

## **Anomalous Surface Behavior of Sr<sub>3</sub>Ir<sub>2</sub>O<sub>7</sub>**

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**Should be considered for poster awards:** Yes

The temperature dependent low-energy electron diffraction (LEED) studies on Sr<sub>3</sub>Ir<sub>2</sub>O<sub>7</sub> show a behavior that contradicts the expected Debye-Waller scattering. A finite Debye temperature would imply a decrease in LEED scattering intensities with increasing temperature, but this is not observed between room temperature and 400 K. Instead, there is a significant enhancement in the intensities of the LEED diffraction spots before a slight attenuation, with increasing temperature, at low kinetic energies. Hence, there is an anomaly in the surface behavior of Sr<sub>3</sub>Ir<sub>2</sub>O<sub>7</sub> which contradicts the Debye-Waller scattering theory. However, at higher kinetic energies, the LEED intensity behavior becomes more characteristic of a finite Debye temperature. This anomaly in the surface behavior of Sr<sub>3</sub>Ir<sub>2</sub>O<sub>7</sub> might be attributed to either temperature-induced surface segregation, a structural transition or an insulator-metal phase transition. We can infer that the surface Debye temperature is significantly lower than the bulk, as expected. By carrying out angle resolved X-ray photoemission spectroscopy, surface segregation has been excluded and electron transport measurements indicate a carrier activation energy in close agreement with LEED.

## Spontaneous Etching of Group V and VI Metal Oxides by Deoxychlorination Using Thionyl Chloride

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**Should be considered for poster awards:** Yes

Group V and VI metal and their respective oxides are of interest in semiconductor and microelectronic devices. Niobium and tantalum oxides possess a high dielectric constant, garnering potential for use in microcapacitors. Vanadium oxide is used as a cathode material in some flow batteries and lithium ion batteries. Molybdenum and tungsten metal and their respective dichalcogenides have recently gained momentum as channel materials. Thermal etching of these materials would provide methods to fabricate precise microelectronics employing said materials.

A quadrupole mass spectrometer (QMS) was outfitted to an ALE chemical reactor to study the etch products present during the exposure of various ALE precursors to nanopowders of group V and VI metal oxides. Spontaneous thermal etching of  $\text{MoO}_3$ ,  $\text{WO}_3$ ,  $\text{WO}_2$ ,  $\text{VO}_2$ ,  $\text{V}_2\text{O}_5$ ,  $\text{Nb}_2\text{O}_5$ , and  $\text{Ta}_2\text{O}_5$  was achieved by the introduction of  $\text{SOCl}_2$  to the powder at as low as  $200^\circ\text{C}$ . ALE was measured by the presence of volatile metal oxychlorides during  $\text{SOCl}_2$  doses in combination with measured mass losses on the nanopowder after exposure. No etching was measured on  $\text{Cr}_2\text{O}_3$  or  $\text{MoO}_2$ .

Volatile etch products varied dependent on the oxidation state of the metal center. Species in the form of  $\text{MO}_2\text{Cl}_2$  was most common for those metals in the +6 oxidation state, such as  $\text{MoO}_3$  or  $\text{WO}_3$ , while exclusively  $\text{MOCl}_3$  species were seen on metals in the +5 oxidation state. Oxidation appears to act as a barrier in this chemistry, as seen in the inability of  $\text{MoO}_2$  and  $\text{Cr}_2\text{O}_3$  to spontaneously volatilize. However, such as in the case of  $\text{WO}_2$  and  $\text{VO}_2$ ,  $\text{SOCl}_2$  was able to act as an oxidizing agent, producing  $\text{WO}_2\text{Cl}_2$  and  $\text{VOCl}_3$ , respectively. QMS results also provide insight into the surface mechanism of these reactions. During the spontaneous etching of  $\text{WO}_3$  and  $\text{WO}_2$ , both  $\text{WO}_2\text{Cl}_2$  and  $\text{WOCl}_4$  are evolved during  $\text{SOCl}_2$  doses, with  $\text{WOCl}_4$  having a significantly larger intensity on the QMS than  $\text{WO}_2\text{Cl}_2$ , suggesting that two sequential ligand exchanges must occur before efficient volatilization of W may occur. Furthermore, the ability to spontaneously etch these oxides provides a pathway for the cleaning of native oxides off of pure metal films deposited via ALD, such as the removal of native  $\text{MoO}_3$  from deposited Mo films.

