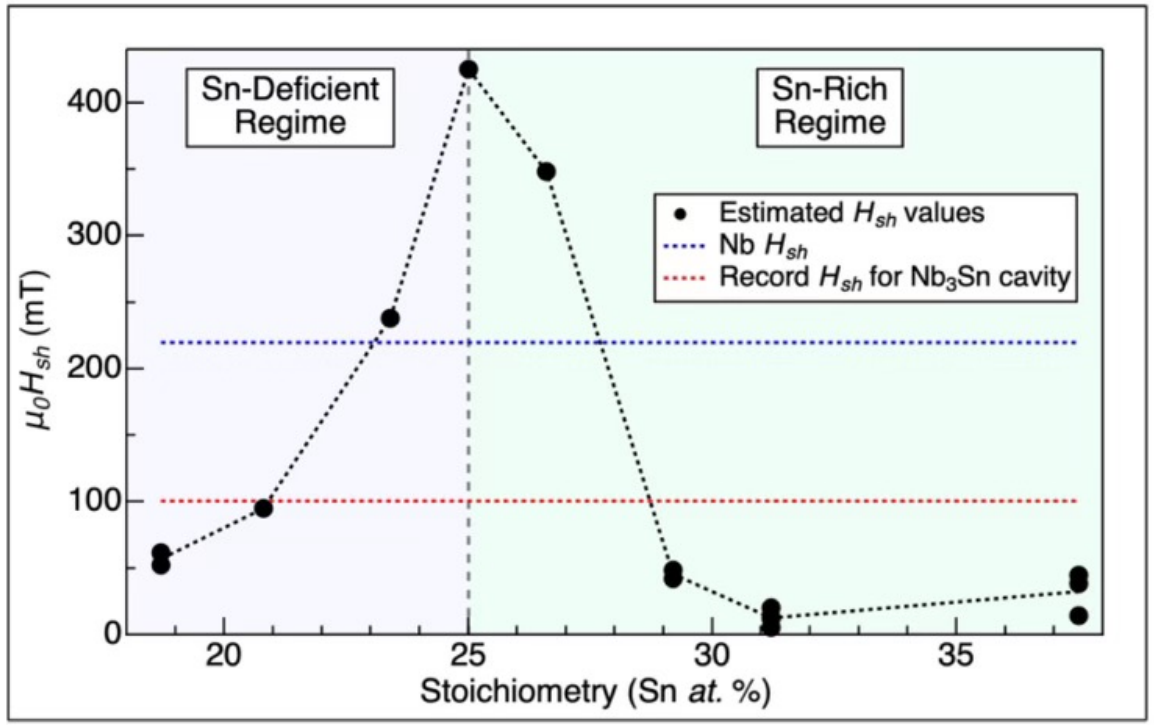
S. Posen and M. Liepe, Phys. Rev. ST Accel. Beams 15, 112001 (2014)

Vapor-diffusion growth leaves tin-depleted regions throughout the film

Small stoichiometry deviations, big performance loss



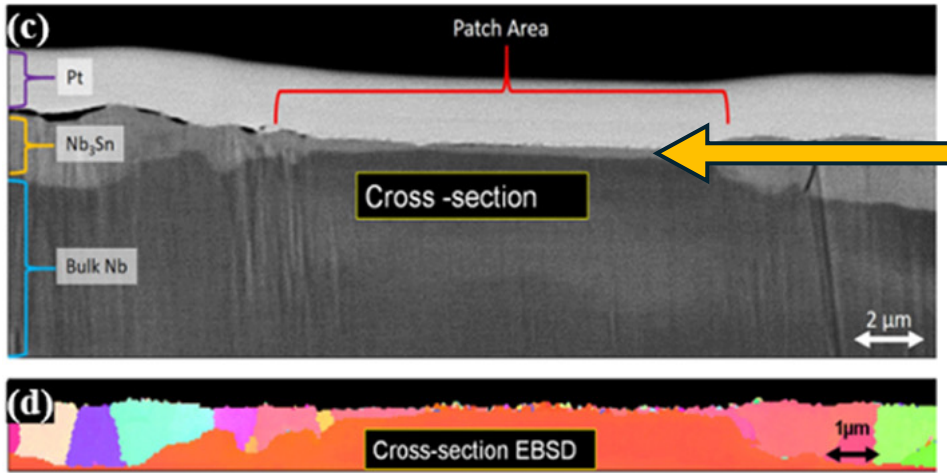
A. Godeke, Supercond. Sci. Tech, 2006



Willson, Harbick et al. 2024 Phys. Rev. Res. 6 043133
***DOI** 10.1103/PhysRevResearch.6.043133*

This tight tolerance is why good growth matters

Nucleation challenge



Pudasaini et al. 2019 J. Vac. Sci. Technol. A 37 051509
DOI 10.1116/1.5113597

Large, thin tin-depleted Nb_3Sn grains

→ Once formed, very hard to 'fill in' (less grain boundaries to assist Sn diffusion)

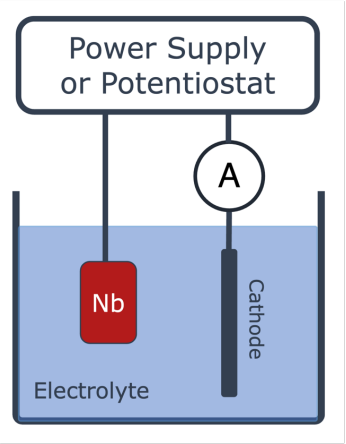
Film quality is limited by non-uniform nucleation in early stages

How can we improve tin nucleation?

Pre-anodization of the substrate

→ Electrochemically growing an oxide on the Nb substrate

This has been found to help with Sn nucleation since the early days of Nb_3Sn research



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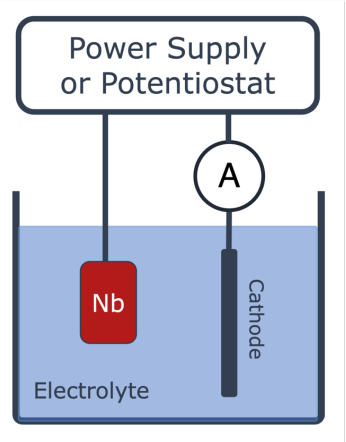
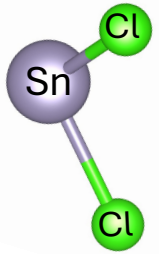


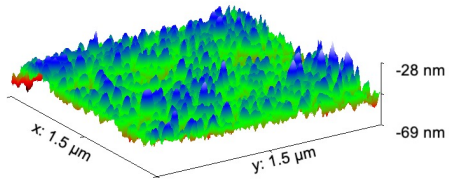
Addition of $SnCl_2$ nucleating agent



→ Higher vapor pressure than metallic Sn at lower temperatures

→ Interacts with the substrate surface at early stages of coating

Does $SnCl_2$ bind preferentially to specific features?



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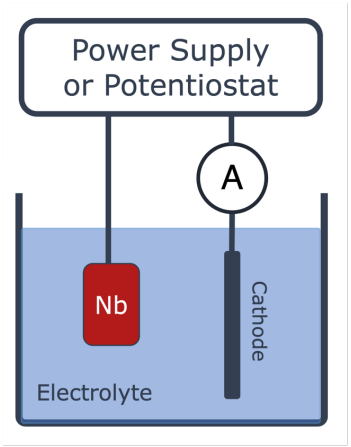
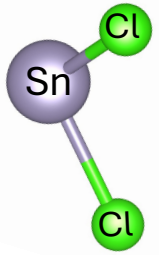


Sets the surface $SnCl_2$ sees

Addition of $SnCl_2$ nucleating agent



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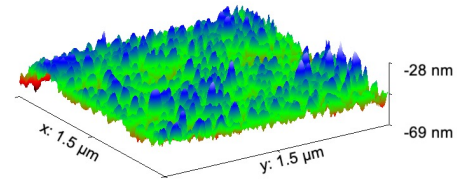
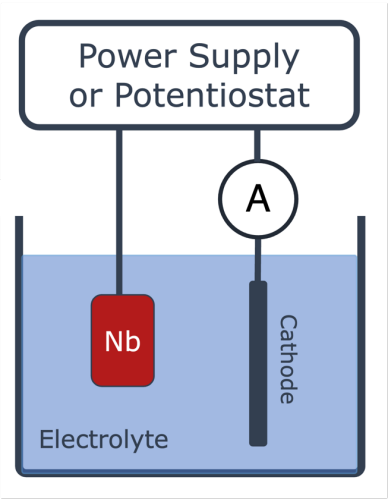


The oxide surface shapes early $SnCl_2$ nucleation

Pre-anodization, in more detail



Relation often cited in SRF literature: thickness ∝ voltage (2-3 nm/V)

→ assumes barrier-type growth

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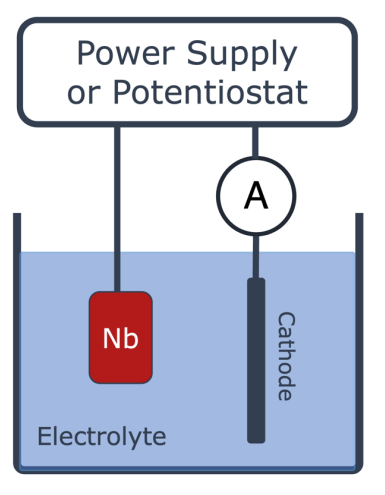
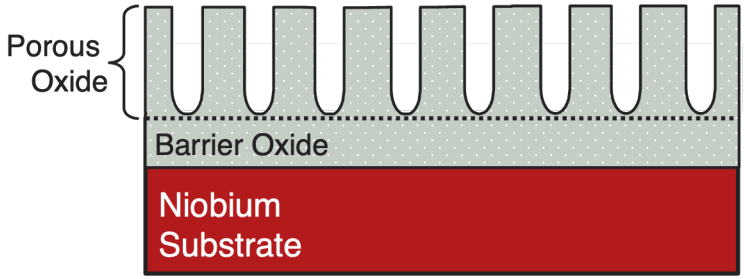


When the oxide is soluble in the electrolyte (e.g. NaOH), you can grow a porous oxide



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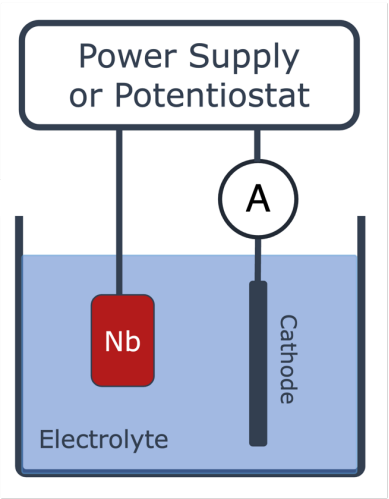

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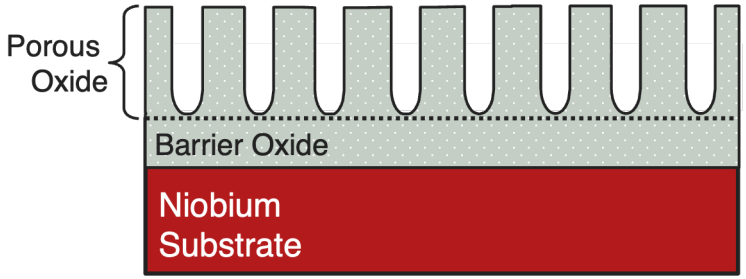

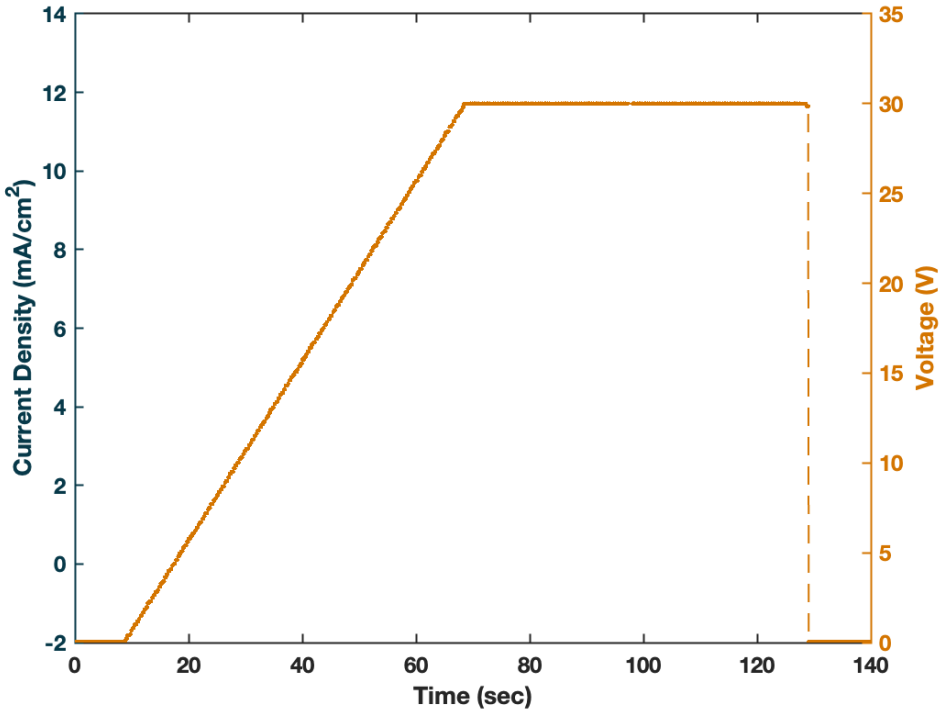

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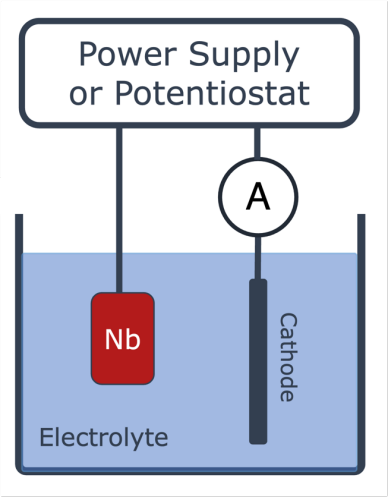

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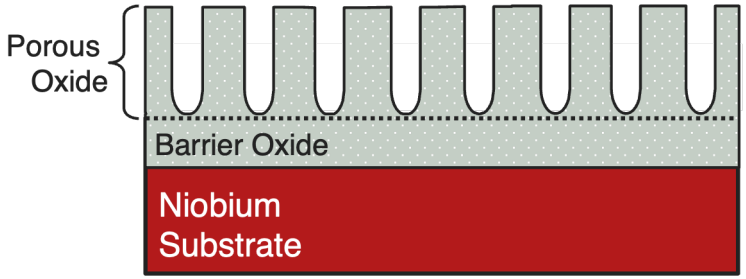

