Poster 1

Multi scale chiral response in switchable local moment molecules.

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Should be considered for poster awards: Yes.

We report on multi scale chiral response in $[Fe(NH_2trz)_3](L\text{-}CSA)_2$ (NH_2trz = 4-amino-1,2,4-triazole, L-CSA = L-camphorsulfonate), which is an Fe(II) spin crossover molecular complex. We report circular dichroism in the visible range which switches as a function of the spin state, confirming previously reported results. Significant differences in the chiral response between the L and D chiral isomer are observed.

Using X-ray absorption spectroscopy, we further reveal a chiral response also exists at the X-ray wavelength, specifically at the Fe L_3 resonance edge. This chiral response is nearly identical in both isomers. However, like the circular dichroism at the visible range, this also switches as a function of the spin state. We attribute this chiral response to the distorted octahedral coordination of the ligand with the metal center. The switching of the chiral behavior is attributed to change in dipole moment across the spin state transition. This is revealed by temperature dependent X-ray photoemission spectroscopy at N 1s core level and capacitance measurements.

Poster 2

Carbonation of Steelmaking Slags using Supercritical Carbon Dioxide for Process Optimization, Chemical Stability, and Heavy Metal Immobilization

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Should be considered for poster awards: Yes

The steel industry produces 190–290 million tons of steelmaking slag annually and contributes about 7 pct of global anthropogenic CO_2 emissions. While steelmaking slag is often reused in aggregate applications, the presence of alkaline calcium and magnesium phases can cause a phenomenon known as the free lime volume instability, where these alkaline phases expand upon exposure to moisture, limiting structural use. Slag fines not suitable for aggregate applications are underutilized and are stockpiled in perpetuity or landfilled. This reactivity, though problematic mechanically, enables CO_2 carbonation. Crushed and mixed with water, reacted particles develop a binding and insulating carbonate matrix that mitigates volume instability and immobilizes heavy metals, expanding reuse potential and reducing environmental risks. The carbonate matrix binds the powdered material together, opening a reuse pathway for slag fines as a CO_2 negative cement alternative. This study optimizes supercritical CO_2 pressure and temperature to accelerate reaction kinetics and maximize CO_2 uptake in three distinct compositions of steelmaking slag from electric arc furnace and ladle metallurgy processes. CO_2 uptake is measured with CS344 LECO and TG-DSC methods. Heavy metal mobility is assessed using EPA Method 1311 to evaluate the effect of carbonation. Preliminary testing shows carbonation exceeding 200 grams of CO_2 per kilogram of slag, approaching 50% of the theoretical maximum while mitigating the leaching of heavy metals.

Poster 3

Controlled Electron Enhanced Etching of GaN and AlN using HCl and BCl_3 as Reactive Background Gases

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Should be considered for poster awards: Yes

A controlled electron enhanced etching process for the gate recessed etch of GaN and AlN in high electron mobility transistors (HEMTs) has been developed by pulsing the reactive background gas (RBG) with a continuous electron current incident on the sample. This process used low energy electrons (100 eV) from a hollow cathode plasma source (HC-PES). In addition, HCl or BCl_3 were employed as the RBGs. In situ spectroscopic ellipsometry (iSE) was used to measure the etch rates. GaN was readily etched linearly using an HCl RBG. This process also showed no significant temperature dependence from 50 to 400°C. A maximum etch rate of 5.12 nm/min was observed and the etch rate could be controlled by the sample stage voltage. AlN was also linearly etched by a combination of HCl and a small amount of BCl_3 as RBGs. The AlN etch rate displayed only minor temperature dependence from 50 to 400°C. This temperature dependence was surprising because $AlCl_3$ is less volatile than $GaCl_3$. We had thought that the low volatility of $AlCl_3$ explained our earlier results where AlN was not etched using only HCl RBG. We now believe that oxygen in the reactor readily grows an oxide film on AlN and prevents the etching by HCl RBG. However, BCl_3 can convert Al_2O_3 to B_2O_3. The B_2O_3 is further volatilized by BCl_3 as trichloroboroxine ($B_3O_3Cl_3$). Without the Al_2O_3 layer blocking the AlN etching, a maximum etch rate of 1.06 nm/min was observed for AlN etching.