## Tunable Electron Enhanced Etching of $\beta$ -Ga<sub>2</sub>O<sub>3</sub> Using HCl Reactive Background Gas and Positive Sample Voltage

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Crystalline  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> is an ultra-wide band gap material with important applications for high power electronics. High precision etching is required for  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> device fabrication. Previous thermal atomic layer etching (ALE) attempts to etch  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> have not been successful. Plasma etching of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> using Cl-containing gases is difficult for Ångstrom-level etching control and can leave surface damage. In this work, electron-enhanced etching of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> is performed using a HCl reactive background gas (RBG) and positive sample bias. The  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> is a (201)-oriented epitaxial film grown by suboxide molecular-beam epitaxy on a single-crystal (0001) Al<sub>2</sub>O<sub>3</sub> substrate. The ~100 eV primary electrons from a hollow cathode plasma electron source (HC-PES) are incident on the  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> sample. The HC-PES is a chemically robust electron source capable of delivering >200 mA over an area >10 cm<sup>2</sup>. The HCl reactive background gas (RBG) is present at ~1 mTorr. A small positive voltage of <50 V is applied to the sample stage.

The  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> film thickness was monitored using in situ spectroscopic ellipsometry during electron exposure. The etching of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> is tunable from 1-50 Å/min by varying the stage voltage from 0 to +40 V, respectively. No etching was monitored from electron exposures without the HCl RBG. Negligible etching was observed without a positive sample stage. The following mechanism can explain these results: (1) The primary electrons at ~100 eV can generate secondary electrons from the substrate. (2) The lower energy secondary electrons can attach to the HCl gas in the reactor. (3) The electron attachment then dissociates HCl into H + Cl<sup>-</sup> through dissociative electron attachment ionization. (4) The Cl<sup>-</sup> negative ions are attracted to the sample by the positive sample stage voltage. (5) The incoming Cl<sup>-</sup> flux leads to an enhancement in etch rate resulting from the formation of volatile chloride species.

The  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> etching was reproducible and only weakly dependent on the primary electron energy from 100-150 eV. The electron current going to ground through the sample also increased with positive sample voltages as expected if the secondary electrons are pulled back to the sample. Surface morphology of the  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> was also investigated after the electron enhanced etching. The RMS roughness decreased after etching. The RMS roughness decreased from 1.88 nm to 1.58 nm after the etching process removed 10 nm at +10 V stage voltage. In contrast, the surface roughness did not change after only electron exposures in the absence of HCl RBG.

## Vacancy Interactions in Two-Dimensional Materials

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**Should be considered for poster awards: Yes**

Point defects in two-dimensional (2D) materials like hexagonal boron nitride (hBN) and MXene can drastically change mechanical, electronic, and optical properties. Surface vacancies specifically affect the electrocatalytic performance of the material. Understanding the interactions between vacancies provides insight into their distribution and transport properties. Here we have developed molecular statics simulations that can approximate elastic power law scaling in various 2D materials. Our simulations show that pure 2D materials like hBN demonstrate agreement with theory while multiple atomic layer MXenes show more complex, thickness-dependent scaling behaviors. These scaling laws inform vacancy separation distributions that assist in design on 2D composites and catalytic applications.