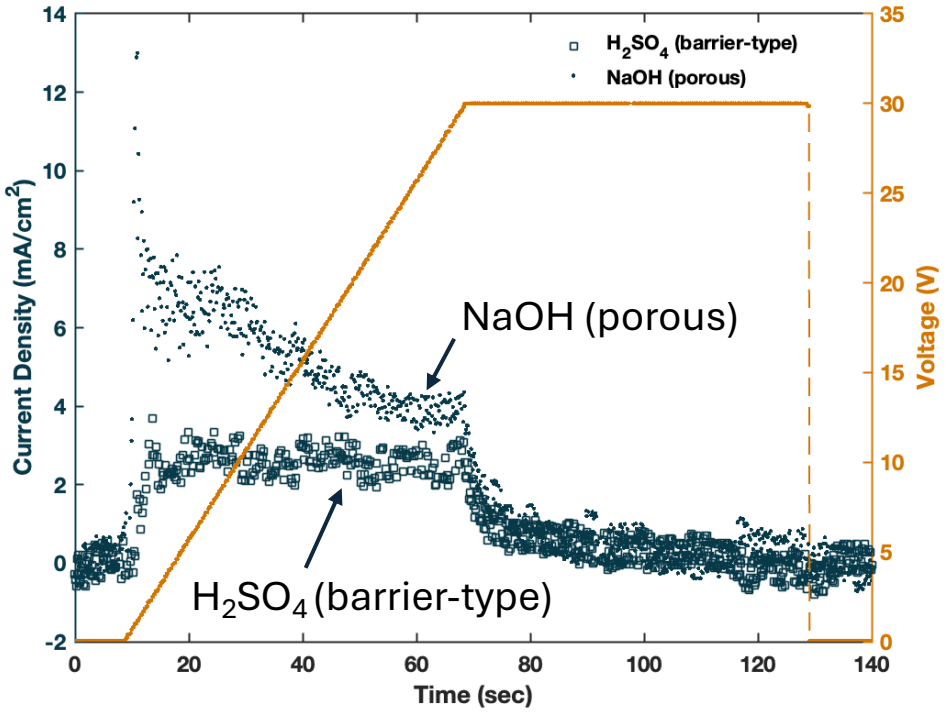

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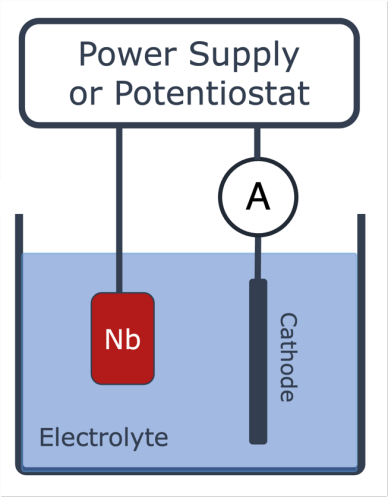

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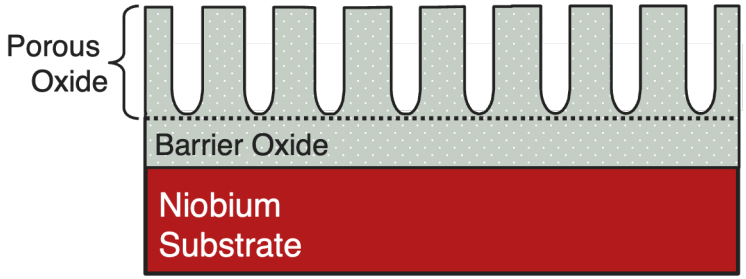

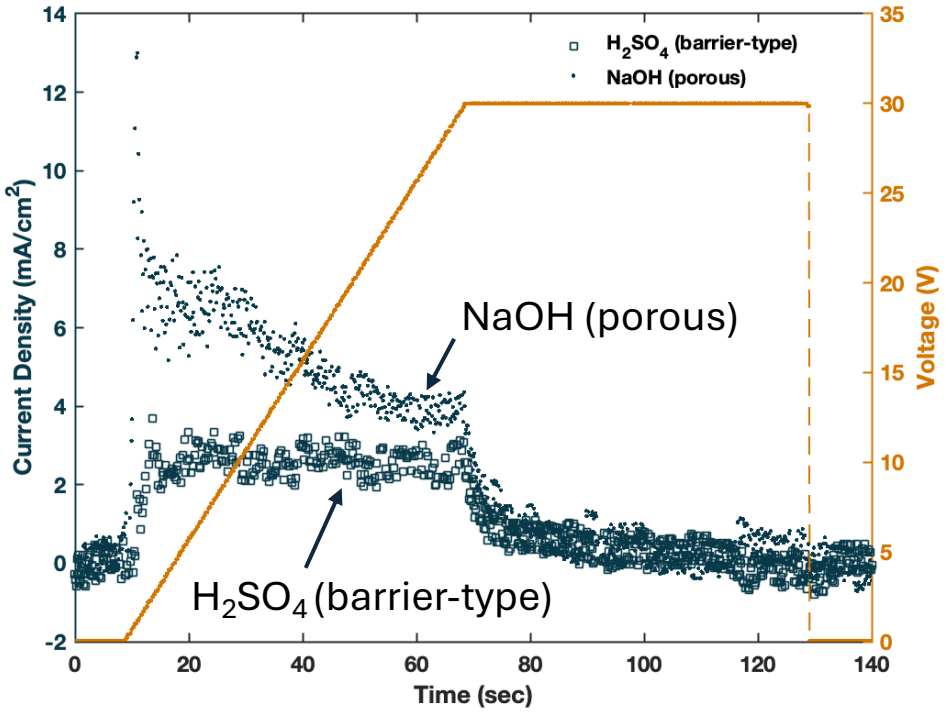

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Same voltage, different oxide: electrolyte controls morphology

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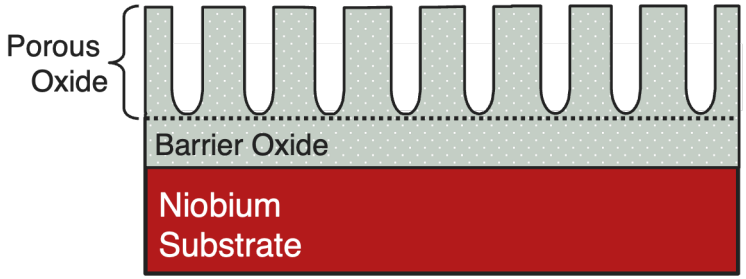
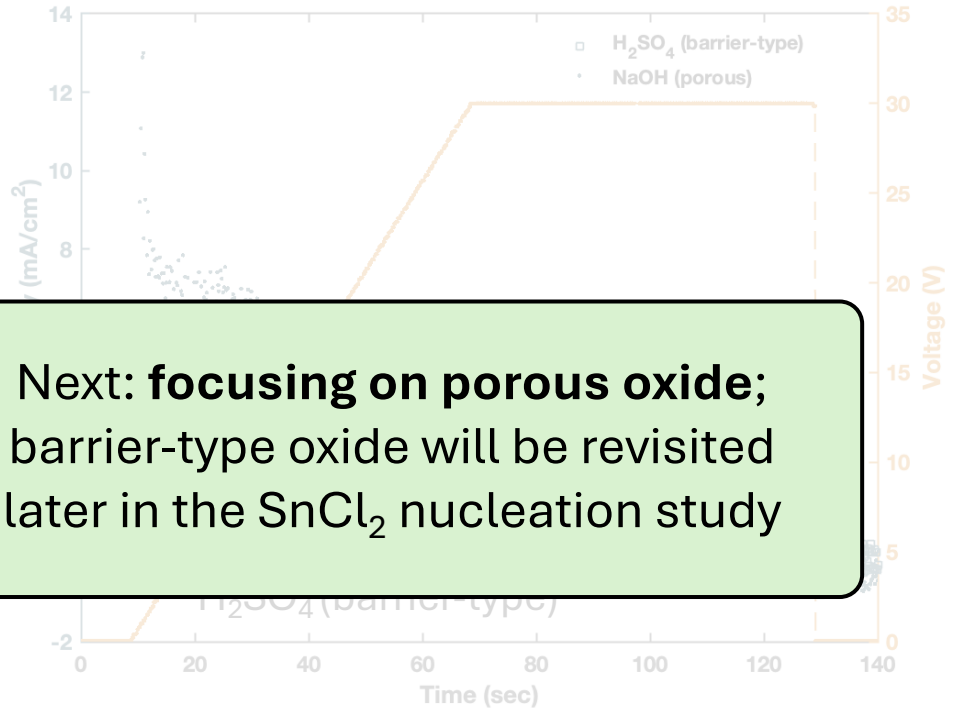
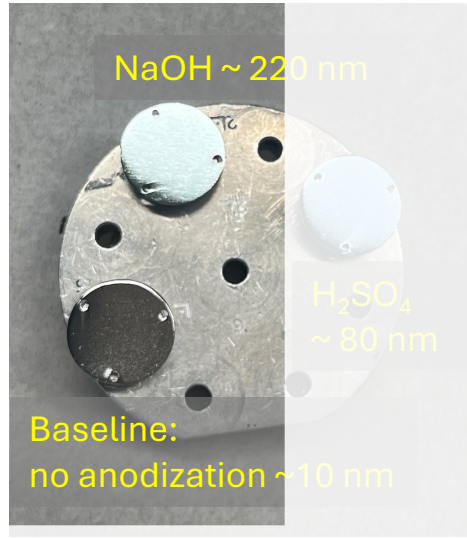




Next: **focusing on porous oxide**; barrier-type oxide will be revisited later in the $SnCl_2$ nucleation study



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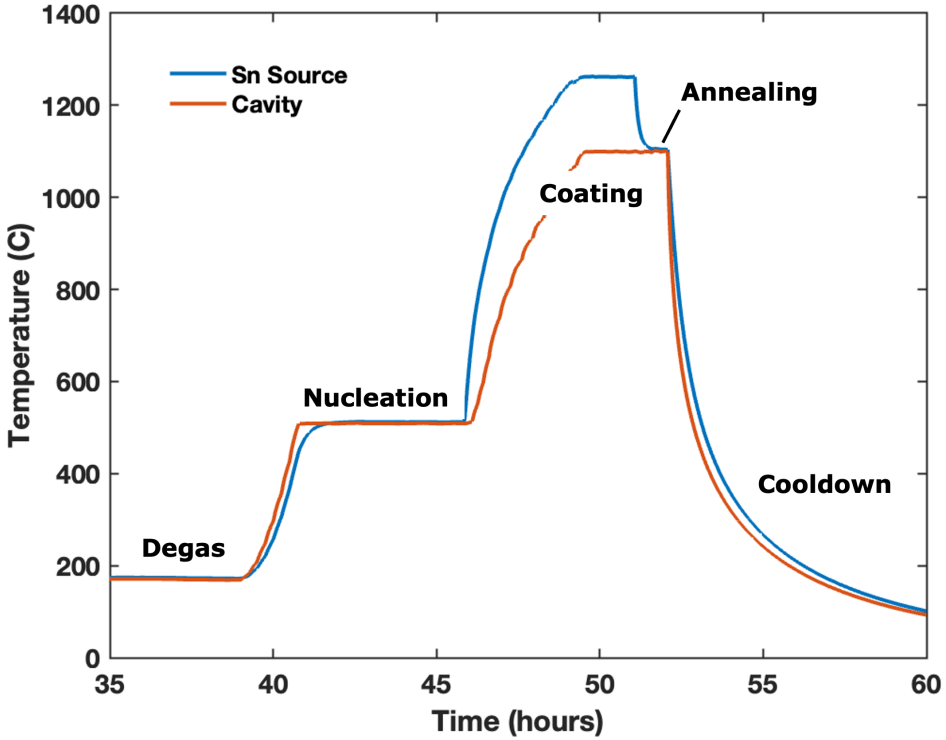
Tracking oxide evolution

Thermal vapor diffusion temperature profile



Do, Brown, Shpani et al. J. Phys. Chem. C (under review)

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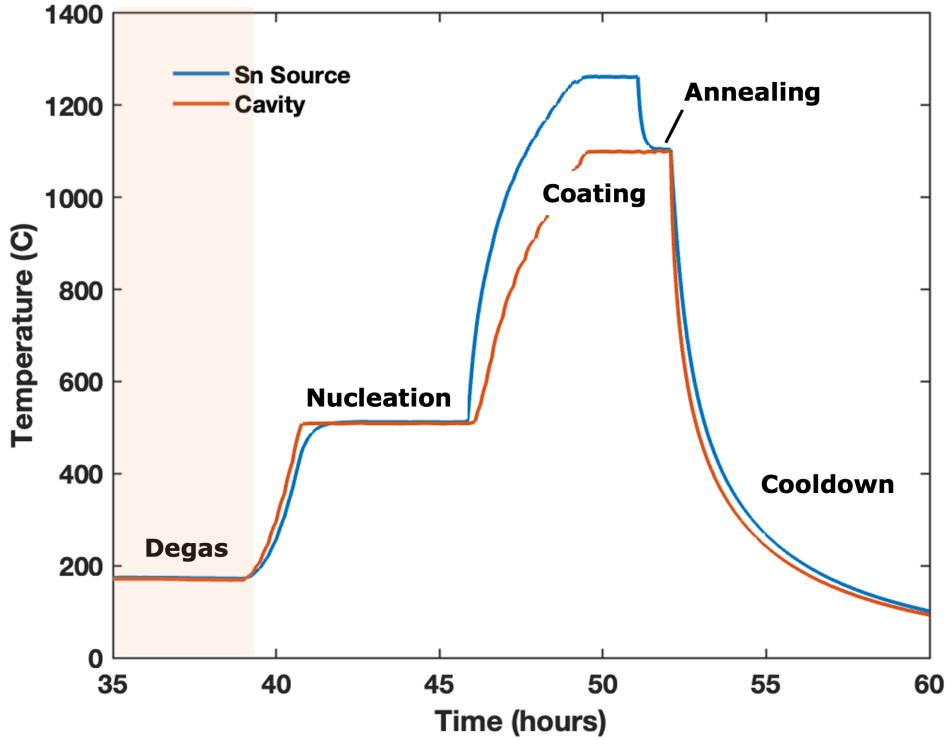

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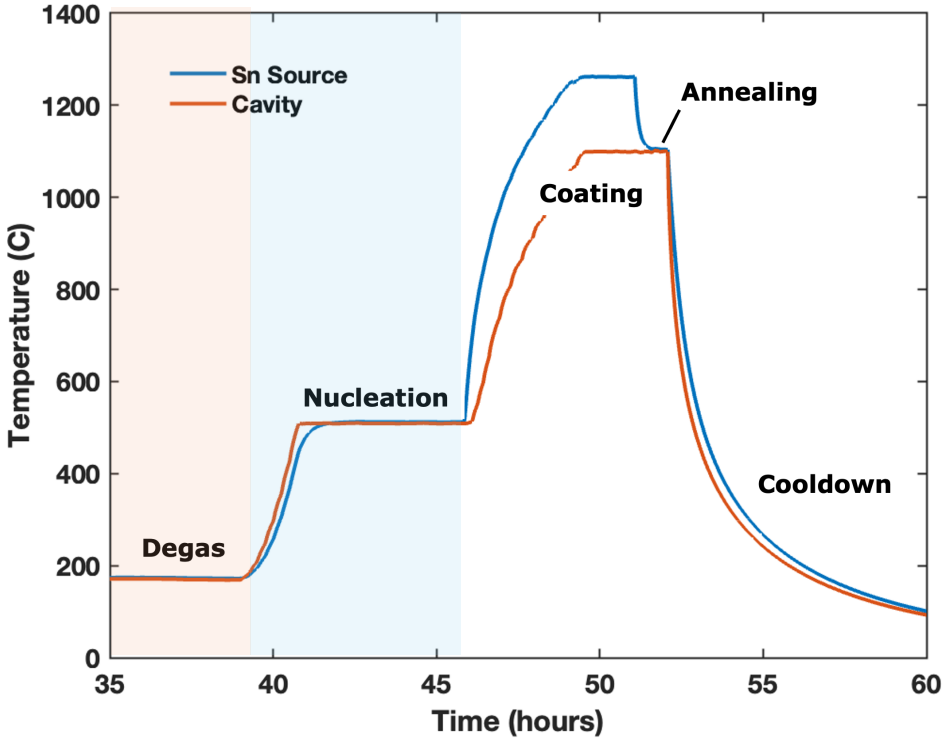

