Bedzyk Research Group

X-ray Interface Science

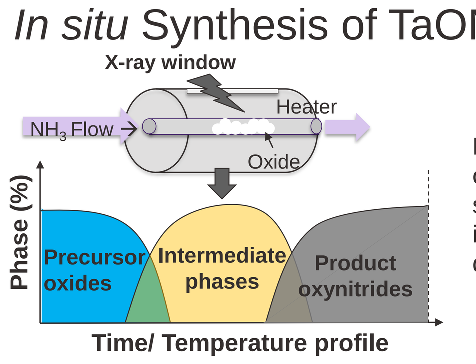
Northwestern

Argonne NATIONAL LABORATORY

Synthesis of oxynitrides for photocatalysis

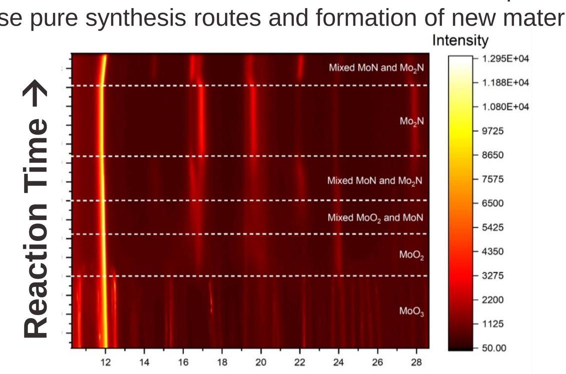
Transition-metal oxynitrides, materials with both O and N anions, are emerging photo- and electro- catalytic materials due to their unique physical, chemical and opto-electronic properties. Oxynitrides are synthesized by flowing NH_3 over an oxide precursor at elevated temperatures. Final products are sensitive to heating profile, precursor, and extent of reaction, making it challenging to obtain single phase products reproducibly, which is key for performing further characterization studies. Probing reaction pathway via in-situ studies corroborated with DFT calculations, allows more controlled synthesis of these oxynitrides.

In situ Synthesis of TaON and Mo-O-N



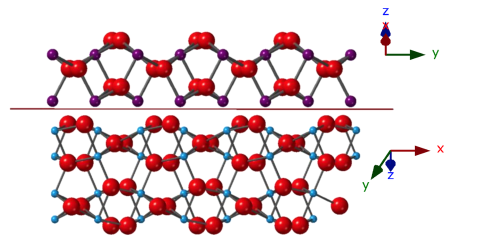
Phase evolution and regions of phase coexistence are studied by taking continuous in-situ XRD measurement during reaction.

Allows direct observation and identification of intermediate phases, thereby guiding phase pure synthesis routes and formation of new materials.

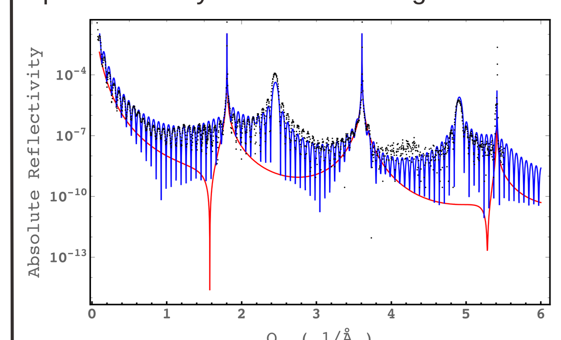


Currently: Elise Goldfine (PhD student) [Collaboration with Prof. Sossina Haile]

Thin Film Growth of Ta-O-N



Single crystal, epitaxial Ta-O-N films are grown by PLD. By matching the TaON lattice constants to the substrate, specific phases of oxynitride can be targeted.



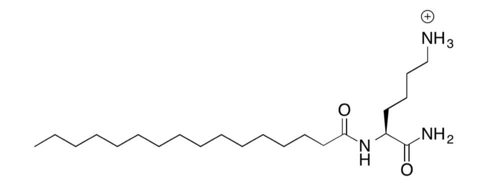
A high quality epitaxial film of TaO2 (101)/Al2O3 (012) provides starting point of oxynitride film growth.