Poster 4

Thermal Atomic Layer Etching of the Semiconductor Oxide Channel Materials by Sequential Surface Modification and Volatile Release Reactions

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Should be considered for poster awards: Yes

Indium gallium oxide (IGO) and Indium Gallium Zinc Oxide (IGZO) are transparent conductive oxides that can be used as channel materials in oxide semiconductor based thin-film transistors (TFTs). These TFTs have high carrier mobility, low leakage current and wider bandgap compared to amorphous silicon. These characteristics are highly desirable for IGO applications in the display industry. During fabrication processes, etching these channel materials to a very precise and controlled thickness is important. We are developing thermal atomic layer etching (ALE) by employing sequential exposures of boron trichloride (BCl_3) and hydrogen fluoride (HF).

The thermal ALE occurs via a sequence of self-limiting surface reactions that leads to formation of volatile products. The first fluorination reaction with BCl_3 results in formation of volatile chlorides ($InCl_3$, $GaCl_3$ and $ZnCl_2$) along with conversion of surface to boron oxide. This reaction is followed by spontaneous etch of boron oxide layer with hydrogen fluoride as shown in Figure 1. The *in situ* spectroscopic ellipsometry (SE) measurements reveal that the IGZO film is etched at a rate of 4.0 Å/cycle at 250 °C.

The etch rates saturate as a function of doing times for BCl_3 and HF which confirms the self-limiting nature of these reactions, thereby ensuring an atomic level control over film thickness. Furthermore, it has been observed that etch rate initially increases with temperature but starts to decline after reaching a maximum (at around 250 °C). The composition and roughness of the films stay constant as the films are etched.

Poster 5

Oxidation State Selective Removal of Molybdenum and Tungsten Oxide Using Chlorination and Deoxychlorination Surface Reactions

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Should be considered for poster awards: Yes

Spontaneous etching of molybdenum and tungsten oxides was done at 200°C using repeated exposures of either thionyl chloride ($SOCl_2$) or sulfuryl chloride (SO_2Cl_2) to form volatile molybdenum and tungsten oxychlorides. Quadrupole mass spectrometry studies of these spontaneous etch processes revealed that $SOCl_2$ and SO_2Cl_2 selectively removed different oxidation states of Mo and W, governed by the chemical mechanism of chlorination. $SOCl_2$ was observed to spontaneously etch the +6 oxides of molybdenum and tungsten, whereas SO_2Cl_2 etched only the +4 oxides. Each precursor did not spontaneously etch the other oxidation state.

The observed volatile products using QMS were MoO_2Cl_2 for Mo, and $WOCl_4$ and WO_2Cl_2 for W. All volatile etch products were in the +6 oxidation state. The mechanism for etch observed using $SOCl_2$ is deoxychlorination, in which oxygen is removed from the substrate in exchange for two chlorines, maintaining the oxidation state of each chemical species. Given that the volatile products exist with a Mo (VI) or W (VI) metal center, deoxychlorination is favorable to spontaneously etch molybdenum and tungsten (VI) oxides. Conversely, SO_2Cl_2 chlorinates by the addition of Cl_2, or by thermal decomposition to form Cl_2. Therefore, to reach the MO_2Cl_2 or $MOCl_4$ products (M = Mo, W), addition of chlorine to molybdenum or tungsten (IV) oxide is more favorable, and chlorination of MoO_3 or MoO_2 is very difficult. As such, $SOCl_2$ selectively etches MoO_3 and WO_3, while SO_2Cl_2 selectively etches MoO_2 and WO_2.

In situ Auger electron spectroscopy (AES) was done during spontaneous removal of native oxides from Mo and W thin films to monitor oxygen content after numerous $SOCl_2$ doses. $SOCl_2$ was selected over SO_2Cl_2, as MoO_3 will form from the oxidation of Mo and MoO_2 in air, and WO_2 disproportionates to form WO_3 and W, so we expect a primarily +6 native oxide. In situ AES showed the selective cleaning of the native oxide from the surface of the Mo and W films using $SOCl_2$.

Poster 6

The electronic band structure and conduction band formation of $HfSe_3$

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Should be considered for poster awards: Yes

Abstract: The anisotropic structure of Group 4 transition metal trichalcogenides (TMTCs) have gained significant interest due to their possible application in optoelectronics. In this work, the band structure of quasi one-dimensional $HfSe_3$ was investigated with nano-spot angle resolved photoemission spectroscopy (nanoARPES). $HfSe_3$ has a rectangular surface Brillouin zone where the effective hole mass along the chain direction is -0.27 m_e, which is smaller compared to the effective hole mass along the direction perpendicular to the chains, -1.17 m_e. The effective hole mass extracted from the band structure along different high symmetry directions is compared with that of TiS_3 and ZrS_3 from prior studies. [1] X-ray absorption spectroscopy (XAS) has been used to characterize the unoccupied states of $HfSe_3$ and will be compared to the XAS spectra of HfS_3 [2] and TiS_3 and ZrS_3. [3] The metal chalcogenide hybridization for Hf differs from the Ti and Zr trichalcogenides. This may be due to the increase in effective atomic numbers leading to strong spin-orbit interaction of Hf based TMTCs.