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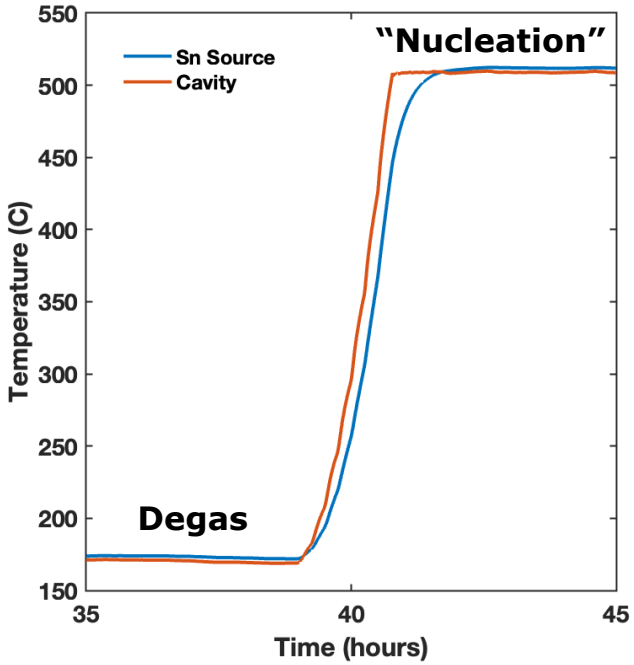

Jasper Brown

Van Do

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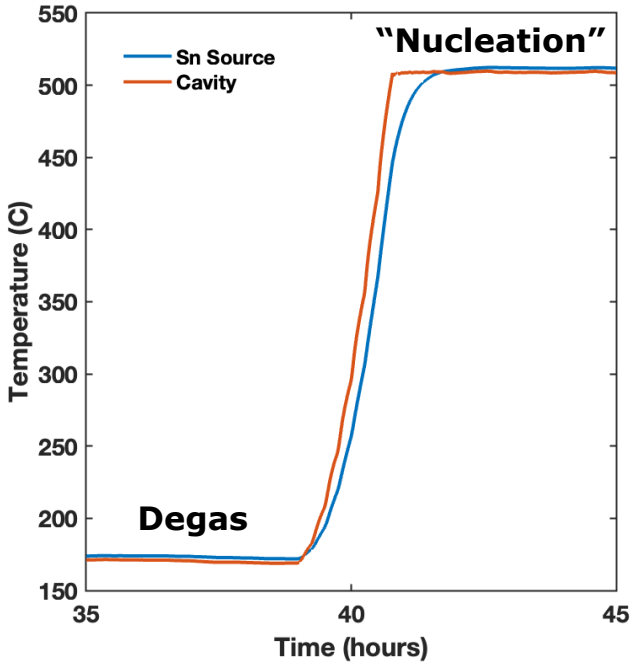
Tracking oxide evolution

Samples were annealed in UHV following the vapor diffusion temperature profile ramp to nucleation temperatures

Sample	Ramp rate
C1 (control)	3 C/min
A1 (anodized, porous)	3 C/min
A2 (anodized, porous)	7 C/min



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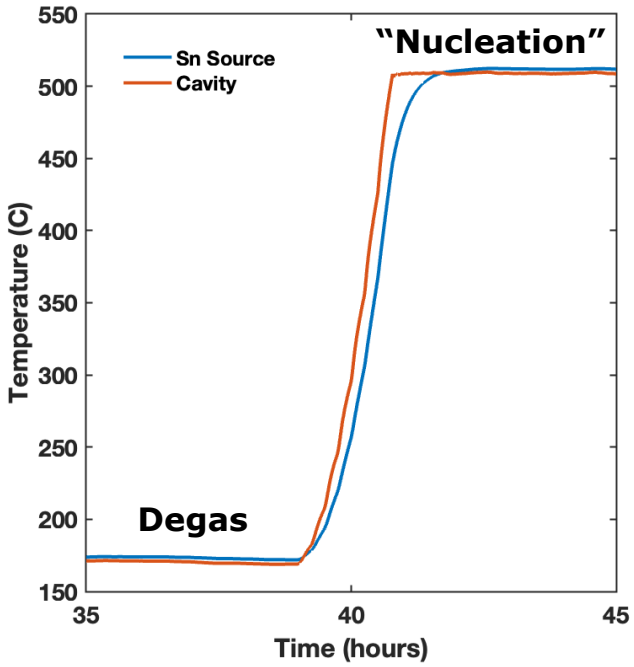

Characterization Methods

in-situ

X-ray photoelectron spectroscopy (XPS)

Oxidation state, throughout heating

Atomic Force Microscopy (AFM)

Surface topography, before/after anneal

ex-situ

Scanning Electron Microscopy (SEM) / Energy Dispersive Spectroscopy (EDS)

Imaging + elemental composition

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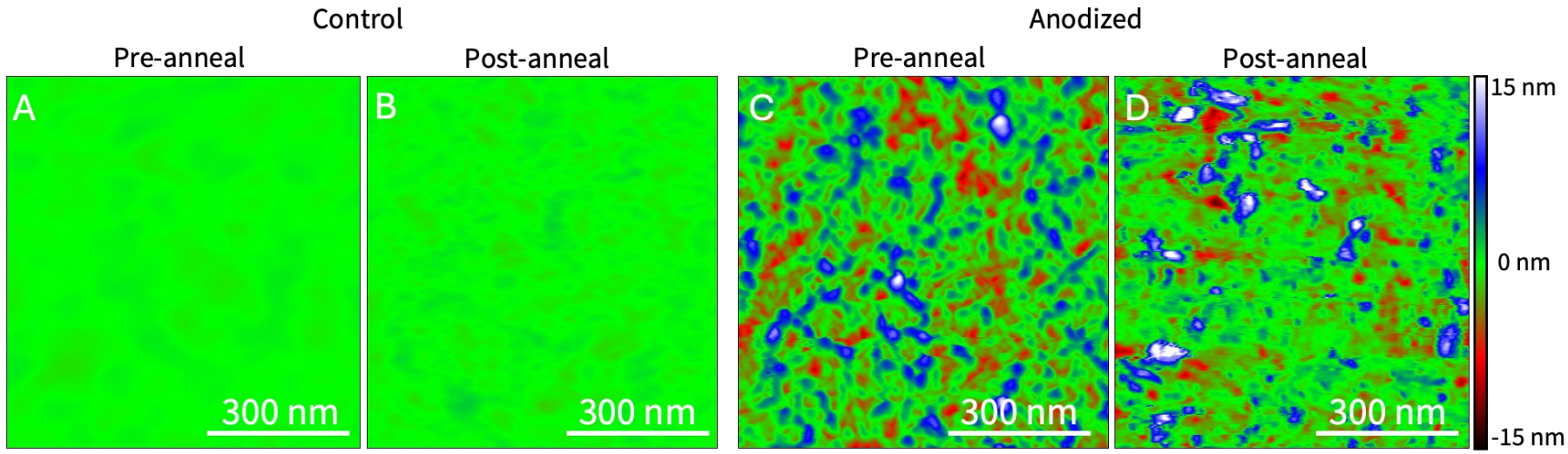
Porous anodization roughness is irreversible



Anodized surface has a rough texture consisting of pores and intersecting bumps, which persist after annealing

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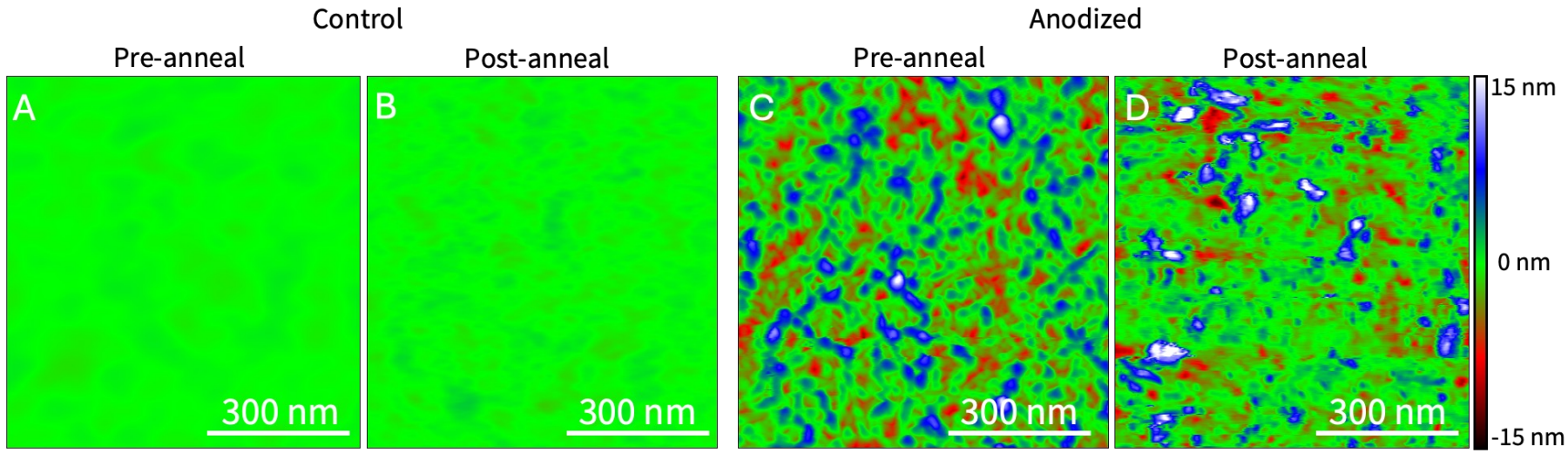

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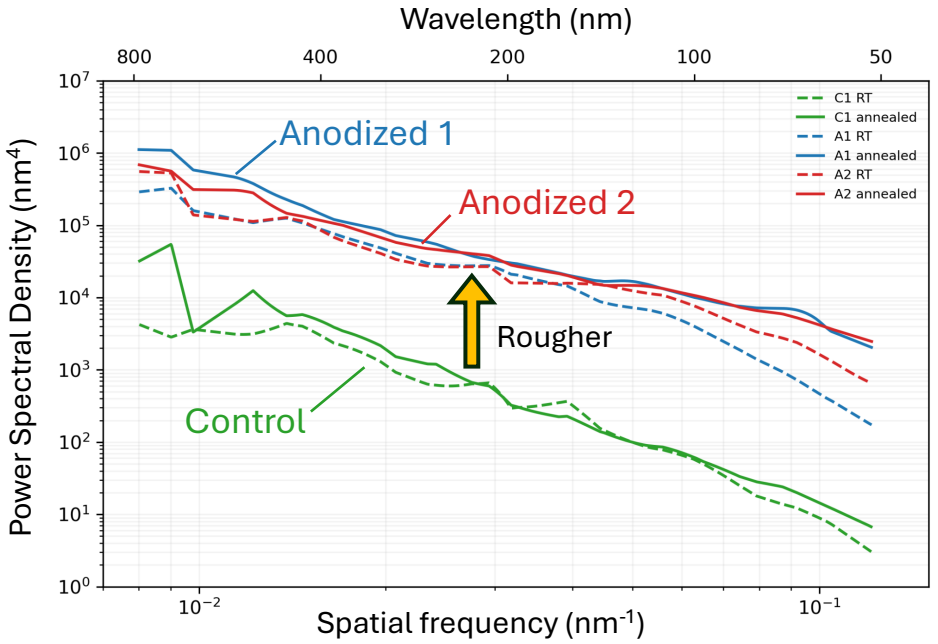

– – Pre-anneal

—— Post-anneal

(without breaking vacuum)

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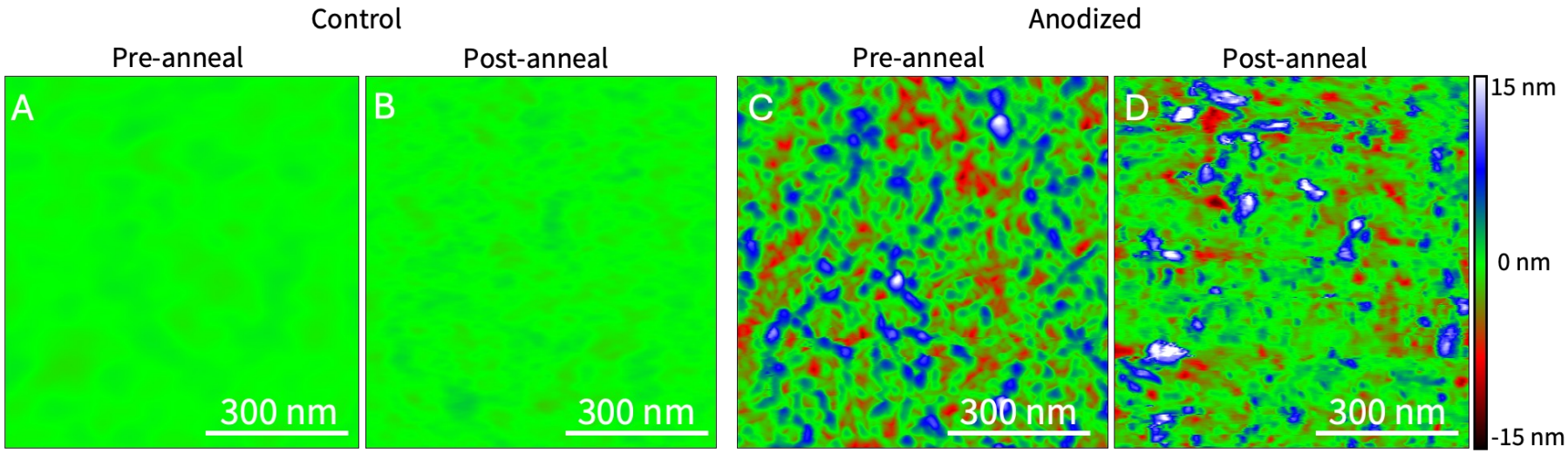