From Left: Guenna, Achari, Prof. Bedzyk, Anusheela, Kathy, Roger, Elise, Bruce, Joey, Rachel, Carlos, Sumit, Yanna, Anthony, Jerry

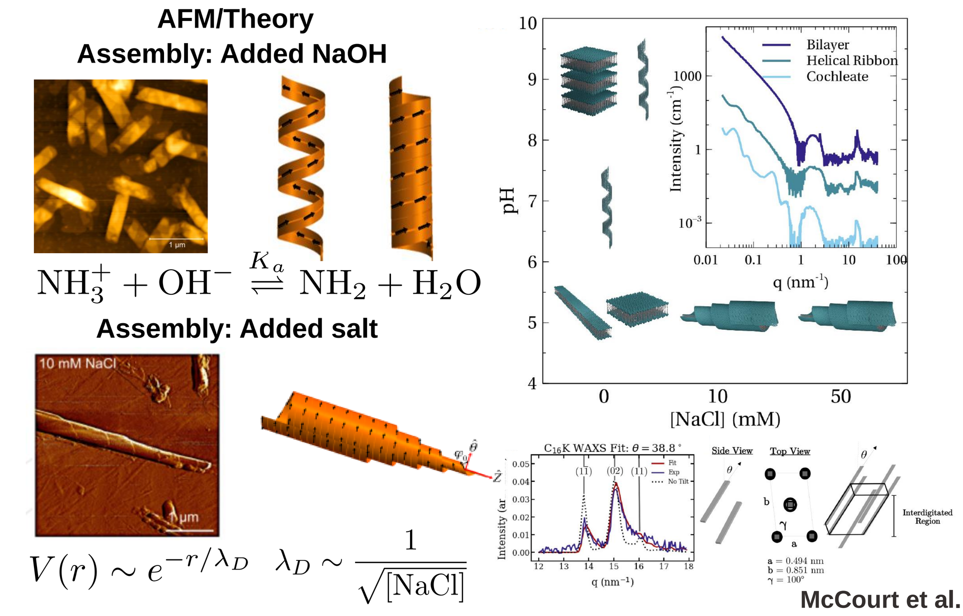
Electrostatic control of assembly of chiral amphiphiles

Charged chiral molecules are abundant in nature. Prime examples are the amino acids. Efficient packing of chiral molecules requires that the neighbors exhibit a twist with respect to each other, leading to helical structures. Here, we show that the nature of the ionic environment determines the type of helical assembly, with weak long-range electrostatic interactions leading to helical ribbons and short-range leading to cochleate.

Chiral amphiphile: C_{16}-Lysine



Approach. The assembly of charged chiral amphiphile C_n-K_1 is examined as a function of NaCl and NaOH concentration from nano-to-meso-scale using a combination of in situ AFM, cryo-TEM, circular dichroism and solution SAXS/WAXS.