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Poster 7

SiO2 Etching by HF in a Liquid-Like H2O Layer in a Vacuum Environment

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Should be considered for poster awards: Yes!

Adsorbed H_2O layers may be employed for etching by a liquid layer in a vacuum environment. Liquid-like H_2O layers can form at H_2O pressures around 10 Torr and temperatures around room temperature. Etchants may then be dissolved in the liquid-like H_2O layers. These conditions allow many etching processes that are conducted in wet aqueous solutions to be extended to liquid-like H_2O layers in vacuum.

This study focused on SiO_2 etching by HF in a liquid-like H_2O layer in vacuum. The experiments were conducted in a warm-wall vacuum chamber designed with a sample stage that allowed for H_2O liquid layer formation only on the cooled stage. The thickness of SiO_2 films was measured using *in situ* spectroscopic ellipsometry as the SiO_2 films were exposed to various H_2O and HF pressures at different substrate temperatures. Studies were conducted at H_2O pressures from 5 to 30 Torr, HF pressures from 2 to 6 Torr and temperatures from 18.1 to 30.4 °C. The SiO_2 films etched readily under these conditions.

The SiO_2 etch rate increased versus HF pressure and versus H_2O pressure. The etch rates varied from <1 Å/Exposure to >3,000 Å/Exposure. The dramatic variation in SiO_2 etch rates suggests that the thickness and composition of the liquid-like layer are changing rapidly with HF and H2O pressure.

The SiO_2 etch rate was also inversely dependent on sample temperature. Experiments were conducted at temperatures of 30.4°C, 29.3°C, 27.2°C, and 18.1°C with a H_2O pressure of 10 Torr, HF pressure of 3.5 Torr, and exposure time of 5 s. These studies yielded SiO_2 etch rates of ~10 Å/exposure, ~23 Å/exposure, ~89 Å/exposure, and ~212 Å/exposure respectively. The large increase of the SiO_2 etch rate is attributed to the thicker liquid-like layer at lower temperatures. The thicker liquid-like layer may be able to more easily solvate the HF reactants and SiO_2 etch products.

Poster 8

Utilizing Pulsed Laser Deposition to Grow Stoichiometric Titanium-doped Ceria Thin Films

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

Pulsed laser deposition (PLD) is a highly controlled and versatile technique for the growth of stoichiometric and structurally well-defined thin films. By employing a high-power pulsed laser to ablate a target material, PLD enables precise control over film composition and thickness. Ceria ($CeO_{2-\delta}$, $0<\delta<0.5$) has attracted increasing attention for catalytic use in various applications, especially in CO_2 conversion, due to its reversible Ce^{3+}/Ce^{4+} redox pairs and tailorable oxygen vacancy concentrations. The incorporation of metal dopants in ceria can cause modifications in the lattice structures and electronic properties of the material, which facilitate the reducibility and enhance oxygen mobility at lower temperatures. Additionally, doped ceria has been reported to exhibit improved thermal stability, further extending its applicability in high-temperature catalytic environments.

In this study, titanium-doped ceria ($Ce_{1-x}Ti_xO_{2-\delta}$, $0<x<0.5$) was synthesized on Si(111) substrates using the PLD technique with controlled key deposition parameters. X-ray diffraction (XRD) and energy-dispersive X-ray spectroscopy (EDS) analyses revealed that the resulting thin films are polycrystalline and stoichiometric with respect to the intended Ti-dopant concentrations. Surface characterization by atomic force microscopy (AFM) and scanning electron microscopy (SEM) imaging showed flat surface morphologies with roughness of about 150 ± 20 pm, consisting of nanostructures with a width average of 30 ± 3 nm. Cross-sectional images using SEM showed the thickness of the thin film corresponding to the specific PLD growth conditions. X-ray photoelectron spectroscopy (XPS) analyses indicated a high degree of reduction in the PLD-grown ceria thin films. O_2 was further introduced into the PLD chamber throughout the thin film growth, which has successfully yielded more oxidized ceria thin films and thus allowed for the study of the behavior with respect to the degree of film reduction in reactions including hydrogen evolution reaction (HER).