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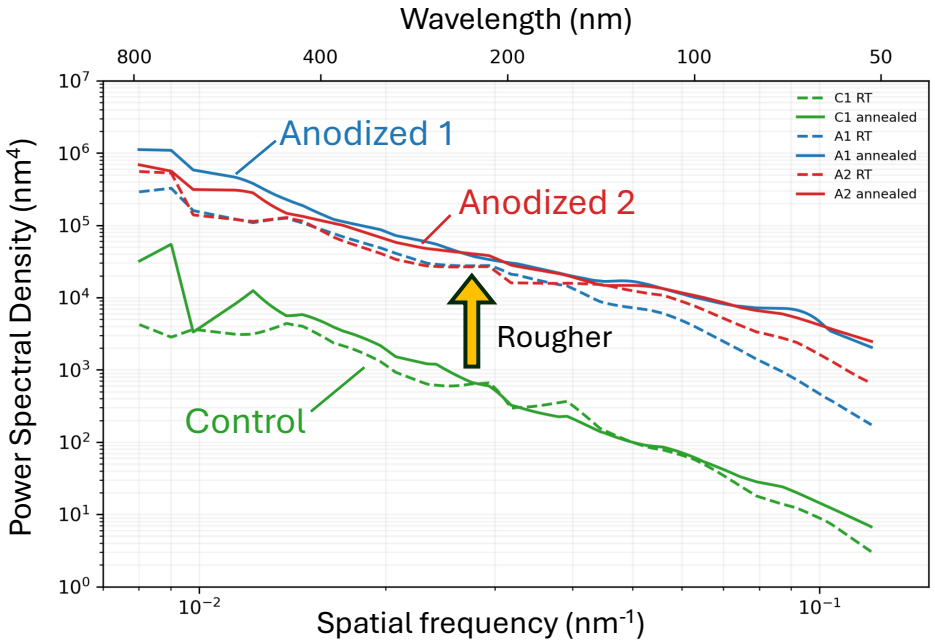
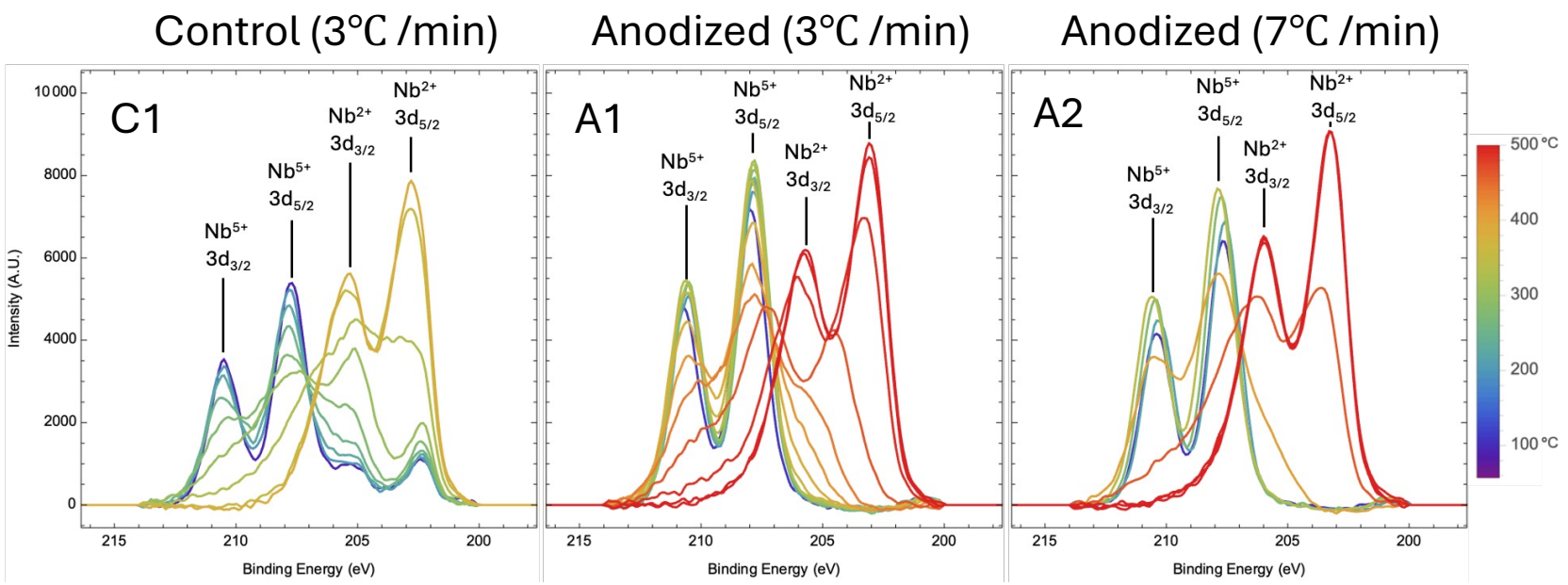
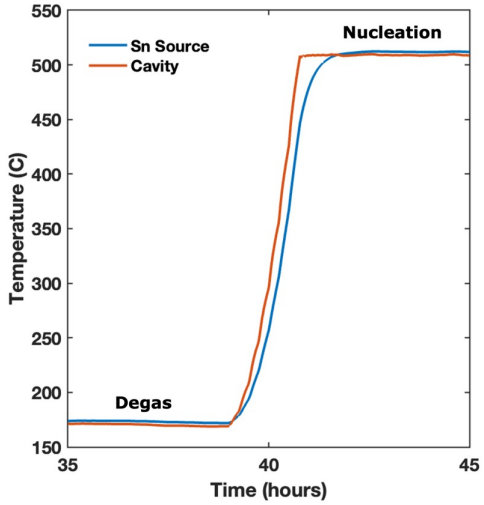


- – – Pre-anneal
- —— Post-anneal (without breaking vacuum)

Anodized samples are rougher than control; roughness does not change substantially after UHV annealing

Oxide dissolution kinetics





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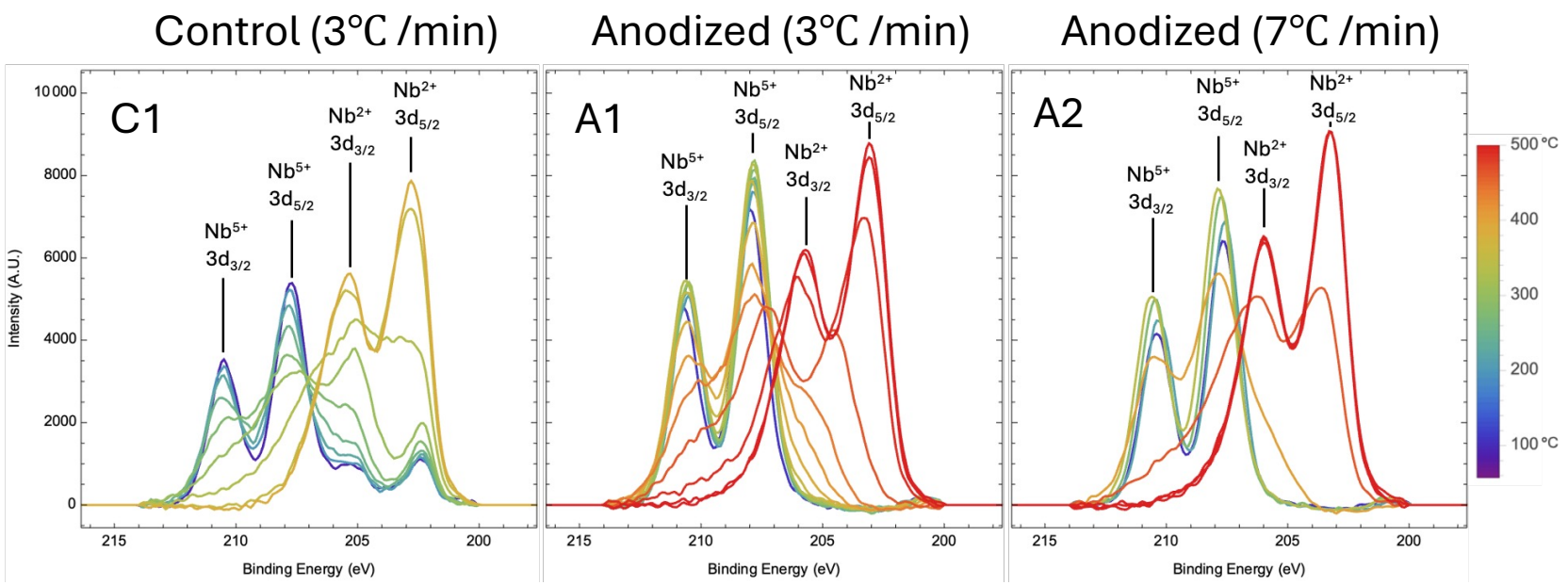

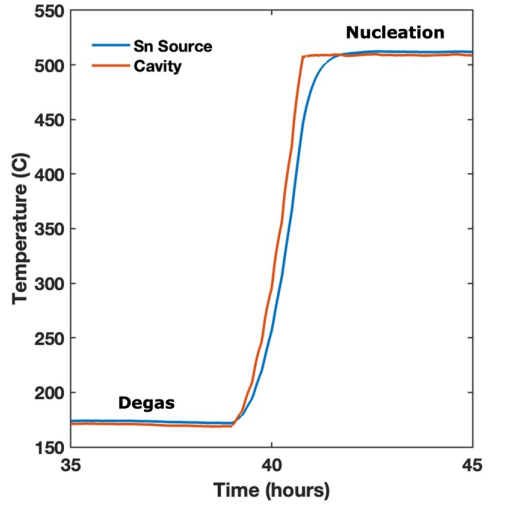

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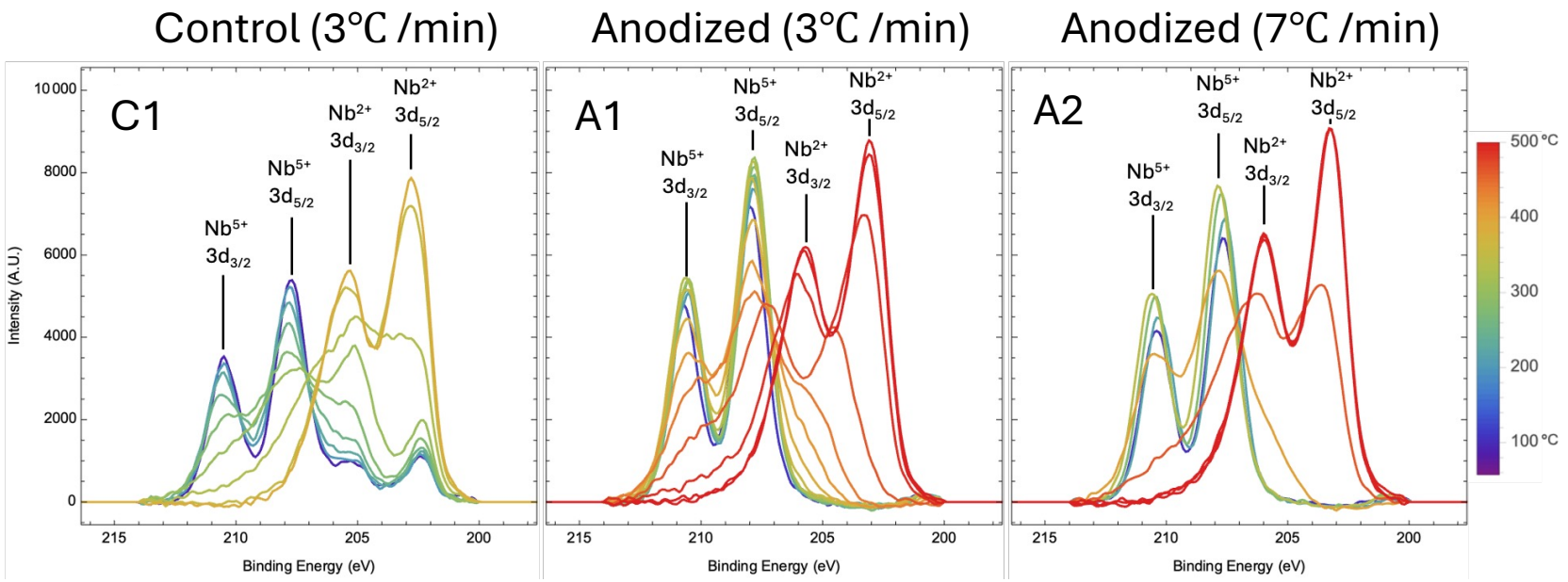

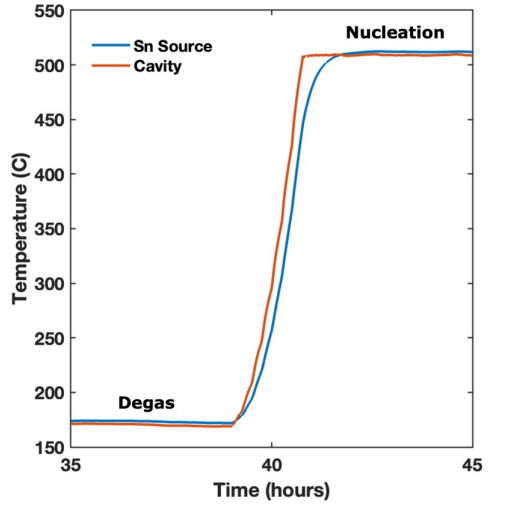

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Assuming first-order kinetics, reduction rate follows Arrhenius form:

Activation energy

$$\frac{d}{dt}[Nb^{5+}] = -Ae^{-\frac{E_a}{RT(t)}}[Nb^{5+}]$$

Frequency factor

Extracted from XPS data

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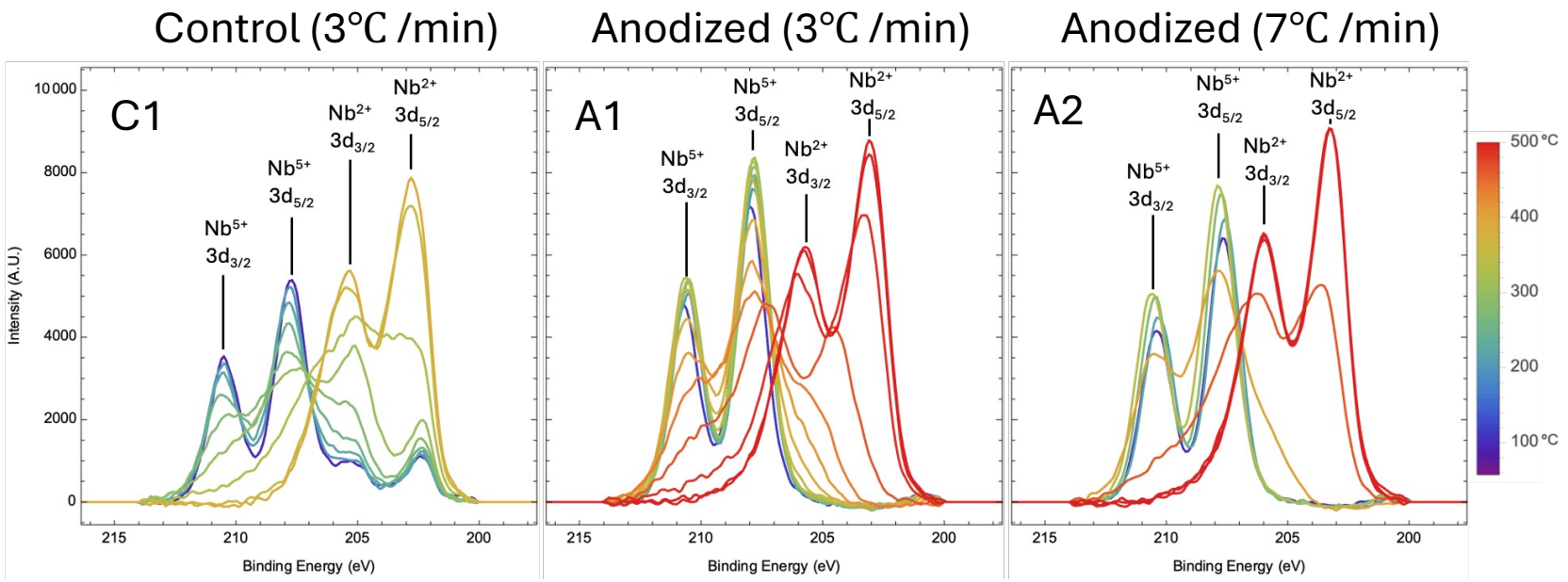

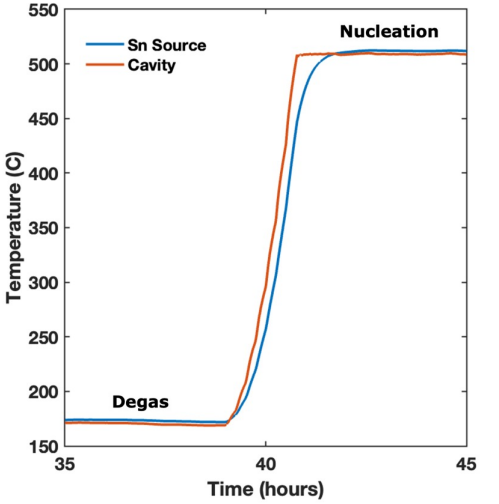

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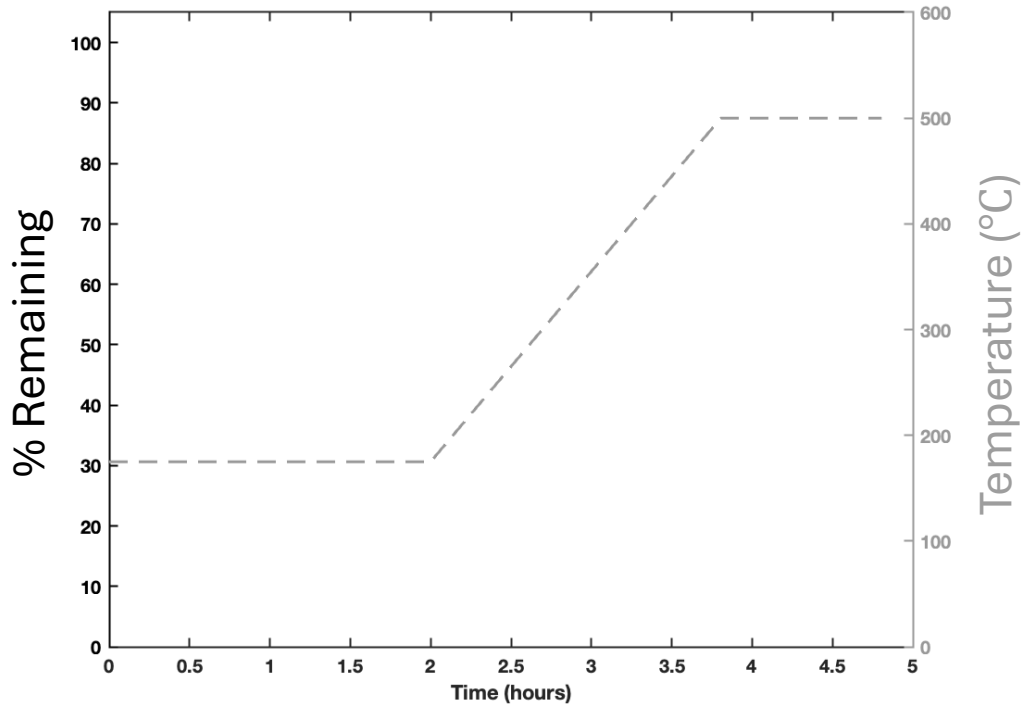
Use fitted parameters to model thickness of Nb_2O_5 as a function of the temperature profile in the furnace