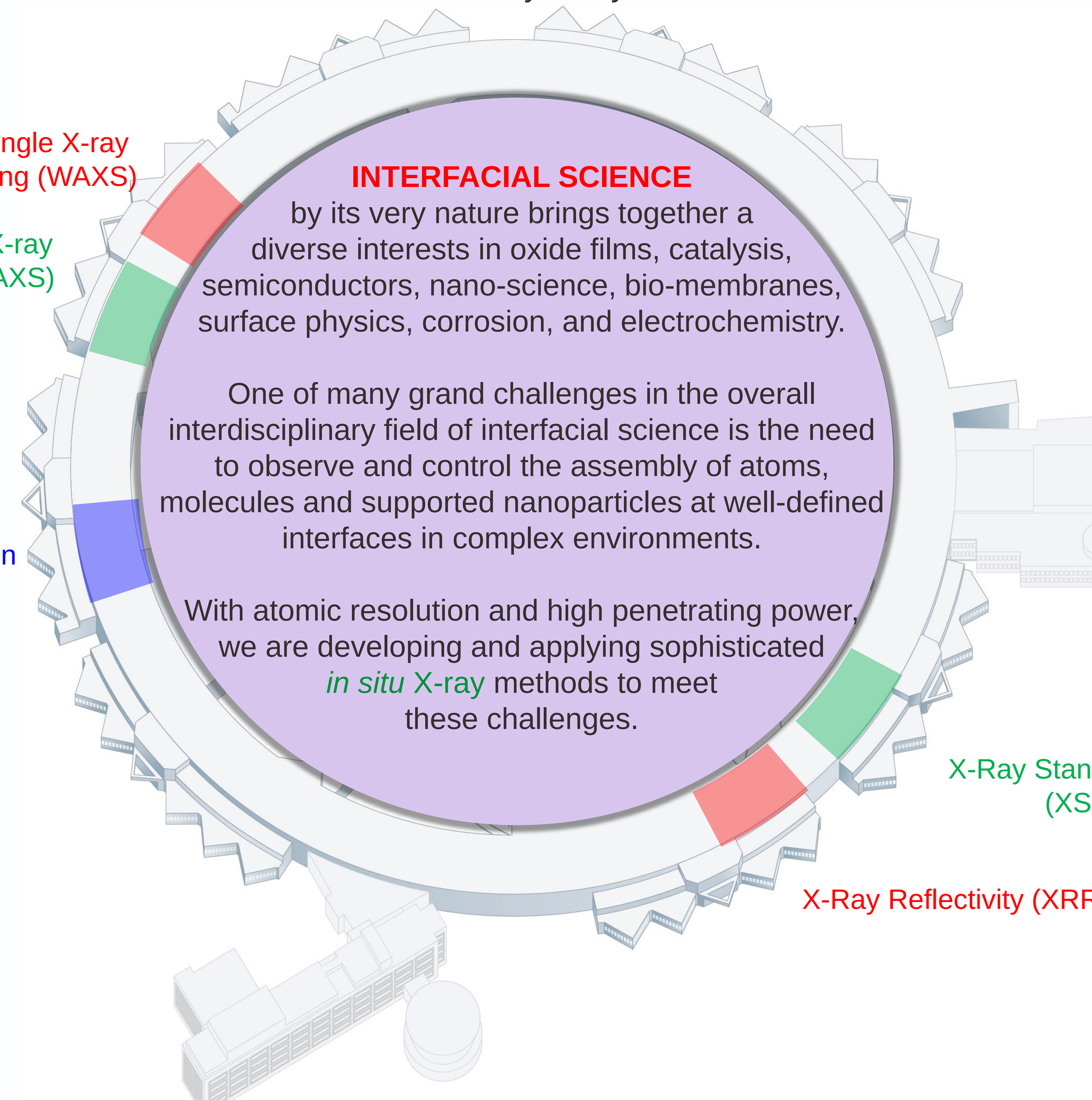
$NH_3^+ + OH^- \overset{K_a}{\rightleftharpoons} NH_2 + H_2O$

$V(r) \sim e^{-r/\lambda_D}$ $\lambda_D \sim \frac{1}{\sqrt{[NaCl]}}$

The molecules assemble into planar, interdigitated, high-aspect ratio, tilted, crystalline bilayer ribbons. With a change in ionic environment, the crystallinity in bilayers reduces and bilayers twist. Depending on whether the change tunes the charge (added NaOH (increased pH)) or screens the charge (added NaCl), the bilayer ribbons form helical ribbons or helicoidal cochleate. The phase the diagram above shows the case for $C_{16}K_1$ (n=16).