Poster 9

HF Plasma Interactions with Polyurea Films deposited by Molecular Layer Deposition

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Should be considered for poster awards: Yes

As the semiconductor industry is transitioning from fluorocarbon (FC)-based plasma chemistries to carbon-free reactive plasmas, new techniques are needed to passivate the sidewalls of high aspect-ratio (HAR) features during etch. Molecular layer deposition (MLD) is a vapor-phase process of alternating surface reactions which can be used to grow organic and hybrid organic-inorganic films. MLD films have several potential applications in semiconductor processing, including as a protective layer during plasma etching. However, MLD films are known to be highly porous and dendritic, as opposed to the graphitic polymer films which can form during FC plasma exposure and act as an etch-stop at sufficiently low ion energies.

In this work, toluene diisocyanate (TDIC) and ethylene diamine (ED) were used as precursors for MLD of polyurea, which was grown on top of either SiO_2 or SiN_x. The films were then exposed to a HF plasma to evaluate their interactions with reactive plasma. During initial HF plasma exposure, only the MLD film was etched, while the underlying SiO_2/SiN_x was protected. Only after the polyurea was completely consumed by reaction was the underlying material etched. SiO_2 and SiN_x showed similar etch delays with a constant polyurea film thickness, and longer SiO_2/SiN_x etch delays were observed when a thicker polyurea film was deposited. Through *in situ* fourier-transform infrared spectroscopy measurements, we were also able to monitor changes in film composition during plasma exposure. Fluorination of the MLD polymer film was observed prior to its removal, which suggests that the polyurea is removed as volatile hydrofluorocarbon fragments. Additionally, we deposited MLD films on HAR holes to evaluate the film conformality and sidewall passivation. While the analogous process of atomic layer deposition requires very high doses to supply necessary diffusive flow into the feature, we found that MLD of polyurea was surprisingly conformal using the saturation doses for a flat surface. Further, the presence of the polyurea was found to protect the sidewalls from being etched, even with just a few nm of deposition. This work presents a new technique for sidewall passivation during plasma etch.

Poster 10

Understanding Etching Mechanism of SiN_x in HF Plasma and the Role of Ammonium Fluorosilicate Layer

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Should be considered for poster awards: Yes

During etching, ammonium fluorosilicate (AFS) forms on SiN_x in both traditional hydrofluorocarbon and HF-based plasmas. The accumulation of this salt on sidewalls can significantly influence etch behavior and profile. Although AFS formation during SiN_x etching has been known for several decades, the underlying mechanism for its formation and the role of AFS during SiN_x etching in a HF plasma remains unclear, especially under ion bombardment over a wide range of energies.

In this study, we have used *in situ* attenuated total reflection Fourier-transform infrared (ATR-FTIR) spectroscopy to study the changes in the chemical bonding on the SiN_x surface during reactive ion etching. We investigated the effect of substrate bias on AFS growth, decomposition, and SiN_x etching in HF plasma. As expected, etch rate is lower at lower bias voltage, and it increases at higher bias voltages. AFS (NH_4^+ bending mode at ~1430 cm^{-1} and NH_4^+ stretching mode at ~ 3000–3300 cm^{-1}) continuously forms under self-bias conditions and etching is dominated by diffusion of neutrals. However, under applied bias, AFS reaches a steady-state thickness. There was a threshold bias where AFS formation and decomposition start to balance.

Here, two processes occur simultaneously — the formation of AFS and its decomposition under energetic ion bombardment. Therefore, to decouple these simultaneous effects, we first deliberately grew a thick AFS layer and then applied different bias voltages. We found that the presence of a thick AFS layer initially suppressed the etch rate, with the etch process being dominated by the diffusion of neutrals both from the plasma and AFS decomposition. As the bias voltage increased, energetic ions were primarily consumed in sputtering away the AFS layer, progressively thinning it until the process transitioned from a neutral-dominated regime to a reactive-ion–dominated regime.