Modeling what's happening in the furnace

We can use temperature profile as an input to predict **% remaining of Nb_2O_5 layer:**

Ramp to nucleation



Modeling what's happening in the furnace

We can use temperature profile as an input to predict **% remaining of Nb_2O_5 layer:**

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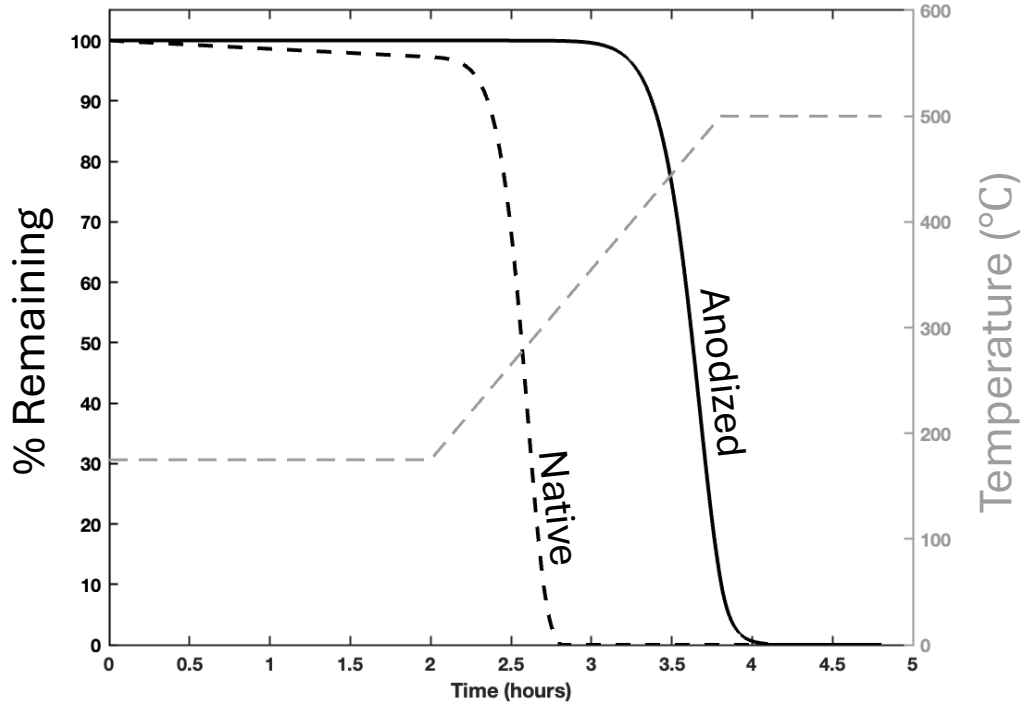
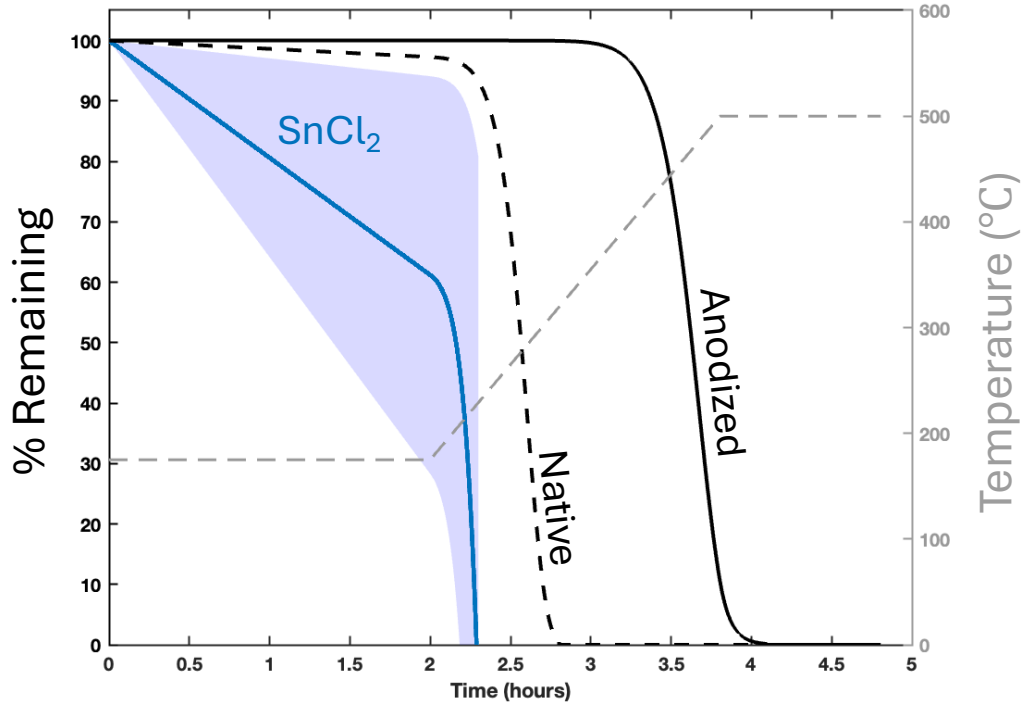


Modeling what's happening in the furnace

We can use temperature profile as an input to predict **% remaining of Nb_2O_5 layer**, and remaining $SnCl_2$ in the crucible**:**

Ramp to nucleation



$SnCl_2$ vapor starts interacting with the Nb_2O_5 surfaces as early as degas

Modeling what's happening in the furnace

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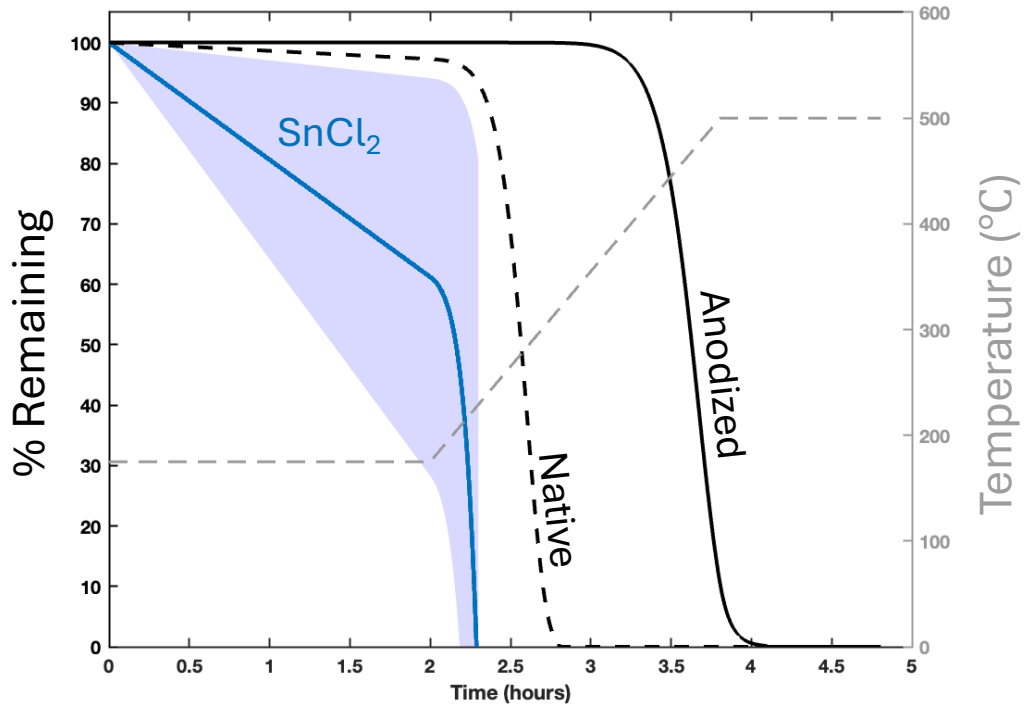
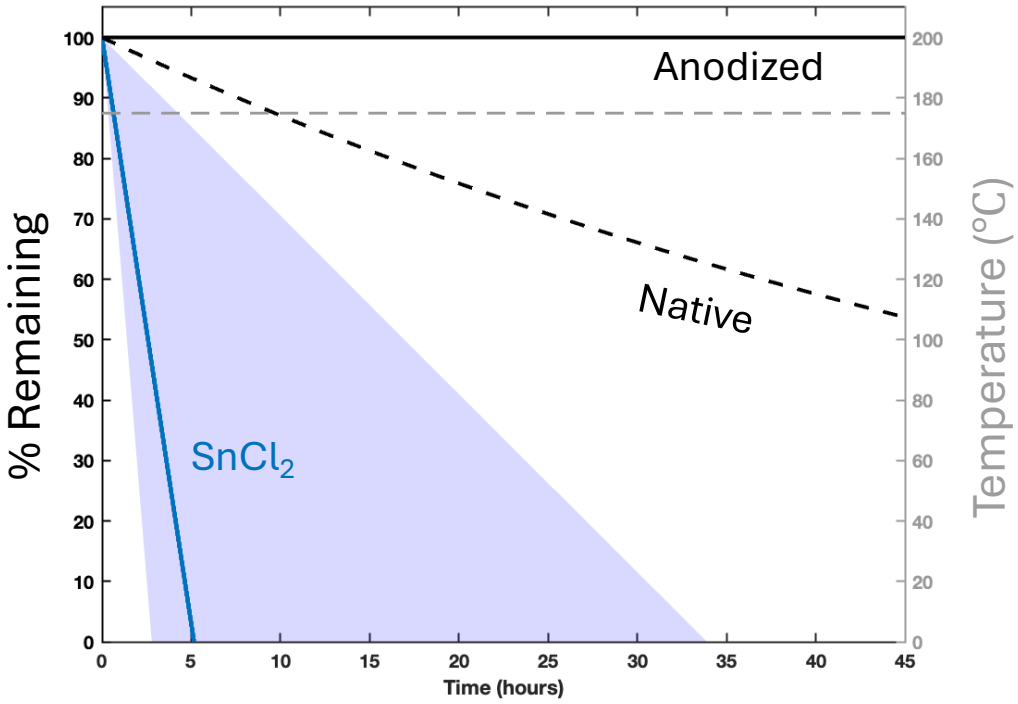


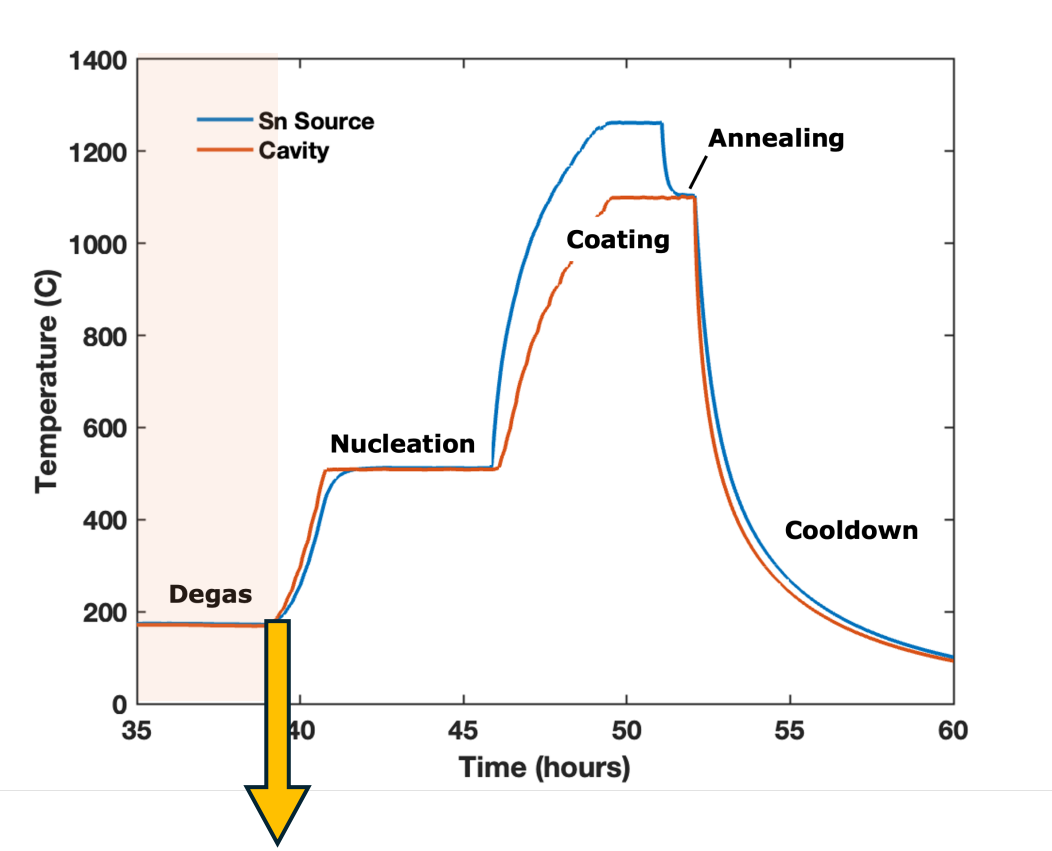
$SnCl_2$ vapor starts interacting with the Nb_2O_5 surfaces as early as degas