McCourt et al., *ACS Central Science*, 2022

Currently: Joey McCourt (PhD student) and Sumit Kewalramani (Research Assistant Professor)



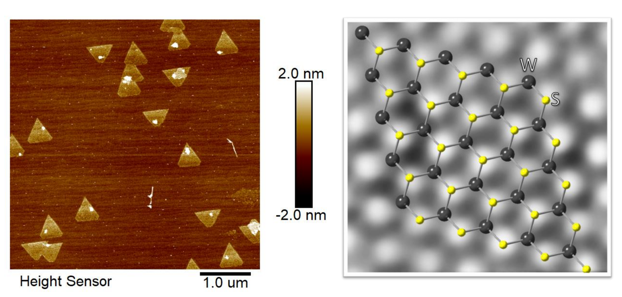
INTERFACIAL SCIENCE by its very nature brings together a diverse interests in oxide films, catalysis, semiconductors, nano-science, bio-membranes, surface physics, corrosion, and electrochemistry.

One of many grand challenges in the overall interdisciplinary field of interfacial science is the need to observe and control the assembly of atoms, molecules and supported nanoparticles at well-defined interfaces in complex environments.

With atomic resolution and high penetrating power, we are developing and applying sophisticated *in situ* X-ray methods to meet these challenges.

Characterization of 2D transition metal dichalcogenides

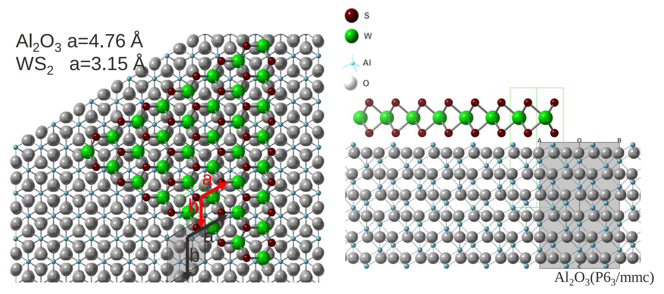
Growing 2D materials epitaxially on single crystal substrates provides a means for controlling their orientation.



AFM image showing the triangular shaped WS_2 monolayer on c-Al_2O_3.

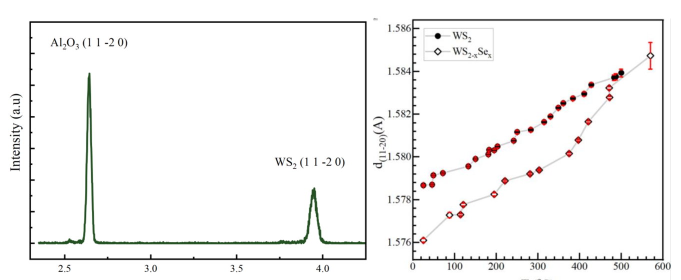
AFM image showing the atomic resolved surface of the WS_2 layer. The overlay shows the atom locations.

- WSe_2 is of interest as a 2D semiconductor (SC) with a direct band-gap. Due to low doping levels, it is an intrinsic SC and shows ambipolar transport. This affords the possibility to realize devices with the Fermi level located in the valence band, where the spin/valley coupling is strong and leads to novel and interesting physics.
- WS_2 and WSe_2 were deposited on sapphire substrates using HT-MOCVD by collaborators at The 2D Crystal Consortium, Penn State University.
- Atomic resolution AFM was carried out with our newly installed VT-AFM.
- Synchrotron X-ray characterization (CTR and XSW) of the structures is ongoing.



WS_2 has a van der Waals epitaxial relation with the substrate c-Al_2O_3. The orientation relation is WS_2(0001)//Al_2O_3(0001) and WS_2()//Al_2O_3().

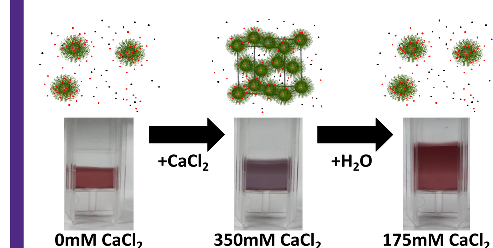
Currently: Achari Kondapalli (Postdoc)



In-plane XRD confirming the orientation relation WS2()//Al_2O_3(). High temperature in-plane XRD elucidating the Se doping effect on the thermal expansion behavior of the WS_2.