## **Enhancing Drug Delivery Targeting and Efficiency: Controlled Delivery with Specific Biopolymer Coated Mesoporous Silica Nanoparticles**

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### **Should be considered for poster awards: Yes**

Traditional drug delivery methods are unable to alleviate challenges associated with the administration of medicine, which include non-target site exposure, adverse effects, environmental impact, and unnecessary cost. In addition to continual drug development, it is equally or more important to consider new methods to use traditional drugs with higher efficiency. Mesoporous silica nanoparticles provide an alluring avenue towards a stimulus specific biomolecule and drug delivery system due to their high surface area (over 1,000 m<sup>2</sup>/g), biocompatibility, and chemical tailor ability. The well-defined pores of MSN materials can host and actively release drug molecules in a controlled manner, reducing non-target site exposure and adverse effects while improving patient compliance and overall treatment effectiveness. To achieve this, various materials have been explored as endcaps to trap payloads within the pores of MSN until reaching a specific stimulus that releases the therapeutic. The biological compatibility and relevance of the biopolymer amylose makes it an ideal candidate for pore coverage. Amylose nanoparticles have been pursued in literature for topical drug delivery and wound dressing. Few methodologies, however, report the formation of biopolymer coatings around porous nanoparticles for internal targeted drug delivery. The physiologically abundant enzyme amylase would degrade the amylose coat and initiate drug delivery appropriate for cases of dysphagia and pancreatitis. Herein we report initial findings and characterizations of an MCM-41 drug delivery system capable of uptake and sustained release of drug surrogate molecules mediated by concentration gradient and pH dependent electrostatics. Amylose displayed suitable surface interactions with bare MCM-41, yielding sufficient pore coverage. A 90% dimethyl sulfoxide solution (DMSO) with PBS was determined to be sufficient for amylose coating of MCM-41 due to amylose solubility in DMSO. Pore volume and pore size distribution of synthesized MCM-41 was determined by nitrogen adsorption. Thermogravimetric analysis was conducted on bare MCM-41, MCM-41 loaded with drug surrogate molecules, and amylose-coated MCM-41 loaded with drug surrogate molecules to calculate pore volume to surface area ratio. Further testing to identify the drug release rate of the amylose-coated MCM-41 in the targeted drug delivery system will be conducted.

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## An Atomic Scale Investigation of Short and Long-Range Order in a CrMnFeCoNi Alloy

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### Should be considered for poster awards: Yes

High entropy materials are a family of materials that were originally studied for their superior mechanical and physical properties. Due to the nature of HEAs necessitating multiple elements, it's easy to change the elemental configurations in order to tune the desired mechanical properties. In more recent studies, HEAs have been found to have many applications in electrocatalysis for energy conversion reactions. The binding energy is dependent on the binding atom and it's neighboring atoms, where in HEAs the energy of binding sites is varied due to the mixing of many elements. It's important to study the surface of HEAs and their atomic elemental distributions to help us understand how the electrocatalytic performance is affected by the structural diversity of the surface. In this work, we use scanning tunneling microscopy (STM) to study the surface of a nearly equimolar CrMnFeCoNi alloy at the atomic scale. We demonstrate a new way to directly study the chemical short-range order (CSRO) at the atomic scale in a HEA system, and also observe unexpected long-range ordering. We report the Warren-Cowley correlation of elements from the first nearest up to the fourth nearest neighbor atomic sites. Using STM, we also demonstrate a method of probabilistically distinguishing elements in highly mixed or disordered systems.

## Heteroepitaxial Growth of ZnTiN<sub>2</sub> on GaN for Optimization of Optoelectronic Properties

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**Should be considered for poster awards:** No

The n-type semiconductor, ZnTiN<sub>2</sub>, has been proposed as a potential photoabsorber in devices for CO<sub>2</sub> reduction. Previous studies of this material focused on the characterization of its properties and optimization of its synthesis. These studies revealed that ZnTiN<sub>2</sub> films form passivating oxide layers under conditions relevant for CO<sub>2</sub>R and that the crystalline quality can be improved both by depositing on sapphire substrates at elevated temperatures and by the addition of ~10 cation % Sn. The study proposed here will build off this work to further characterize the optoelectronic properties of ZnTiN<sub>2</sub> films that are heteroepitaxially grown on GaN substrates. The films in this study have been deposited by reactive RF co-sputtering at elevated temperatures onto p-type, insulating, and n-type GaN substrates, and the properties of these films will be explored via capacitance-voltage measurements, hall measurements, and photoelectrochemical experiments, respectively. Characterization of ZnTiN<sub>2</sub> via multiple complementary techniques will lead to fundamental insight into the structure-property relationship of this material. Future efforts will focus on further optimizing the synthesis of ZnTiN<sub>2</sub> to reduce dopant density to improve its efficiency for PEC applications and on studying the effect of growing on different facets of sapphire on the polarity of ZnTiN<sub>2</sub>.