Character Count: 2332/2700

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Poster 11

Ge Etching by Anhydrous HF Vapor Studied Using Quadrupole Mass Spectrometry

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Should be considered for poster awards: Yes

The fabrication of next-generation gate-all-around (GAA) field effect transistors (FETs) employs stacks of crystalline Si and SiGe layers. Formation of the Si nanosheets in the GAA FETs is accomplished by removing the sacrificial SiGe layers. The etching of these sacrificial SiGe layers requires dry thermal etching. Our previous work has discovered the facile dry spontaneous etching of Si using anhydrous hydrogen fluoride (HF) vapor at temperatures above 150°C. In this work, we explore the dry spontaneous etching of Ge using HF.

These studies of Ge etching utilized quadrupole mass spectrometry (QMS) to identify the volatile etch products. The reactor used high surface area powders and molecular beam techniques to increase the sensitivity of the QMS detection. The sample could also be heated to explore etching at various temperatures under different reactant gas exposures. Temperature-ramped QMS studies identified two main products during exposure of Ge nanopowder to ~1 Torr of HF vapor. (1) GeF_3^+ ion species indicating the formation of GeF_4 was observed at low temperatures <100-150°C. (2) GeF^+ ion species indicating volatile GeF_2 as an etch product was monitored at higher temperatures >200°C. Thermochemistry calculations confirmed the reaction pathways leading to these GeF_4 and GeF_2 reaction products.

The puzzling aspect of these results was the lack of GeF_4 etch products at temperatures >150°C during the temperature ramps. This disappearance of GeF_4 at >150°C was explored by varying the temperature ramp rate, performing isothermal experiments, and running reverse temperature ramp experiments. These experiments suggested that Ge etching terminates itself by the buildup of a non-volatile GeF_2 polymer. However, the GeF_2 polymer can be volatilized at temperatures >200°C.

Experiments were also performed by co-dosing H_2O with HF. Under these co-dosed conditions, GeF_4 formation appeared to be independent of the ramp rate and there was no indication of self-termination by GeF_2 polymer formation. In addition, an increased GeF^+ ion signal indicated the formation of volatile GeF_2 with H_2O co-dosing. Therefore, the introduction of H_2O may counteract the GeF_2 polymer buildup, allowing for a spontaneous etch of Ge at lower temperatures without surface poisoning.

Poster 12

Optical Constants and Thickness of Partially Oxidized Ultrathin Thermally Evaporated Iron Catalyst Films

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Should be considered for poster awards: Yes

Vertically aligned carbon nanotube (VACNT) forest growth is a chemical vapor deposition process that uses a thin-film iron catalyst on an alumina support. The iron catalyst thickness for VACNT growth is typically 1–10 nm, and thickness strongly affects forest morphology. Consequently, the metrology of iron thin films could improve process control of VACNT growth. In this study, we explored the use of spectroscopic ellipsometry (SE) to measure these ultrathin iron films because the technique is rapid, highly sensitive, and non-destructive. SE does have challenges, however, as it is difficult to break the correlation in the analysis between the optical constants and the thickness of ultrathin films. The partial oxidation and the absorptive nature of the iron–iron oxide films add further complexity. We performed a multisample analysis of thermally evaporated iron films with target thicknesses of 1, 2, 4, 7, and 14 nm. To improve sensitivity, we used interference enhancement by incorporating a 350 nm silica film on a silicon substrate under the iron film and alumina support. We used the consecutive-layers approach, collecting SE data and fitting the model for each layer before depositing the next. We found high sensitivity to iron thickness with SE, with repeatable thickness results. We modeled the iron–iron oxide composite film with a Bruggeman effective medium approximation layer. Our SE model fits the data well with a relatively low mean squared error of 24.7. We explored the sensitivity of iron–iron oxide thickness results to errors in the underlying alumina thickness while using the consecutive-layers approach. We found that thickness errors in underlying layers could explain the variance we found when measuring iron thickness in different spots on the same sample.

Poster 13

Corrosion Behavior of Cu-Ni Alloys Produced by Wire Arc Additive Manufacturing

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Should this be considered for poster awards: Yes

Copper nickel alloys such as Cu-30Ni are widely used in marine environments because copper forms a Cu_2O-rich passive film and nickel stabilizes the surface oxides. Persistent challenges with domestic casting have motivated exploration of additive routes, particularly Wire Arc Additive Manufacturing (WAAM). Here we apply post-build heat treatments to relieve residual stress and tune passivity in WAAM Cu-30Ni. WAAM produced a columnar/dendritic microstructure, consistent with expectations for Cu-Ni. These microstructural features were comparable to wrought Cu-30Ni. The corrosion behavior of Cu-30Ni with and without heat treatment was evaluated by potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). The surface chemistry was probed by X-ray photoelectron spectroscopy (XPS). Under specific conditions, heat treatment reduced the corrosion rate, which we correlate to changes in oxide speciation identified by XPS. Long-term EIS further shows that corrosion rates for all specimens decrease with immersion time and converge to similar low values. These preliminary results indicate that WAAM, combined with appropriate post-processing, can deliver Cu-30Ni with seawater corrosion resistance comparable to wrought material.