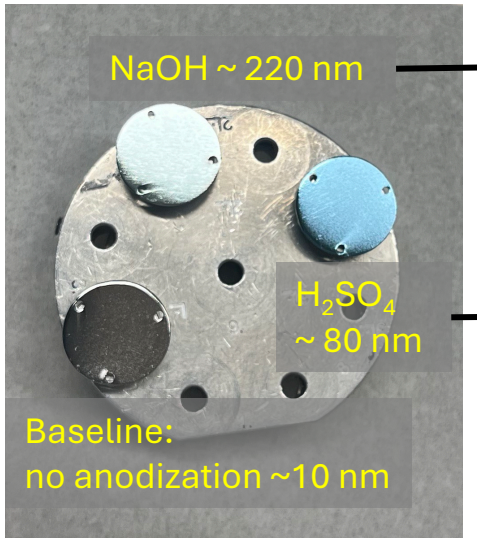
Degas



In this example, $SnCl_2$ vapor is exhausted early in the degas process

Checking experimentally what happens after degas





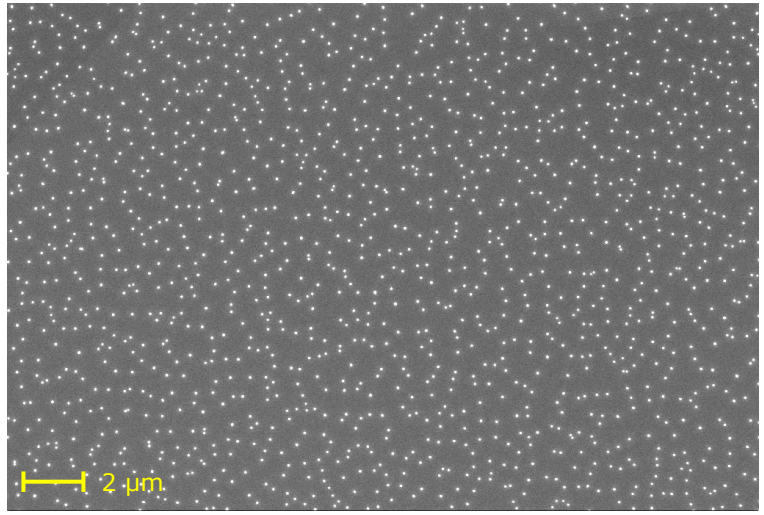
Porous oxide

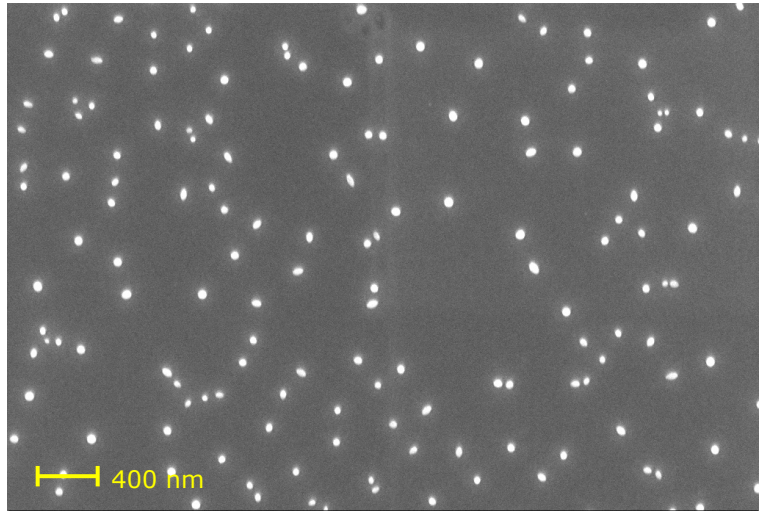
Barrier type, Smoother oxide

Samples taken out of furnace and underwent surface characterization

Post 170℃ degas with $SnCl_2$ results

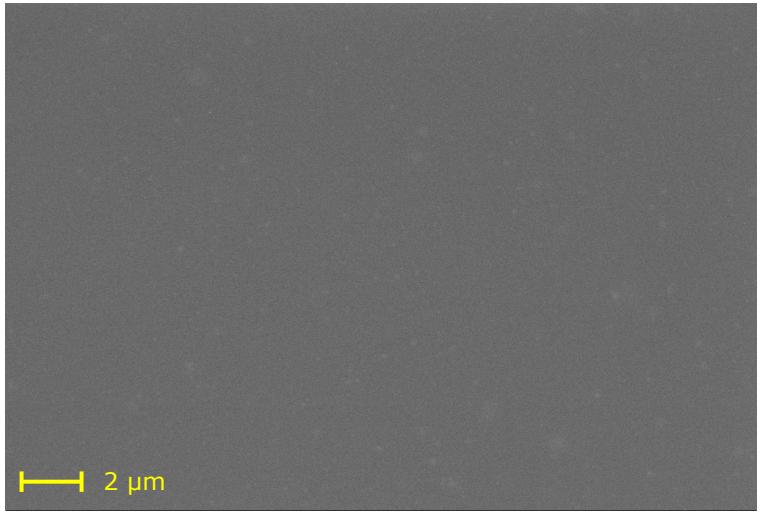
Native Oxide

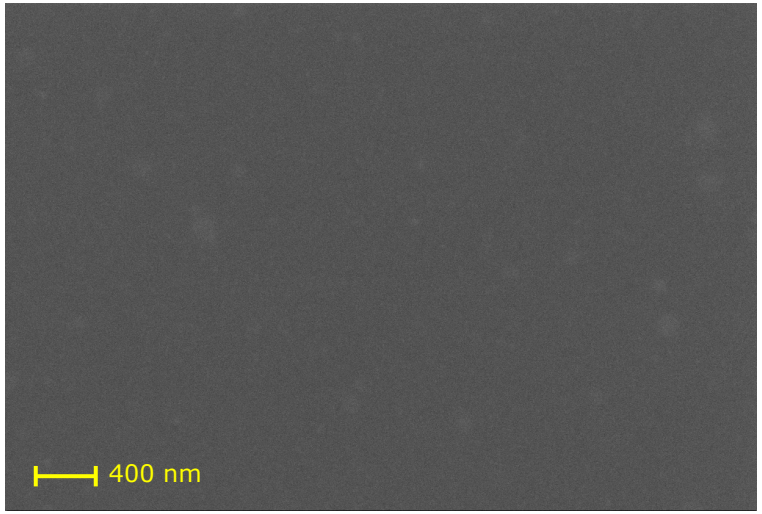




Sn3d/Nb3d (XPS at. %) = 0.25

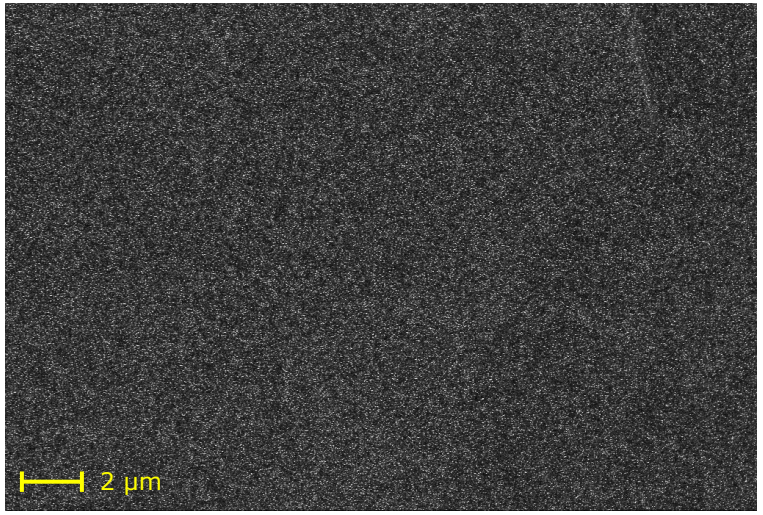
H_2SO_4 Anodized (Smooth Oxide)

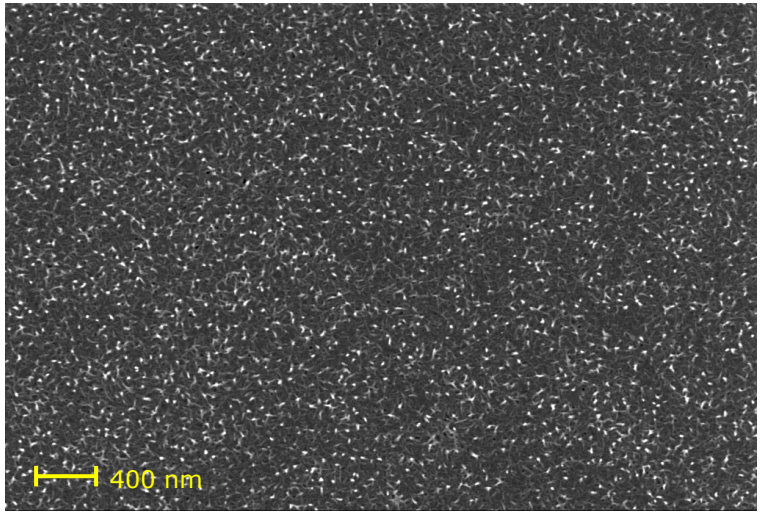




Sn3d/Nb3d (XPS at. %) = 0.38

NaOH Anodized (Rough Oxide)





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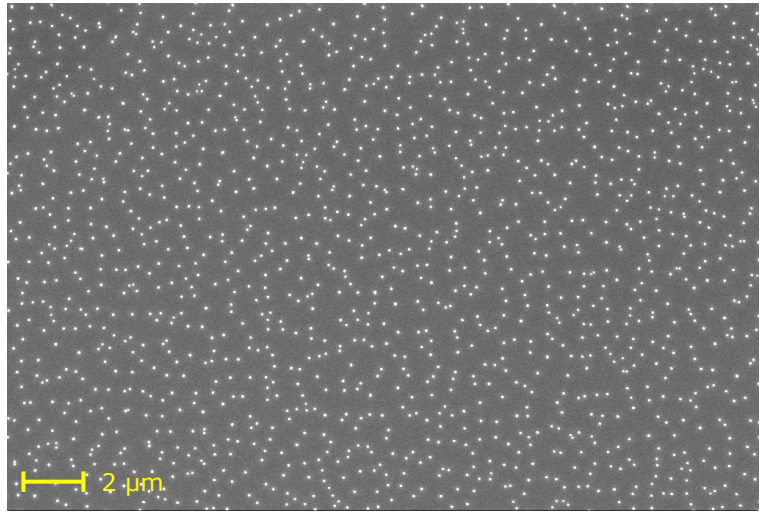
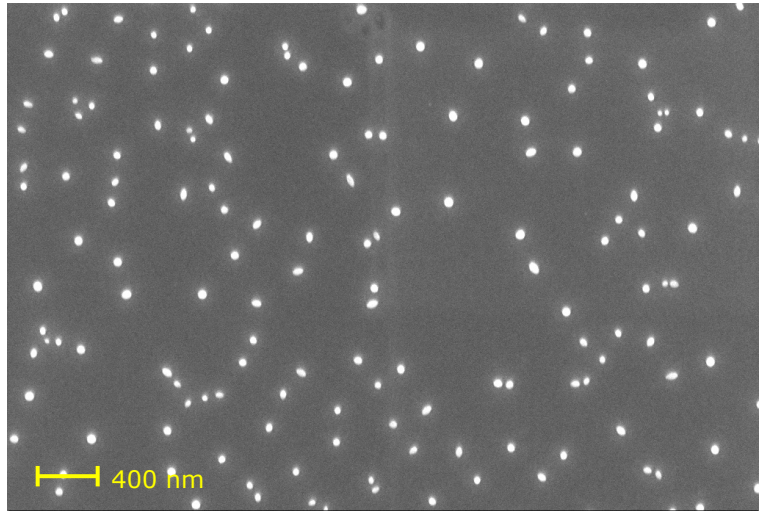
Post 170℃ degas with $SnCl_2$ results

Native Oxide





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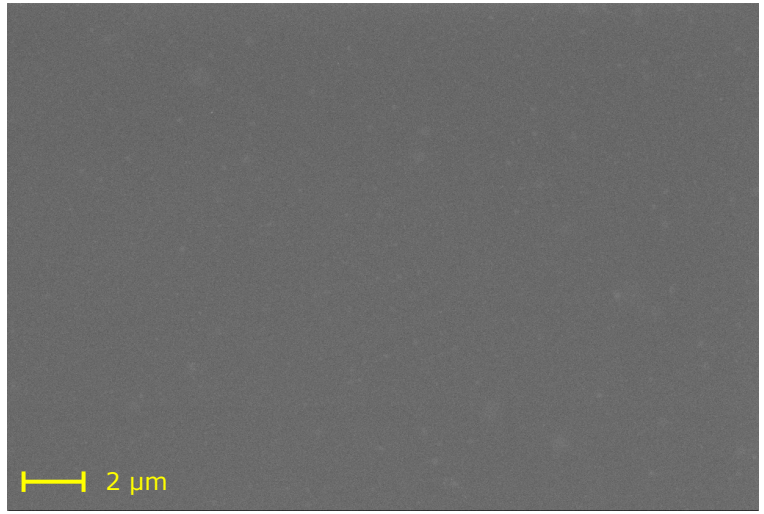

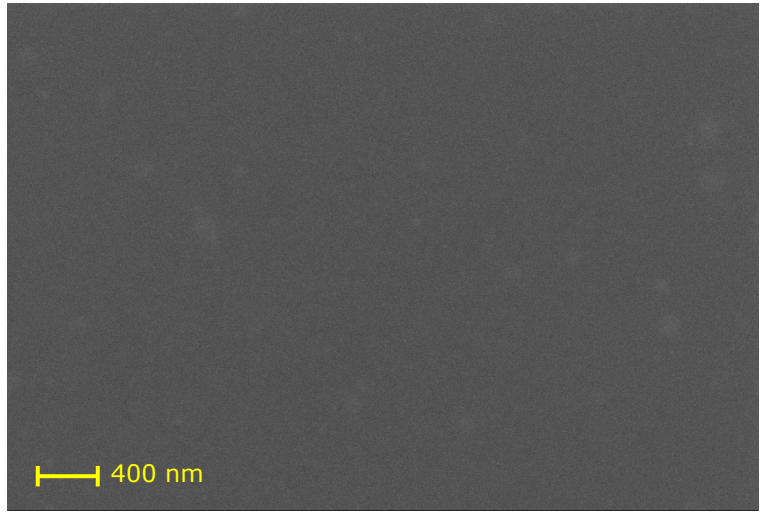

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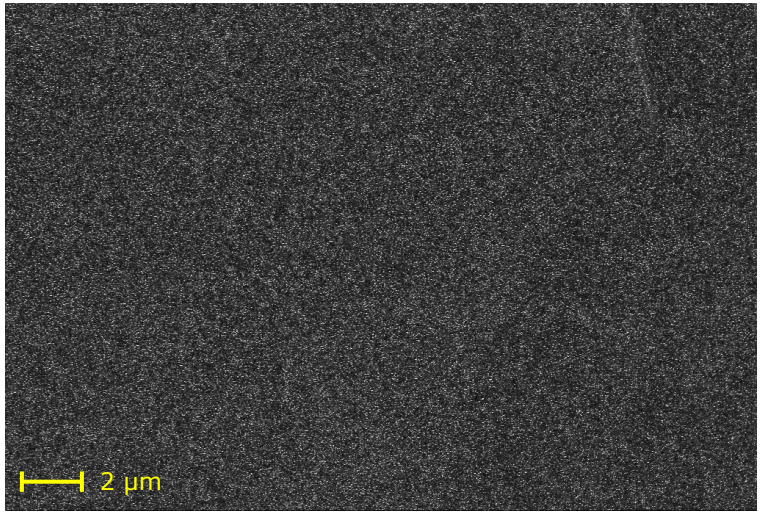