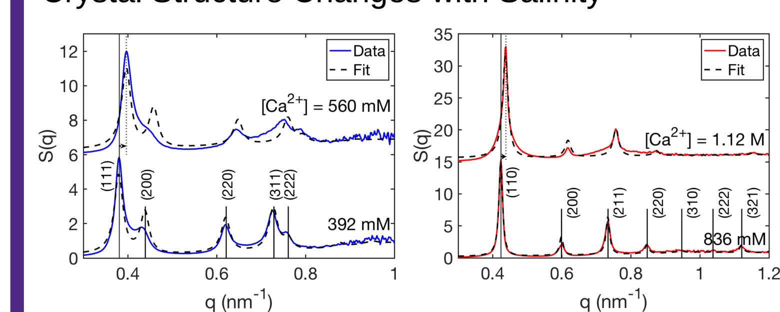
Interparticle Interactions in Concentrated Electrolytes

Ca^{2+} ions induce crystallization



- Dissolved ions act as mediators of electrostatic forces in aqueous systems. Ions can induce exotic behavior, such as attractions between like charges.
- Small angle X-ray scattering (SAXS) is utilized to investigate the crystal symmetries and effective particle separations of DNA-functionalized gold nanoparticles assembled in divalent salt solutions.

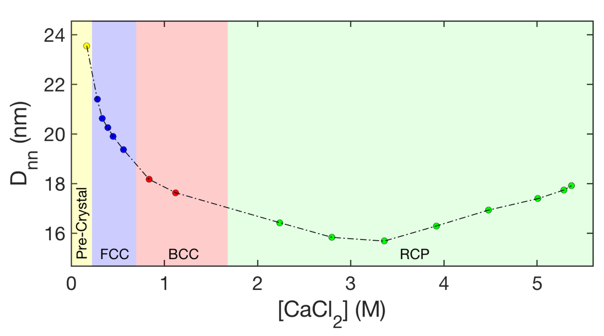
Crystal Structure Changes with Salinity



- Increasing the solution ionic strength changes the lattice type from FCC to BCC, eventually eliminating long-range-order

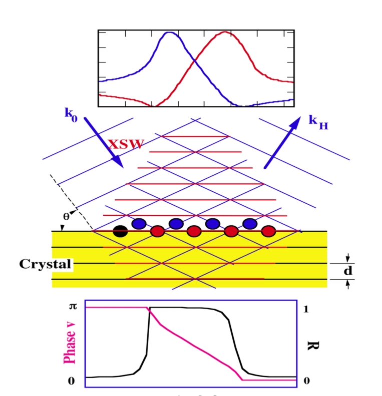
Extraction of Effective Particle Sizes

- The nearest-neighbor distance (D_{nn}) in the assemblies initially decreases with $CaCl_2$ concentration (expected from classical theory), but eventually reaches a minimum and begins to increase.



Currently: Roger Reinertsen (PhD student) and Sumit Kewalramani (Research Assistant Professor)

Atomic-scale x-ray interface studies of heterogeneous catalytic systems



X-ray standing wave → Interference between incident and Bragg reflected X-ray planes waves, XSW period = *d*