## Thermal Atomic Layer Etching of ZrO<sub>2</sub> Using HF and TiCl<sub>4</sub>

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### Should be considered for poster awards: Yes

Thermal ALE can be accomplished using sequential surface modification and volatile release reactions. Thermal ALE of high dielectric constant materials such as ZrO<sub>2</sub> and HfO<sub>2</sub> has been demonstrated using sequential, self-limiting fluorination and ligand-exchange reactions. A variety of fluorination reactants have been used such as HF, SF<sub>4</sub> and XeF<sub>2</sub>. The ligand-exchange reactants include TiCl<sub>4</sub>, Sn(acac)<sub>2</sub>, SiCl<sub>4</sub> and AlCl(CH<sub>3</sub>)<sub>2</sub>. However, there have been few studies of the effect of processing parameters on the etch rate. Most of the studies have only been conducted at one temperature or a limited range of temperatures. In this project, the etch rate of ZrO<sub>2</sub> ALE is being evaluated as a function of various processing parameters such as reactant exposure times, temperature and reactants pressures.

This study demonstrated the thermal ALE of ZrO<sub>2</sub> thin films using sequential, self-limiting thermal reactions with HF and TiCl<sub>4</sub> as the reactants. The initial ZrO<sub>2</sub> films were grown by atomic layer deposition (ALD) using tetrakis(diethylamino) Zirconium and H<sub>2</sub>O. The thermal ZrO<sub>2</sub> ALE processes under different process parameters were then studied using various techniques including quartz crystal microbalance (QCM) and quadrupole mass spectrometry (QMS).

In situ QCM experiments monitored ZrO<sub>2</sub> ALE with HF pressure from 0.1 Torr to 0.9 Torr with fixed TiCl<sub>4</sub> pressure and TiCl<sub>4</sub> pressure from 0.2 Torr to 2 Torr with fixed HF pressure, respectively. The higher HF and TiCl<sub>4</sub> pressure led to higher ZrO<sub>2</sub> etch rates. At HF pressure of 0.6 Torr and TiCl<sub>4</sub> of 1.2 Torr, the ZrO<sub>2</sub> thermal ALE reactions were saturated at 250°C. The QCM studies also showed that the sequential HF and TMA reactions were self-limiting versus reactant exposures. The ZrO<sub>2</sub> etching rates were increasing with higher etching temperatures. At higher precursors pressure, the QCM analysis measured mass change per cycle (MCPC) values that varied from -49.4 ng/(cm<sup>2</sup> cycle) at 200 °C to -118.6 ng/(cm<sup>2</sup> cycle) at 300 °C. These MCPCs correspond to ZrO<sub>2</sub> etch rates from 0.87 Å/cycle at 200 °C to 2.09 Å/cycle at 300 °C.

QMS analysis revealed the volatile etching products during the sequential HF and TiCl<sub>4</sub> exposures on ZrO<sub>2</sub> at 200, 250 and 300 °C. Etch products were observed at all three temperatures with the signal intensity increasing as the temperature increases. H<sub>2</sub>O was monitored during HF exposures confirming that the HF has fluorinated the ZrO<sub>2</sub> surface. ZrCl<sub>4</sub> as the etch product and TiFCl<sub>3</sub> as the ligand-exchange products were observed during TiCl<sub>4</sub> exposures confirming the successful ligand-exchange reaction between ZrF<sub>4</sub> and TiCl<sub>4</sub>.