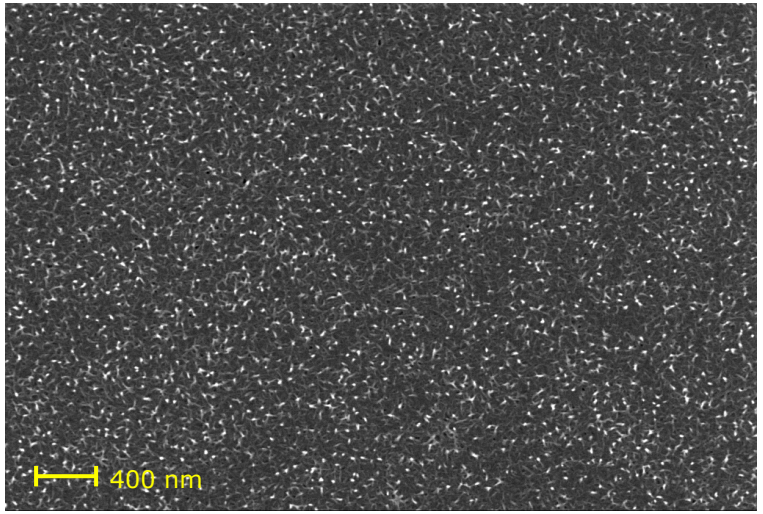

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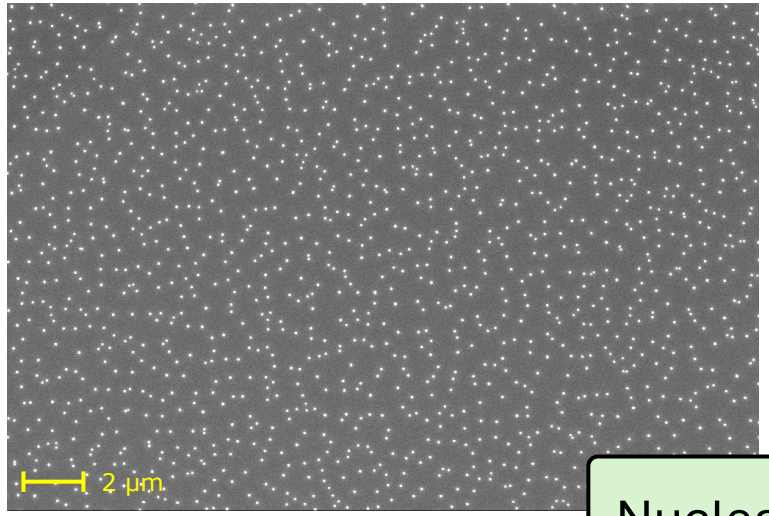
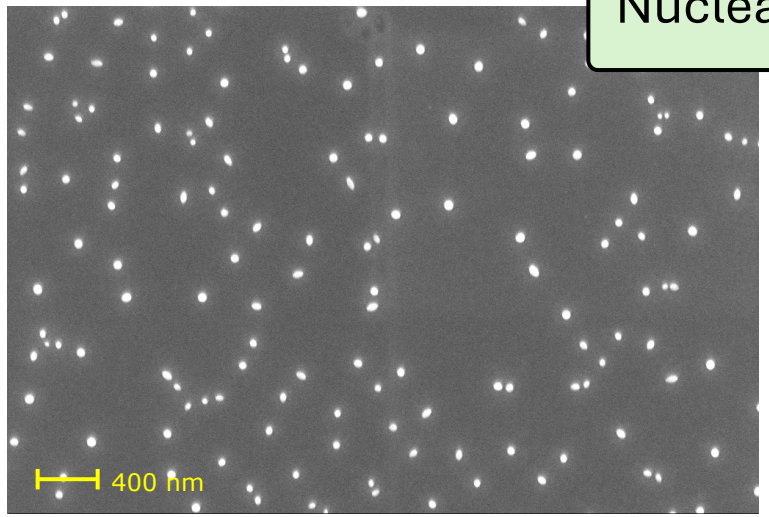
Post 170℃ degas with $SnCl_2$ results

Native Oxide





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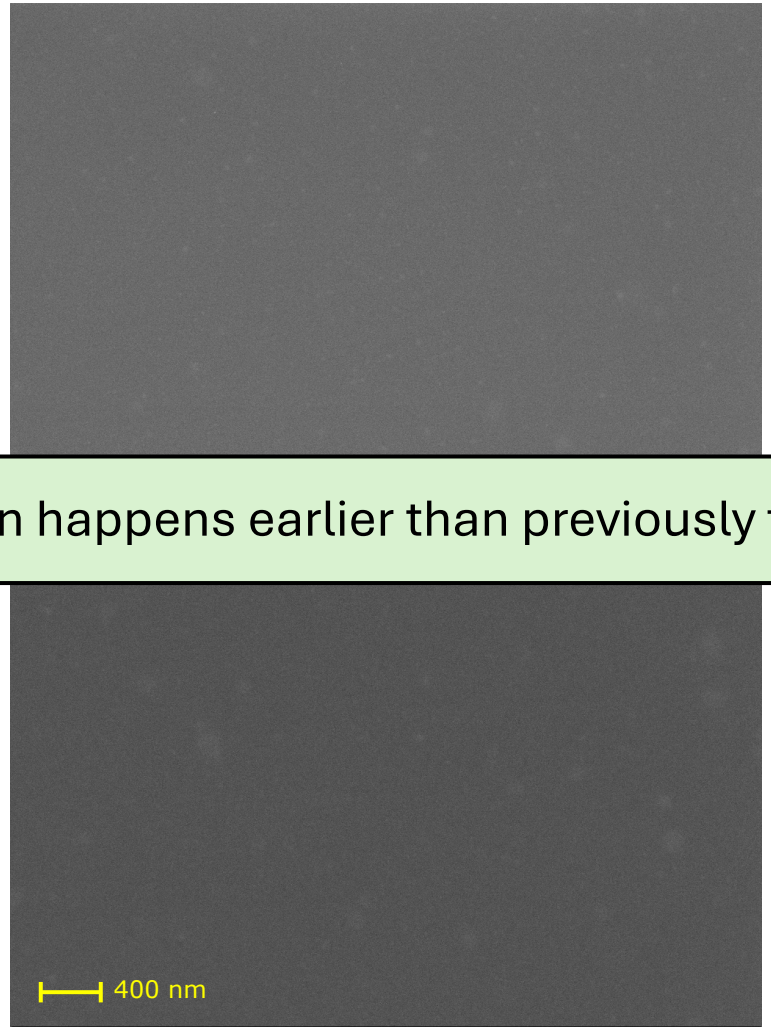

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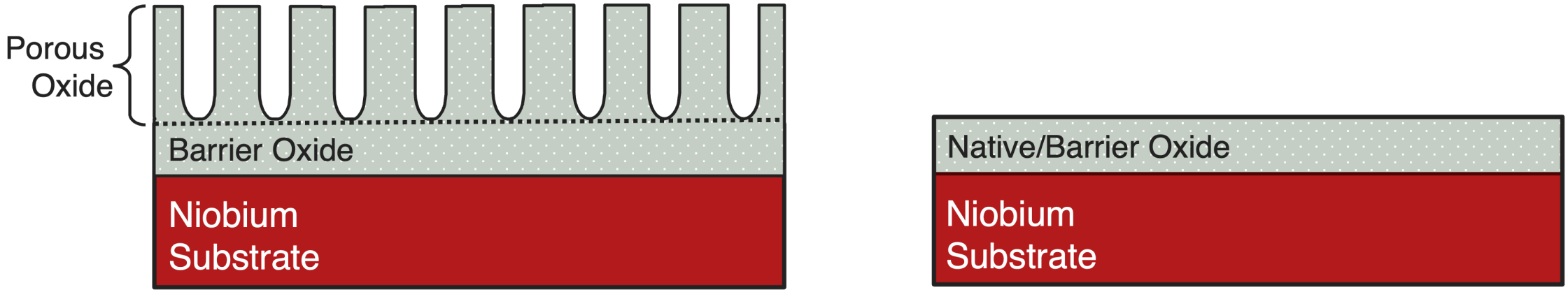
NaOH Anodized (Rough Oxide)

Sn3d/Nb3d (XPS at. %) = 0.89

Nucleation happens earlier than previously thought!

Porous oxide takes in more $SnCl_2$: simplified picture



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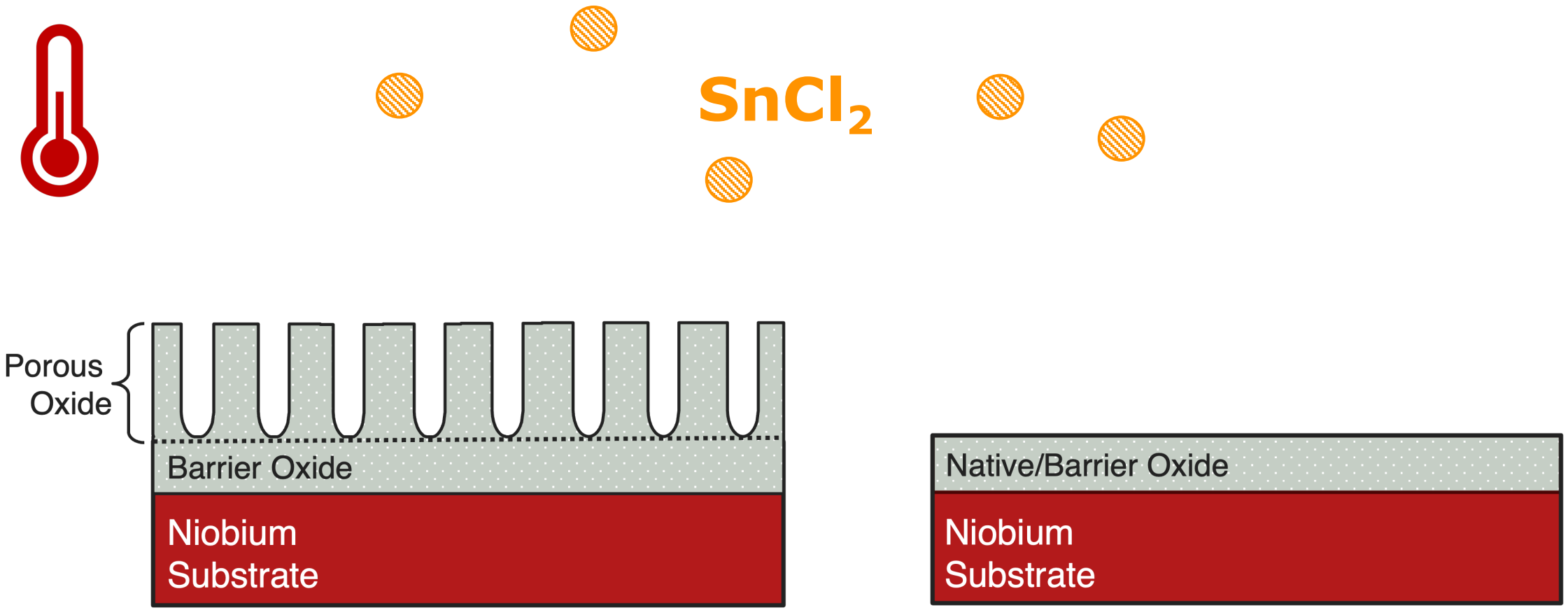

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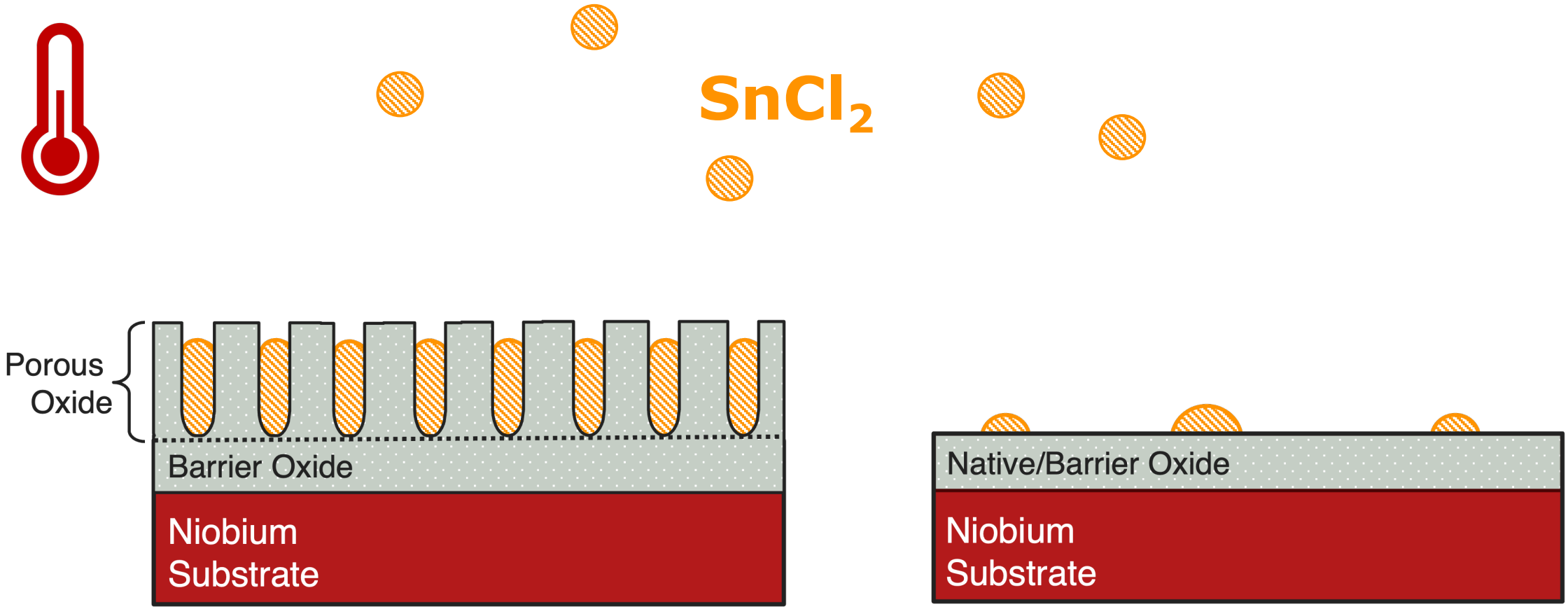
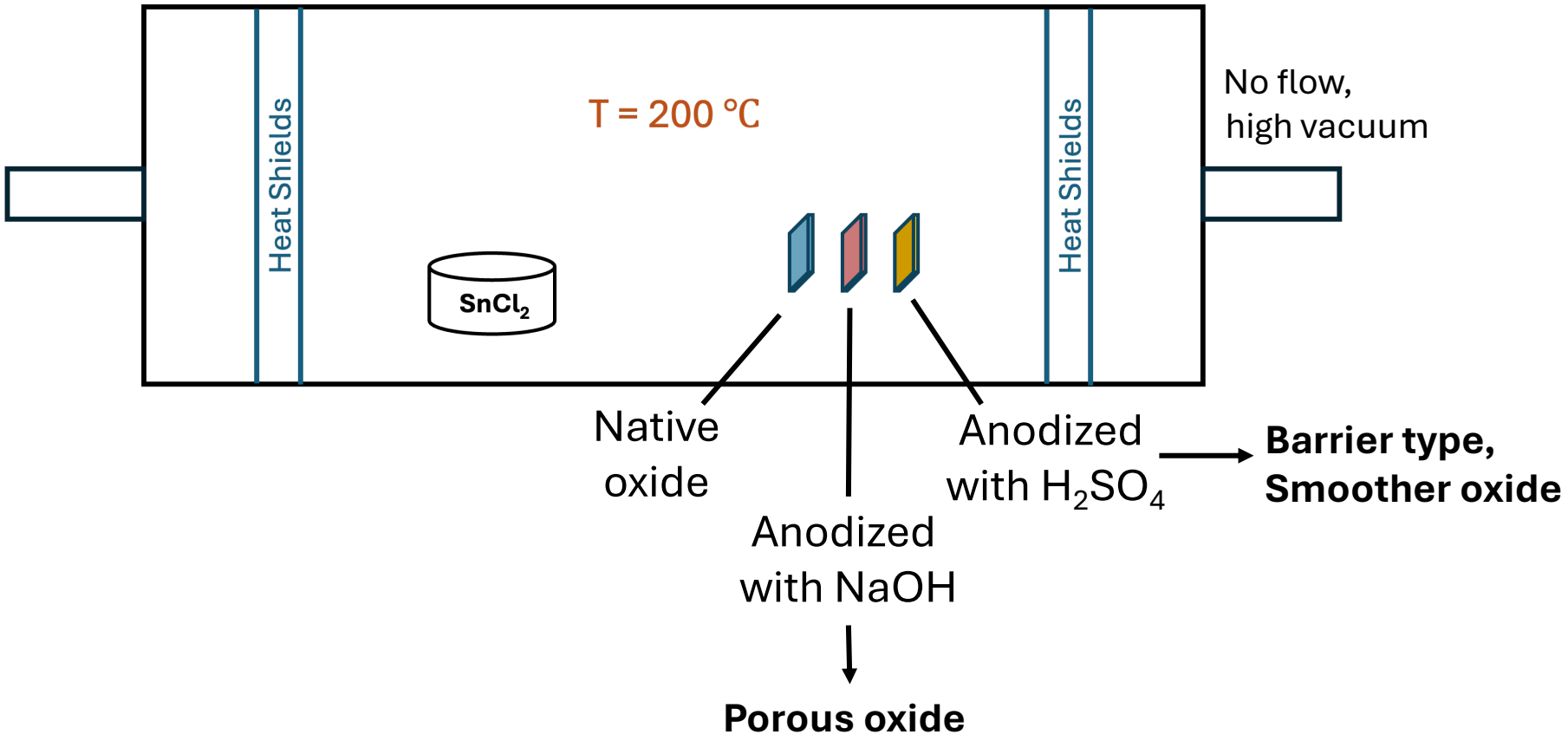
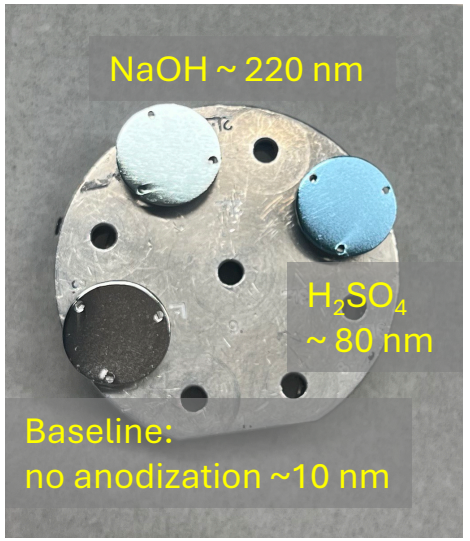