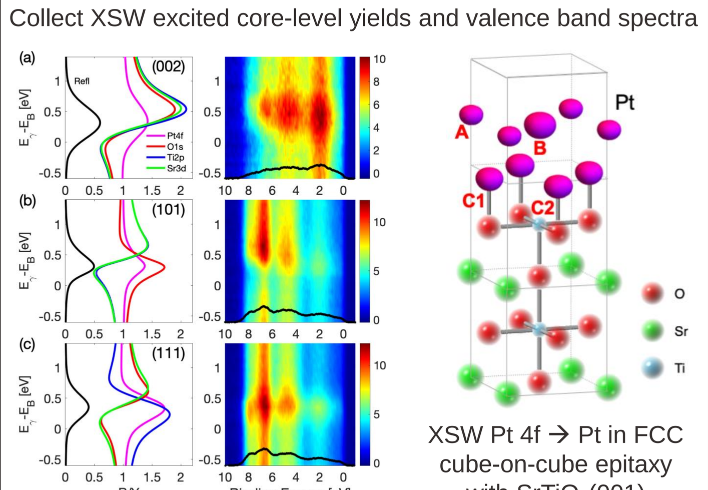
Scanning in q thru Bragg peak → *XSW phase shift by $^d/_2$* → modulation in XRF (element specific) or XPS (chemical state specific) yield

Fourier summation of multiple planes → 3D, model-independent, real-space map of emitter atoms with sub-Å

A novel method to determine site-specific valence electrons contribution to density of states

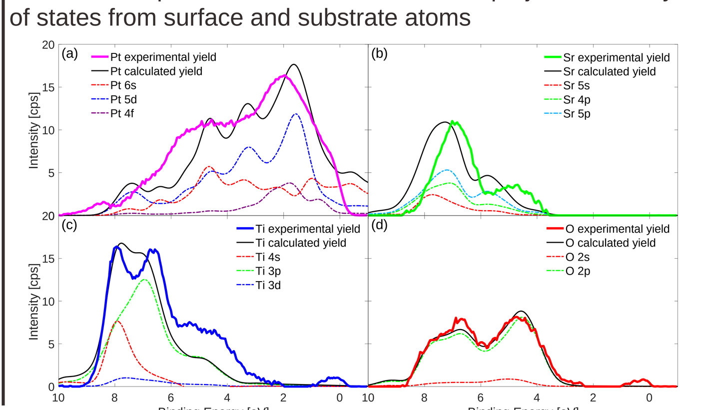
PLD ½ ML Pt on $SrTiO_3$ (001)

Collect XSW excited core-level yields and valence band spectra

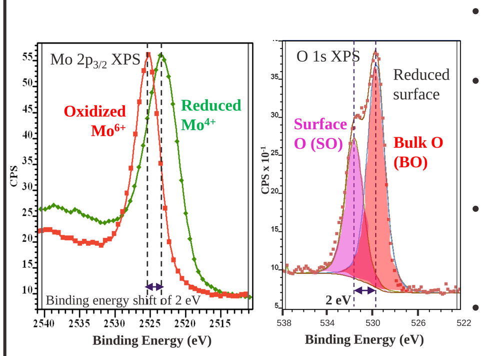


XSW Pt 4f → Pt in FCC cube-on-cube epitaxy with $SrTiO_3$(001)

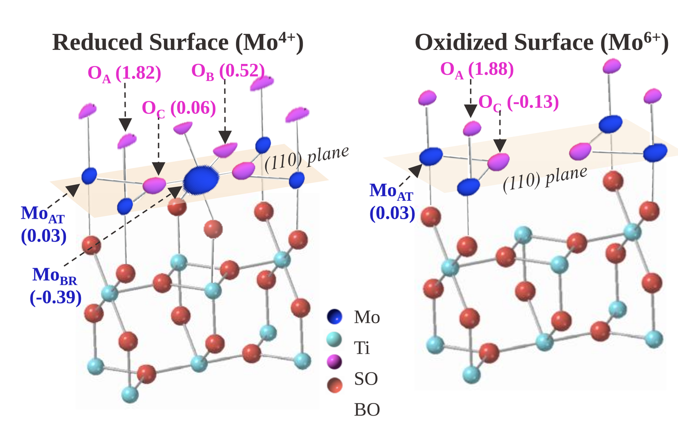
XSW VB compares well to a DFT calculated projected density of states from surface and substrate atoms



ALD 1 ML of MoO_x on α-TiO_2 (110)