Poster 14

Molecular Beam Epitaxy Growth of IrO_2 using Plasma-Only Oxidation

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Should be considered for poster awards: Yes

Epitaxial thin films of IrO_2 are researched for application in electrocatalysis, spintronics, and superconductors. Previously, these films have been prepared via molecular beam epitaxy (MBE) using ozone or metal-organic sources in conjunction with oxygen plasma sources to fully oxidize the iridium. In this work, we present for the first time plasma-only oxidation for growth of IrO_2. While the thermodynamics of ozone-assisted IrO_2 growth are well documented, constructing a model for plasma-assisted MBE growth is more challenging due to the variety of species present in the plasma. We use optical emission spectroscopy to determine the relative composition of different reactive species in the oxygen plasma, and construct an Ellingham diagram of the atomic oxygen driven reaction to describe the predicted growth window relative to molecular oxygen. Since Ir is a noble metal, growth of IrO_2 is a good test case to determine whether plasma-only MBE can produce high-quality epitaxial oxide films. We present chemical and structural characterization of optimized (110) IrO_2 films. These findings improve our understanding of plasma-assisted MBE and support broader use of this reactive MBE technique to grow functional oxide films for research in a variety of applications.

Poster 15

Thermal Atomic Layer Etching of Magnesium Oxide Using Hydrochloric Acid and Acetylacetone

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Should be considered for poster awards: Yes

The thermal atomic layer etching (ALE) of magnesium oxide (MgO) was accomplished using sequential exposures of hydrochloric acid (HCl) and acetylacetone (Hacac). MgO is used as a tunneling barrier in magnetic tunneling junctions (MTJs) in magnetoresistive random access memory (MRAM) and spin-transfer torque MRAM (STT-MRAM) devices. MgO has a high-volume resistivity and large bandgap (7.8 eV) that reduces leakage current across the barrier. Having precise control of the tunneling barrier thickness allows manipulation of the MgO performance, including its resistance in MTJs.

The initial MgO film was grown by atomic layer deposition (ALD) using sequential exposures of bis(cyclopentadienyl) magnesium and water. The deposition and etching were monitored *in situ* with a quartz crystal microbalance (QCM) and quadrupole mass spectrometry (QMS). The QCM monitored etching for temperatures ranging from 180°C to 240°C. The sequential exposures of HCl and Hacac resulted in a linear decrease of film thickness versus number of ALE cycles. The measured etch rates were -0.28 Å/cycle at 180°C and increased to -0.56 Å/cycle at 220°C. *In situ* QMS studies also revealed the volatile etching products. The QMS results support the etching mechanism where HCl chlorinates MgO according to $MgO + 2HCl \rightarrow MgCl_2 + H_2O$. Then Hacac reacts with $MgCl_2$ to produce volatile $Mg(acac)_2$ species according to $MgCl_2 + Hacac \rightarrow Mg(acac)_2 + 2HCl$.

Poster 16

X-Ray Photoelectron Spectroscopy Analysis of Degradation in Polymer Electrolyte Membrane Fuel Cell Catalyst Layers

Dylan Kuiken, Jayson Foster, Matthew Coats, Jonathan Braaten, Lei Chang, Christina Johnston, Svitlana Pylypenko

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Should be considered for poster awards: Yes

X-ray Photoelectron Spectroscopy (XPS) is a surface analysis technique that uses the photoelectron effect to characterize and identify a materials elemental composition and chemical state in the top 3-10nm of the material. XPS is a vital tool for research in polymer electrolyte membrane fuel cells (PEMFCs) due to its ability to provide elemental and chemical speciation of the main components of the catalyst layer (CL), including catalyst, support and ionomer. Analysis of the CL is paramount due to the necessity of a highly efficient and long-lasting CL to make PEMFCs economically viable. Within this project, XPS was used to study the effects of degradation on a Pt nanoparticle catalyst supported by high surface area carbon (Pt/C) as a function of different degradation conditions, including temperature, nitrogen flow rate, voltage limit and hold times, as well as relative humidity. This presentation will showcase how XPS can be used to study surface level changes of the CL due to degradation through visual inspection of spectra, elemental peak ratio comparisons, and novel peak fitting approaches. Analysis of the CLs with XPS provides complimentary information to electrochemical testing and electron microscopy characterization. A multi-technique approach is paramount for improving understanding of degradation and enabling further improvements of CLs and PEMFCs performance and long-term durability.