$SnCl_2$ sublimation study

Using the annealing functionality of the Chemical Vapor Deposition (CVD) furnace, we can mimic vapor-diffusion conditions and study $SnCl_2$-Nb surface interactions

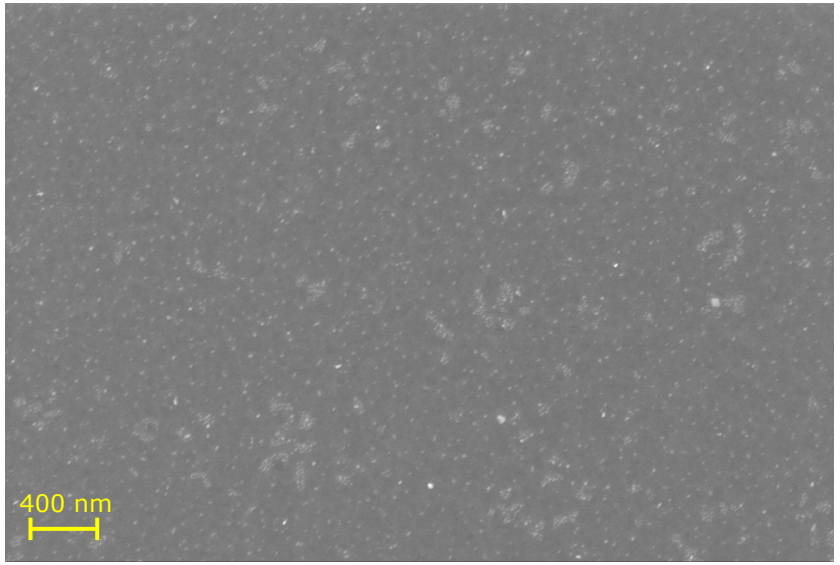




Gabriel Gaitan

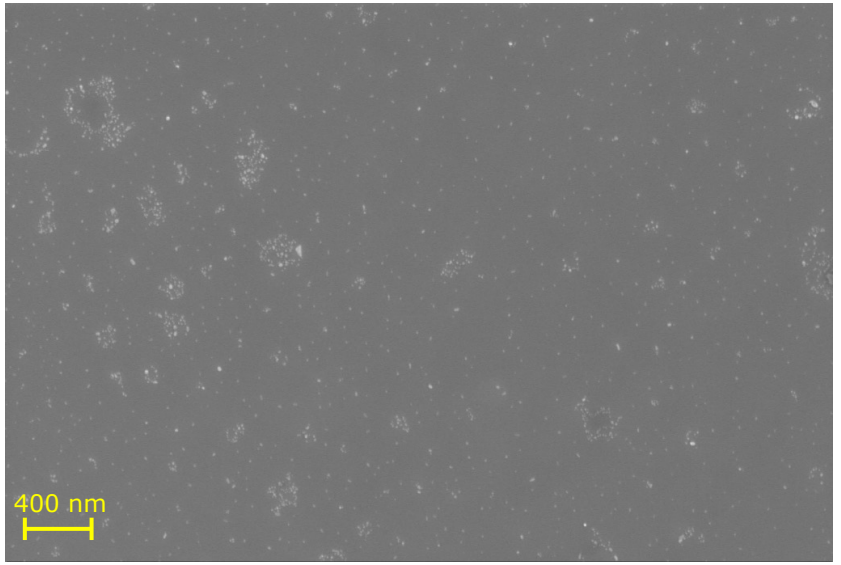
Post 200℃ bake with $SnCl_2$ results

Native Oxide



Sn3d/Nb3d (XPS at. %) = 0.24

H_2SO_4 Anodized (Smooth Oxide)



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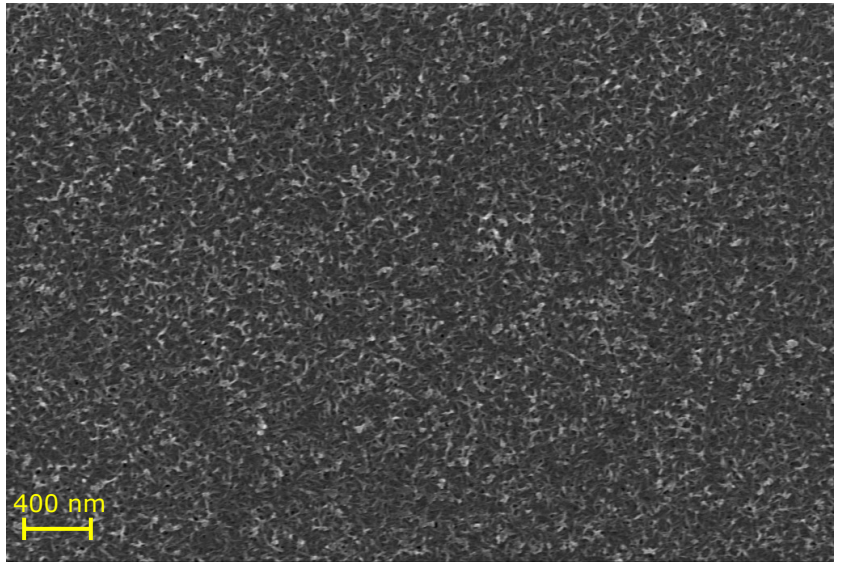
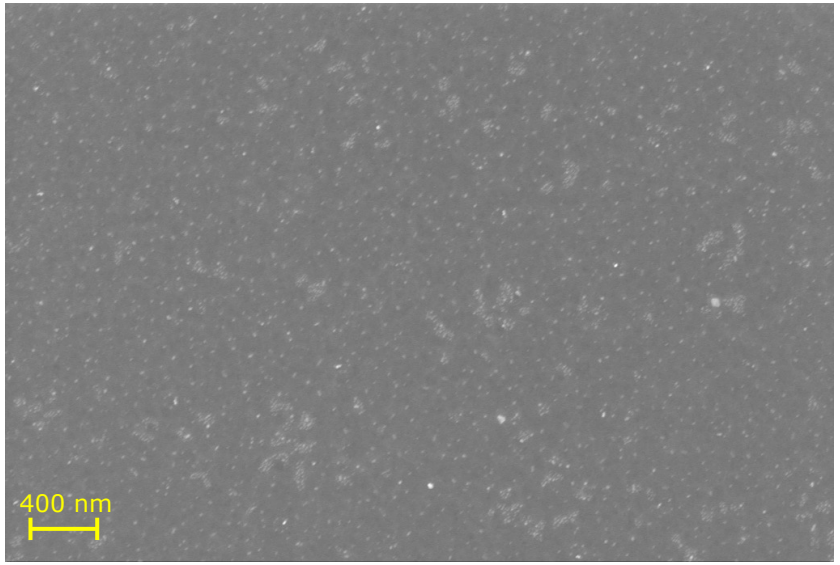


Sn3d/Nb3d (XPS at. %) = 0.93

Same effect was observed: porous oxide has most Sn content

Post 200℃ bake with $SnCl_2$ results

Native Oxide



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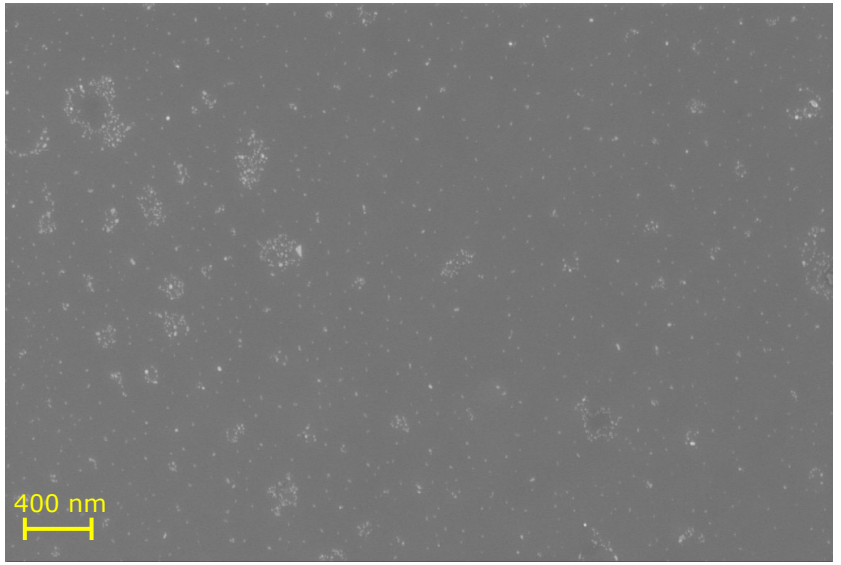

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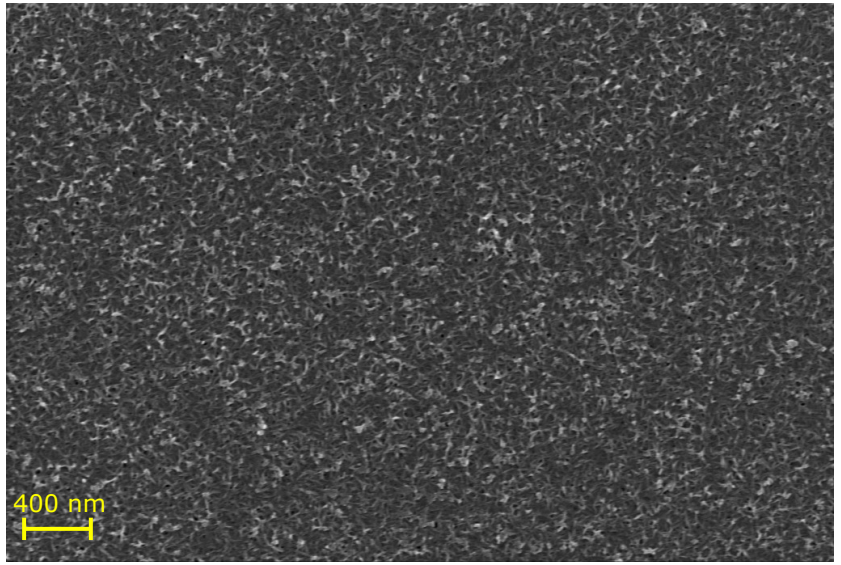

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Same effect was observed: porous oxide has most Sn content

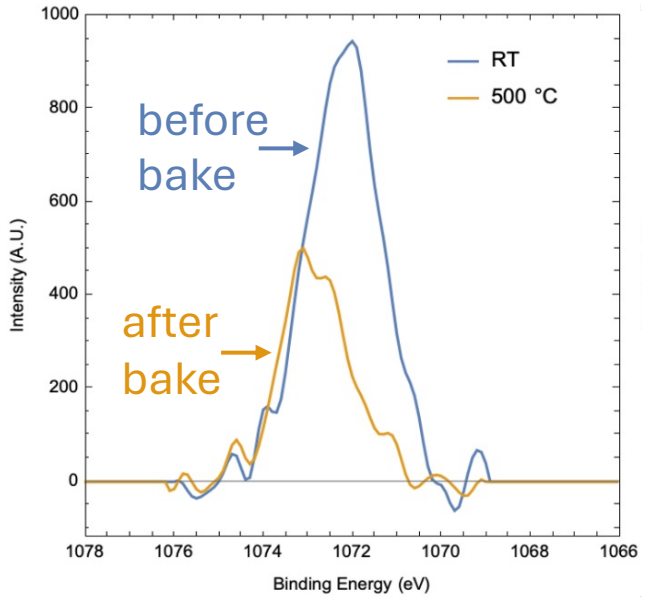
Challenge we faced with multiple runs: degradation of $SnCl_2$ (lower sublimation rates) due to handling in atmosphere

Some more observations

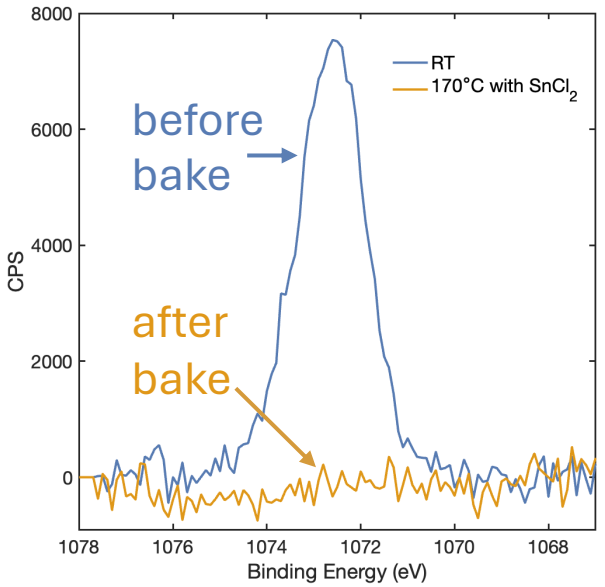
Surface chemistry reveals Na in porous oxide

Electrolyte incorporation in the oxide during anodization

Na 1s, UHV



Na 1s, $SnCl_2$ present



Na persists after annealing in UHV; however, it goes away when $SnCl_2$ is present in the chamber!

Takeaways and outlook

Surface roughness persists after oxide reduction through annealing:

→ helpful to separate chemical vs roughness effects in future nucleation studies (using the Chemical Vapor Deposition furnace)

$SnCl_2$ interacts with the Nb surface earlier than previously assumed (as early as degas stage):

→ important for understanding what actually drives nucleation

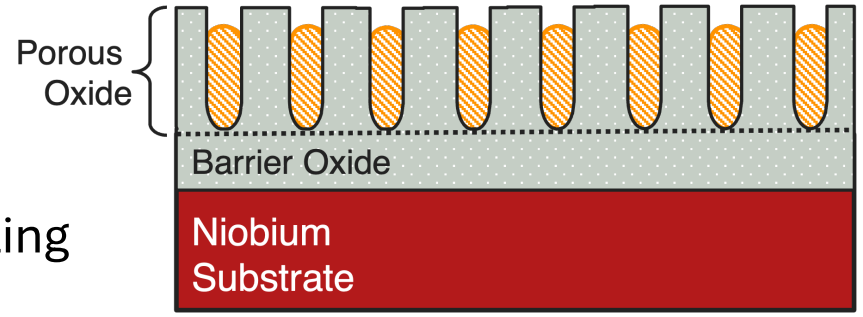
Porous/rough oxides show potential for improved nucleation: no droplets but more tin

→ promising direction to engineer the substrate surface for better (thinner, more uniform) final films

Some things to keep in mind moving forward:

→ Na incorporation in porous oxide surface: does it play a role?

→ $SnCl_2$ degradation: important consideration for storage and handling



Takeaways and outlook

Thank you for your attention!

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