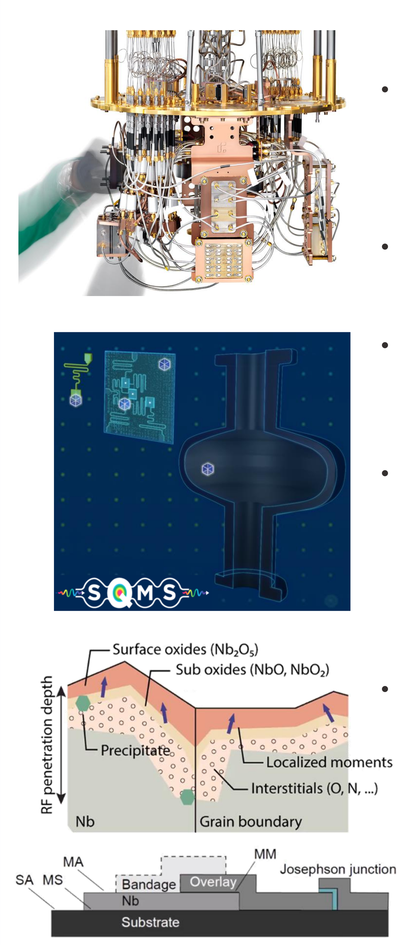


- SO peak shifted to by 2 eV from BO peak
- 3x higher coverage of correlated SO in the reduced surface than the oxidized surface
- No oxygen at B site in the oxidized surface
- Upon reduction all 3 surface sites have oxygen



- Mo $2p_{3/2}$ peak shifted by 2 eV lower by reduction
- No bridging Mo in the oxidized surface
- Upon reduction, most Mo from AT site → BR site

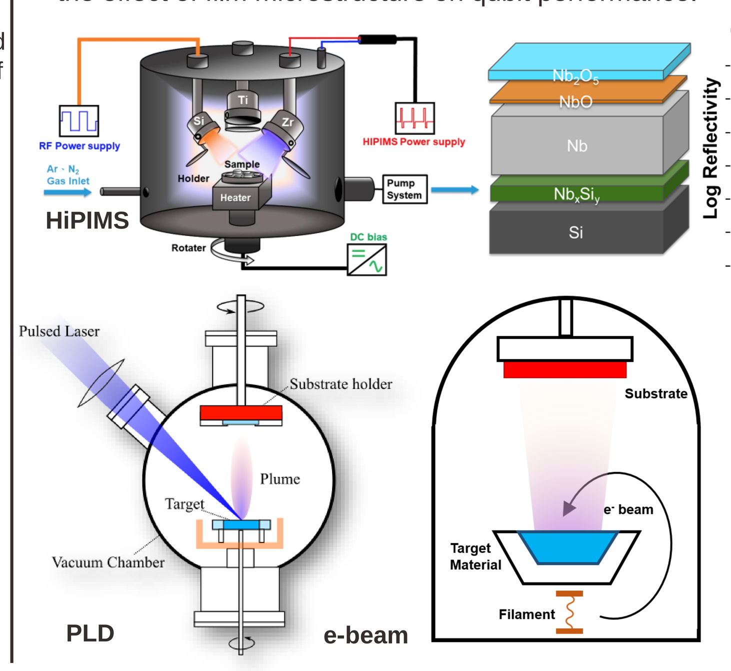
Improving the coherence time of superconducting qubits through materials characterization and optimization