## Custom Fluidized Bed Reactor for Particle Atomic Layer Deposition on Lithium-Ion Battery Cathode Active Materials

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**Should be considered for poster awards: Yes**

The first fluidized bed reactor for atomic layer deposition (ALD) on particles was developed almost two decades ago, which helped the ALD technology expand beyond the semiconductor industry to catalysis and energy storage. In particular, particle ALD can be applied to energy materials like nickel-rich cathode active materials like  $\text{LiNi}_x\text{Mn}_y\text{Co}_{1-x-y}\text{O}_2$  (NMC) to stabilize the surface and improve electrochemical performance for Li-ion battery applications. With sufficient cycles, the ALD process deposits conformal, pin-hole free films with Angstrom-level precision. However, nickel-rich NMC such as  $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$  (NMC811) is an air-sensitive material that requires handling under inert conditions to prevent growth of surface contaminants like hydroxides and carbonates. Here, we show a fluidized bed reactor design that allows inert (un)loading of material and real-time quantification of vapor species evolved from the ALD reactions. NMC811 was coated using the trimethylaluminum (TMA)/water chemistry. We investigated the effect of ALD temperature, number of ALD cycles, and termination chemistry on powder and electrochemical properties using a variety of techniques including inductively coupled plasma optical emission spectroscopy (ICP-OES), Brunauer-Emmett-Teller (BET) analysis, and electrochemical cycling. Our present work showcases a fluidized bed reactor capable of performing ALD on air-sensitive particles, which can help inform the design of future fluidized bed reactors.

## Identifying Suitable Front Contacts for Cd(Se, Te) Solar Cells on Space-Qualified Cover Glass

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**Should be considered for poster awards:** Yes

To employ solar cells in space, achieving high specific power (W/kg) and radiation hardness is crucial. CdTe thin-film solar cells are expected to demonstrate the capability of achieving high specific power and radiation hardness comparable to Si and III-V solar technologies, which currently dominate in space applications. Although CdS/CdTe solar cells have been studied extensively for performance degradation, and somewhat for radiation tolerance, the more modern, higher efficiency architecture based on Cd(Se, Te) (CST) remains relatively unexplored for space application. The maximum efficiency achieved by CdTe-based solar cells under standard terrestrial test conditions is 23.1% at the laboratory scale. However, for terrestrial applications, CdTe is generally deposited on commercially available fluorine-doped tin oxide (FTO)-coated ~3 mm thick glass substrates. Because ultra-thin and lightweight glass substrates do not come with a transparent conducting oxide (TCO) layer, the TCO and emitter choice becomes crucial.

Here, we report the fabrication of CST solar cells, based on multi-source evaporation, on space-qualified cover glass, with a matrix of different front TCOs and emitters to determine the optimum working combination for high-efficiency superstrate-configured CST solar cells on thin glass substrates. The aim is to monitor the effects on UV transmission, while balancing it with the sheet resistance, determine their stability to high temperature and reactive ambients in the processing, and then calculate figure of merit to determine the quality of TCOs. The device structure will then be optimized to achieve maximum device performance under AM0 atmospheric conditions with minimal losses compared to that under the AM1.5G condition.

## Tuning the Sintering and Chemical State of Ni via the Bimetallic Particle Growth over CeO<sub>2</sub>(111) Thin Films: Design of Thermally Stable Bimetallic Catalysts

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### Should be considered for poster awards: Yes