Poster 17

Adhesive Strength of Carbon Nanotubes to Stainless Steel Substrate

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Should be considered for poster awards: Yes

The adhesive strength of carbon nanotubes (CNTs) to the substrate on which they are grown is an important characteristic to know in many applications, particularly in biomedical applications where detached CNTs could pose a potential health risk. In this work, we develop a procedure for testing the adhesive strength of CNT films to a substrate, and present initial results of that procedure for CNTs grown on 316L stainless steel. Testing was conducted for CNTs grown at temperatures ranging from 700-800°C for times ranging from 3-40 minutes. The procedure involves pressing a 2x2mm square of adhesive tape onto a CNT sample up to a standard force using an Instron tensile tester, then raising the tape back up and examining the resulting force data to obtain an adhesive strength. Trends from our initial data include, for a given growth time, an increase in adhesive strength with increasing growth temperature. We also find that, in general, adhesive strength increases with growth time for a given temperature up to 20 minutes, then levels off, though for 700°C and possibly 750°C we find a decrease in adhesive strength after 20 minutes. We propose some possible causes of this decrease, though further testing and electron microscopy will be needed to verify the existence of this phenomenon.

Poster 18

Methodological Approach for XPS Characterization of Nickel and Iron Metal, Oxide, and Hydroxide Systems

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Should be considered for poster awards: Yes

In this study, nickel-based electrodes used in liquid alkaline water electrolysis (LAWE) were analyzed to investigate role of iron contamination effect on surface speciation. Comparative analyses were performed on anodes and cathodes tested under three conditions: no added Fe, Fe added to the anolyte, and Fe added to the catholyte. X-ray photoelectron spectroscopy (XPS) was used as the primary method to investigate surface composition, complemented by Raman spectroscopy and corroborated with results of electrochemical testing.

Despite its potential, XPS analysis of transition metals remains difficult and often underutilized. XPS chemical state analysis of transition metals is inherently challenging due to multiplet splitting, overlapping and shifting binding energies, and mixed chemical speciation. To address these challenges, peak-fitting parameters were developed with rigid constraints to accurately determine material composition. These parameters were compiled from literature and validated using experimental reference materials, with minor adjustments applied to account for pass energy differences. The resulting fitting profiles enabled consistent and reliable surface composition analysis with several important findings for the samples investigated. When iron was introduced into either the anolyte or catholyte of nickel foam electrodes, distinct changes in nickel and iron speciation were observed. Complex Ni $2p_3/_2$ peak fitting demonstrated presence of NiO, NiOOH (Ni^{2+} and Ni^{3+}), and $NiFe_xO_y$ and in most of the samples. Additionally, analysis revealed similar compositions in NiOOH oxidation ratios between anode and cathode sample tested with Fe added to anolyte, anode tested with Fe added to catholyte, and cathode with no added Fe. Unique speciation was observed in anode with no added Fe which showed high metallic nickel content and cathode tested with Fe added to catholyte which had significant $NiFe_xO_y$ content. The Fe $2p_3/_2$ spectra also showed unique differences between samples, despite limited intensity of this peak due to low concentrations. This investigation confirmed crossover effects of iron during testing, impacting the performance of Ni electrodes.

Poster 19

Elucidating Hydrogen Adsorption Mediated Phase Transitions in MIL-53(Al) via *In Situ* Synchrotron Diffraction

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Should be considered for poster awards: Yes