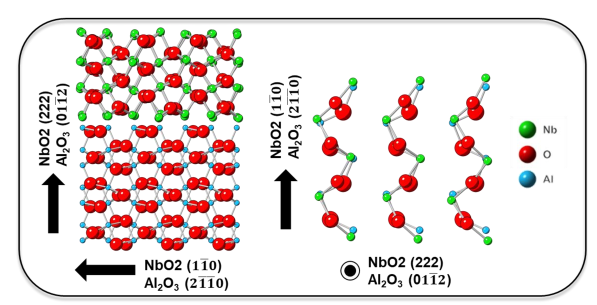


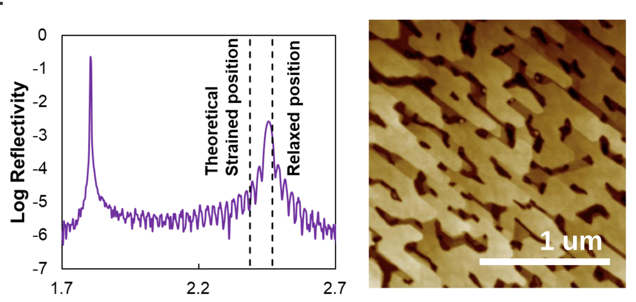
- Superconducting qubits use Josephson junction (JJ) circuit elements to create controllable and readable qubits.
- Qubit architecture of 2D and 3D transmon designed limit noise.
- Materials defects, loss, and participation are sources of substantial decoherence in qubits.
- Fabrication of JJs, resonators, and transmons are used to measure quality of synthesized material and compare thin film structures for future chip fabrication.
- Northwestern University has partnered with Fermilab and Rigetti Computing to fundamentally understand the source of decoherence and implement mitigation strategies.

Niobium thin films are grown via Pulsed Laser Deposition (PLD), Magnetron Sputtering, High-power Impulse Magnetron Sputtering (HIPIMS), and electron beam evaporation (e-beam) on silicon and sapphire substrates.

These techniques are used to compare growth techniques for use in industry as well as to compare the effect of film microstructure on qubit performance.

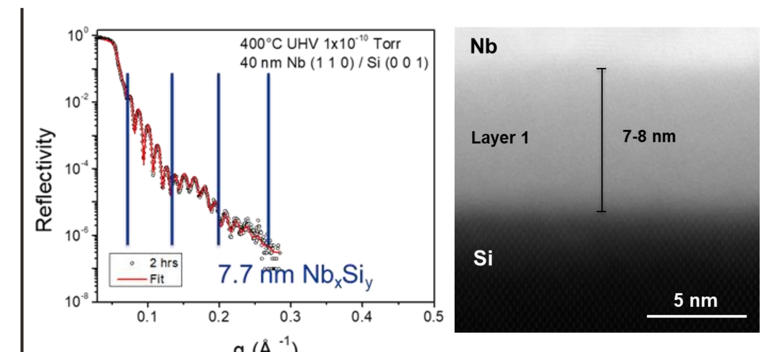




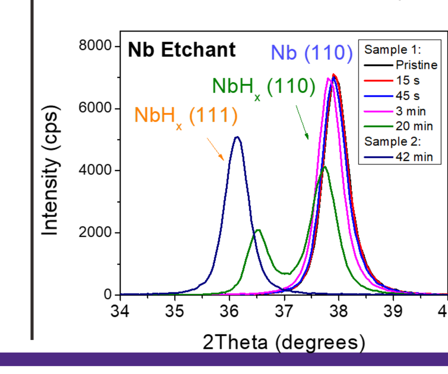


Depending on the substrate and growth technique, the films may be epitaxial, textured, polycrystalline, or amorphous.

X-ray diffraction is used to determine the crystal structure, crystallinity, and lattice mismatch. Control of the structure is studied for the use in superconducting qubits.



Formation of unwanted phases in the film interfaces and bulk such as niobium hydrides and silicides are studied with numerous techniques including X-ray Reflectivity, Cross-section TEM, Atomic Force Microscopy, and X-ray Diffraction, and X-ray Photoelectron Spectroscopy. Interdiffusion of silicon at the substrate interface causes the formation of amorphous Nb_xSi_y. Hydrogen can be incorporated into the bulk via chemical and cryogenic experiment, creating Nb_xH_y.



rigetti Fermilab

Currently: Carlos Torres (PhD student), David Garcia Wetten (PhD student), K.V.L.V Narayanachari (Postdoc)