Ceria-supported Ni and Co nanoparticles have been of great interest in heterogeneous catalysis as they catalyze many reactions including dry reforming of methane (DRM), steam reforming of ethanol, and Fischer-Tropsch synthesis. Ni and Co supported over ceria exhibit promising reactivity owing to unique redox properties of ceria as well as the strong metal-support interaction. We have carried out the detailed study of nucleation, growth, and sintering of monometallic Ni and Co particles over well-defined CeO<sub>2</sub>(111) thin films under ultrahigh vacuum conditions using scanning tunneling microscopy (STM) and x-ray photoelectron spectroscopy (XPS). Both Ni and Co with metal coverages of 0.3 ML can form small particles at room temperatures and are well dispersed over the CeO<sub>2</sub>(111) surface. Compared to Ni, Co particles show a slightly smaller particle height indicating three-dimensional (3D) growth of Ni from low coverage. XPS study indicated the presence of Co<sup>2+</sup> species up until 0.3 ML Co coverage. However, for Ni, both Ni<sup>2+</sup> and Ni<sup>0</sup> species were present as major species with higher concentration of Ni<sup>0</sup>. This is consistent with density functional theory results as the adsorption energy of Co adatom is slightly higher than Ni indicating slightly higher metal-support interaction for Co. Furthermore, the minimum-energy configurations for a series of small Ni and Co particles up to ca. 20 atoms indicated a strong tendency for Ni to form particles than Co. We also investigated the growth, thermal stability, and chemical state of NiCo bimetallic particles as Ni-based bimetallic catalysts could exhibit interesting chemical behavior compared to Ni counterparts due to the synergistic effects between these two metals. Bimetallic NiCo particles can be prepared by depositing Co over the Ni/CeO<sub>2</sub>(111) surface or vice versa. Deposition of Co over the Ni/CeO<sub>2</sub>(111) surface induced the reduction of Ni<sup>2+</sup> species to Ni<sup>0</sup> indicating the formation of Ni-Co interface sites. Despite the deposition order, Ni<sup>0</sup> was found to be the predominant species for NiCo bimetallic particles. Annealing the monometallic Ni/CeO<sub>2</sub>(111) surface to 700 K and above causes Ni particles to grow extensively in size indicating pronounced sintering of Ni. Sintering of Ni at higher temperatures is one of the major reasons behind catalytic deactivation. However, the addition of Co can better inhibit the sintering of Ni particles. Our fundamental understanding of bimetallic NiCo particles supported on ceria can help on providing insightful ideas in the potential design of Ni-based catalysts with improved thermal stability leading to less deactivation in DRM.

## **Weakly and Strongly Adsorbed H<sub>2</sub>O Layers on Hydroxylated SiO<sub>2</sub> Surfaces: Dependence on H<sub>2</sub>O Pressure at Various Temperatures**

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**Should be considered for poster awards: Yes**

While H<sub>2</sub>O adsorption on SiO<sub>2</sub> surfaces has been studied, questions about the nature of the H<sub>2</sub>O layer remain. In this study, in situ spectroscopic ellipsometry (SE) on a warm-wall vacuum chamber with a temperature-controlled sample stage was used to examine the H<sub>2</sub>O layer thickness on flat hydroxylated SiO<sub>2</sub> surfaces. The H<sub>2</sub>O layer thickness was measured versus pressure at various temperatures. The H<sub>2</sub>O pressures used were varied. The H<sub>2</sub>O layer thickness versus relative humidity was consistent with general expectations from the BET adsorption isotherm model.

The SE measurements demonstrated that there were two distinct H<sub>2</sub>O layers: a weakly adsorbed layer and a strongly adsorbed layer. The weakly adsorbed layer could be added or removed by increasing or removing the water pressure. The strongly adsorbed layer could only be desorbed by heating the sample stage to 120°C. Complimentary FTIR studies corroborate these findings.

Upon repeating H<sub>2</sub>O exposures, the strongly adsorbed layer reached an approximate plateau at ~1 Å at various temperatures. In contrast, the weakly adsorbed layer continued to become thicker at larger pressures. For example, the weakly adsorbed layer thickness was 7 Å at 92% relative humidity at 30.4°C (30 Torr). These studies confirm the existence of a strongly adsorbed vicinal H<sub>2</sub>O layer and a weakly adsorbed H<sub>2</sub>O layer explained by the BET model on hydroxylated SiO<sub>2</sub>.

## Vacuum Systems for Quantum Sensing Experiments @ FRIB

Abigail Gillespie and Caitlyn Stone-Whitehead

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### **Should be considered for poster awards: Yes**

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Instructions for abstract submission: Click on the “Submit Abstract” button on the website to bring up an email template. Please attach your abstract in Microsoft Word format. Be sure to include the presenting author’s contact email address and institution in this email. We look forward to seeing you in September!