Hydrogen (H_2) is a promising fuel source for the emerging energy landscape due to its high gravimetric energy density and lack of CO_2 production upon use. However, the low volumetric density of H_2 limits its utility, requiring extreme pressure and temperature swings to store and deliver working amounts. Microporous materials such as Metal–Organic Frameworks (MOFs) have been proposed as adsorbents to densify H_2 at milder conditions, enabling its practical storage and delivery. Microporous frameworks typically exhibit Type I Langmuir adsorption–desorption profiles in which gas adsorption and desorption primarily occur at low pressures. Consequently, low pressures are needed to deliver the full payload, limiting their usable capacity to much lower than their total uptake capacity. Cooperatively flexible MOFs can, in theory, obviate this shortcoming through structural transitions during adsorption and desorption, resulting in appreciable changes in accessible porosity. These structural changes can produce "step-shaped" adsorption–desorption profiles, thereby increasing usable capacities. MIL-53(Al) is a cooperatively flexible framework of interest as it exhibits step-shaped H_2 adsorption, has a high total capacity for H_2, and is composed of earth-abundant aluminum. However, MIL-53(Al) is limited by its Type I desorption profile, which mitigates the benefit of step-shaped adsorption to its usable capacity. To intuitively modify this framework to improve usable H_2 capacities, we must first understand the structural changes as a function of gas pressure. Herein, we have undertaken *in situ* synchrotron X-ray diffraction to deconvolute the phase changes of MIL-53(Al) during H_2 adsorption. Our study has revealed the phase changes responsible for the multi-stepped H_2 adsorption behavior of MIL-53(Al) and revealed the presence of a previously uncharacterized intermediate phase. This work sets the stage for the intuitive derivatization of MIL-53(Al) with attention to how modifications will impact the deconvoluted structural transitions.

Poster 20

Direct visualization of the existence of surface local chemical order in CoCrFeMnNi

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Should be considered for poster awards: Yes

High entropy materials are a novel family of materials that were originally studied for the superior mechanical and physical properties of high entropy alloys (HEAs). In order to fulfil the 'high-entropy' name, these materials require five or more unique and equimolar elements that form a solid solution. In more recent studies, HEAs as well as other high entropy materials have been found to have many applications in electrocatalysis for energy conversion reactions, where the binding energy is dependent on the binding atom and its neighboring atoms, where in HEAS the energy of binding sites is varied due to the mixing of many elements. It's important to carefully study the elemental distributions on the surface of HEAs, to understand how surface properties such as electrocatalytic performance, corrosion, and oxidation resistance will be 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 CoCrFeMnNi alloy at the atomic scale, and directly observe two surface local chemical ordering domains with corresponding $\sqrt{5} \times \sqrt{5}\, R \pm 26.6°$ quasi-long-range orderings. Density functional theory calculations identify the local chemical orderings and provide evidence of the existence of surface chemical order. This work paves the road towards directly observing local chemical order and understanding how local chemical order influence surface-based properties, facilitating the design of HEAs with tailored functionalities.

Poster 21

FIBXTEM Investigation of the Carbon Nanotube to Substrate Interface for Layered Silicon and Stainless Steel Substrates

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Should be considered for poster awards: Yes

We investigated the growth of carbon nanotubes (CNTs) on silicon and stainless steel substrates. This analysis included creating FIBXTEM cross-sections of the CNT-substrate interface, which were imaged and analyzed by STEM and EDX. Samples with various lengths of CNT growth time were compared to understand how CNT growth and the substrate surface changed over time. The growth mechanisms of the two substrates were compared.

CNTs were grown on silicon by depositing an alumina buffer layer, followed by a layer of iron catalyst. The substrate was then heated in hydrogen gas to 750 °C, and then a flow of ethylene was added to initiate CNT growth through catalytic chemical vapor deposition (CCVD). Imaging of the samples shows that the iron layer breaks up into nanoparticles of two size categories: large (20-60 nm) and small (5-15 nm). Only a fraction of the small particles acted as CNT catalysts. When CNT growth continued for a long time (25 mins.), iron particles that did not act as CNT catalysts disappeared. Iron particles were found incorporated in the cores of the CNTs, so it is likely that excess iron particles migrated to the active base catalysts and were pulled into the CNTs.

CNTs were grown on stainless steel by inserting it into a preheated furnace and oxidizing it for 4 minutes at 800 °C. The furnace was then purged of air, and ethylene was flowed to initiate CNT growth by CCVD. Cross-sections of the CNT-substrate interface show that these CNTs grow from iron particles embedded in an oxide layer on the steel surface. These iron particles were reduced out of the oxide by the ethylene precursor, allowing them to act as CNT catalysts. This behavior shows that oxidation and reduction of the steel surface prior to CNT growth helps isolate iron-rich particles that promote CNT growth. The embedded nature of the catalyst limits its access to the ethylene precursor, quickly stopping CNT growth. This embedded property also significantly improves the CNT-substrate adhesion.