The new Superconducting Array for Low-Energy Radiation (SALER) experiment at FRIB aims to directly embed short-lived isotopes in superconducting tunnel junction (STJ) sensors to measure nuclear recoil energies from weak decay as a search for BSM physics. Like the Beryllium Electron capture in Superconducting Tunnel junctions (BeEST) experiment, a calibration laser (262nm) is used to achieve sub-eV resolution in spectra captured by STJ sensors. The SALER experiment brings forth new challenges due to the experiment being operated and calibrated while being implanted with short-lived isotopes. Additionally, calibration methods with an x-ray source are being investigated for SALER. In order to provide feedthrough mechanisms to sub-Kelvin temperatures for the RIB, laser and x-ray source; it is necessary to design custom vacuum parts and optics. The vacuum system ensures that interfaces are hermetic and allows for clean transitioning between various sources (RIB, laser, x-ray) without breaking vacuum. Once inside the fridge, the sources must be able to reach the STJs without allowing for IR radiation through cold stages. This led to the design of custom LiF/C optics for allowing the passing of rare isotopes as well as light with wavelengths shorter than 300nm. This poster will discuss the design and fabrication of the full cryogenic system for SALER @ FRIB.

## Understand SiN<sub>x</sub> Etch with CH<sub>2</sub>F<sub>2</sub>/Ar Plasma and SF<sub>6</sub>/H<sub>2</sub> Plasma

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**Should be considered for poster awards:** Yes

During the etch of SiO<sub>2</sub> and SiN<sub>x</sub> in a fluorocarbon plasma, the selective etch is believed to be realized by the accumulation of a fluorine-deficient graphitic carbon layer on the SiN<sub>x</sub> surface. While the hydrofluorocarbon gases are also widely used in the selective etch of SiO<sub>2</sub> to SiN<sub>x</sub>, the mechanism of SiN<sub>x</sub> retardation is still unclear. It has been hypothesized that in addition to the graphitic carbon layer, another blocking layer—ammonium fluorosilicate (AFS)—may form on the SiN<sub>x</sub> surface. These layers can retard or even fully stop the etching of SiN<sub>x</sub>. The formation of an ammonium salt layer has been reported in some atomic layer etching and reactive ion etching (RIE) processes. However, the mechanism of formation of AFS, the role of AFS in SiN<sub>x</sub> etching, and the stability under directional ion bombardment are not fully understood.

In this work, we investigate the effect of bias voltage on the formation of AFS during RIE of plasma-deposited SiN<sub>x</sub> in a CH<sub>2</sub>F<sub>2</sub>/Ar plasma. Using *in situ* attenuated total reflection Fourier-transform infrared spectroscopy (ATR-FTIR) spectroscopy, we monitor the surface bonding changes of SiN<sub>x</sub> film during RIE at bias voltages over the range of 100–250 V. As expected, the etch rate is lower at a lower bias voltage, and the etch stops with rapid accumulation of AFS layer (NH<sub>4</sub> bending mode at ~1430 cm<sup>-1</sup> and NH<sub>4</sub> stretching mode at ~3000–3300 cm<sup>-1</sup>) and graphitic hydrofluorocarbon layer (C=C stretching mode at ~1600 cm<sup>-1</sup>). To further identify the formation mechanism and role of AFS, we also study the SiN<sub>x</sub> etch in a SF<sub>6</sub>/H<sub>2</sub> plasma at bias voltages ranging from 100 to 250 V. Interestingly, SiN<sub>x</sub> is linearly etched in the SF<sub>6</sub>/H<sub>2</sub> plasma, accompanied by the rapid formation of AFS on SiN<sub>x</sub> surface. Comparisons between SiN<sub>x</sub> etch in CH<sub>2</sub>F<sub>2</sub> plasma and SF<sub>6</sub>/H<sub>2</sub> plasma leads to the following conclusions: 1) HF and etch products are the key for AFS formation; 2) under ion bombardment, accumulation of AFS does not lead to etch-stop, and graphitic carbon is required for etch-stop to occur under ion bombardment.