Thursday Evening, November 9, 2023

Undergraduate Poster Session
Room Oregon Ballroom 203-204 - Session UN-ThP

Undergraduate Poster Session

UN-ThP-2 Enhancing the Durability of Nitrogen Plasma-Treated PLA Films: Investigating Hydrophobic Recovery Reduction Methods*, **Mina Abdelmessih**, M. Hawker,* California State University, Fresno

Polylactic acid (PLA) is a promising eco-friendly biopolymer as it is produced from renewable feedstocks. The use of PLA in biomedical-related applications is increasing due to its non-toxicity *in vivo* and biodegradability. Nevertheless, the surface hydrophobicity of PLA limits its utility in the biomedical field, especially in applications related to tissue engineering. Although PLA scaffolds have potential for bone reformation and angiogenesis, a hydrophilic surface would further assist in developing *in vivo* applications. For instance, valuable properties such as cell adhesion and growth could be promoted on a hydrophilic PLA surface. Previous research has demonstrated promise in increasing hydrophilic surface properties on PLA utilizing radio frequency nitrogen plasma treatment. Nitrogen plasma-treated polymers, however, exhibit hydrophobic recovery where the plasma modified polymer surface is thermodynamically unfavorable, reverting back into its hydrophobic state with age. Hydrophobic recovery of treated PLA surfaces is detrimental, especially for biomedical applications. Methods of preventing this phenomenon in PLA are widely unexplored.

This work analyzed the effectiveness of different preservation methods in maintaining the hydrophilic character of nitrogen-plasma treated PLA. PLA films were prepared as model substrates and plasma-modified under optimized nitrogen plasma parameters (power, pressure, and treatment time). Following plasma treatment, samples were aged in different environments (e.g., cold temperature, under inert gas) for a period of one month. Samples exposed to different preservation environments (along with controls aged under ambient conditions) were subjected to multiple surface analyses throughout the aging period. Film surface wettability was analyzed utilizing water contact angle goniometry. X-ray photoelectron spectroscopy was utilized to determine plasma-treated PLA surface chemical composition as well as composition throughout the aging process. Expanding these preservation methods to PLA scaffolds has the potential to positively impact the use of PLA for tissue regeneration.

UN-ThP-3 Applying Ammonia Plasma to the Surface of PTFE to Enhance Amine Content*, **Sannad Jawad**, A. O'Regan, M. Hawker,* California State University, Fresno

The World Health Organization reports cardiovascular diseases to be among the most prevalent global health issues, with an estimated 17.9 deaths annually. Such diseases include congenital heart defects such as atrial or ventricular septal defects. Treatment options for these conditions include surgical intervention in which a patch made of a synthetic polymer or biological tissue is secured over the affected area. Among the most commonly used polymers is polytetrafluoroethylene (PTFE). This material is well known to be inert, exceedingly flexible, and highly resistant to wear. Although PTFE is widely recognized for its good qualities, it does have the potential to elicit a negative immune response that can be harmful to the body. This study aims to reduce the immune response by utilizing ammonia plasma to increase the concentration of amine groups on the surface of PTFE. Prior studies have shown success in introducing amine groups using different ammonia plasma parameters (e.g., power, pressure, and time). However, an optimized set of parameters that produce the maximum quantity of amine groups on the PTFE surface has yet to be realized.

This study focused on varying the ammonia plasma parameters in a systematic manner to establish the correlation between these parameters and the extent of amine group integration. A range of parameters was studied (pressure 70-500 mTorr, applied power 20-100 W, plasma exposure time: 0.5 - 5 min). After treating PTFE sheets with varying plasma exposure times, applied powers, and feed gas pressures, surfaces were characterized to investigate the presence and quantity of amine groups. First, Fourier transform infrared spectroscopy (FTIR) was used to detect the presence of IR active functional groups. Then, X-ray photoelectron spectroscopy (XPS) was used to identify the elemental composition of the surface. Contact angle goniometry was then conducted to evaluate the polymer surface hydrophilicity. Lastly, the acid orange II colorimetric assay was performed to determine the quantity of primary amine groups.

UN-ThP-4 Reporting of Parameters Related to Data Acquisition and Peak Fitting in XPS: A Further Evaluation of the Literature*, **B. Maxwell Clark**, G. Major,* Brigham Young University*; D. Baer,* Pacific Northwest National Laboratory*; M. Linford,* Brigham Young University

X-ray photoelectron spectroscopy (XPS) is a widely used spectroscopic technique for analyzing thin films and materials. Because XPS peak widths and chemical shifts are often of about the same magnitude, spectra acquired in XPS typically require peak fitting. In recent years, significant challenges with reproducibility in XPS analyses have been identified. We recently surveyed about 400 papers from 2019 to understand the quality of peak fitting/data analysis in the literature. We have now surveyed an additional ca. 900 papers from 2021 to understand the reporting of important peak fitting and data acquisition information. Parameters investigated include X-ray source type, pass energy, spot size, vacuum level, and the types of baselines and synthetic fit components used in fits. In general, there is a severe lack of reporting of much of this essential information in the literature.

UN-ThP-5 Analyzing the Surface Roughness and Surface Chemistry of Oxygen Plasma-Treated Silk Fibroin Films for Corneal Epithelial Tissue Regeneration*, **Gurneet Kaur**, M. Hawker,* California State University, Fresno

Corneal epithelial damage is common due to ocular surface injuries that prevent tissue regeneration. These corneal surface injuries could lead to corneal defects and potential blindness. Current treatments for corneal epithelial tissue regeneration are amniotic membrane implants, however, these have limitations regarding mechanical strength, transparency, and infectious disease transmission risk. A biomaterial that has similar bulk mechanical properties to those of the cornea is silk fibroin. Silk fibroin is biodegradable and optically transparent. Additionally, prior studies indicate that silk fibroin promotes corneal epithelial cell proliferation. Current research, however, indicates a decrease in initial cell attachment when compared to the amniotic membrane. We propose the use of oxygen plasma treatment to enhance epithelial cell adhesion. Notably, this strategy has proved successful for other polymers but has not been extended to silk surfaces. This study was inspired by conflicting evidence in previous literature about the roles of surface roughness and surface chemistry in epithelial cell attachment. In this work, silk fibroin films were fabricated and plasma treated with oxygen plasma to explore the impact of both film surface roughness and surface chemistry. First, silk fibroin films with high and low surface roughness values were fabricated by dissolving silk fibroin into water and hexafluoroisopropanol, respectively. Solutions were then dropcast onto glass slides and dried overnight. Films were then oxygen plasma treated using varied plasma parameters (e.g., exposure time, applied power). Surface wettability was analyzed using contact angle goniometry. Surface roughness was qualitatively and quantitatively measured using scanning electron microscopy and profilometry, respectively. Surface chemistry was analyzed by using x-ray photoelectron spectroscopy. Overall, findings demonstrate successful fabrication of a silk fibroin film library with systematically-varied surface roughness and surface chemistry. Future analysis of corneal epithelial cells attachment on these surfaces will be performed to evaluate efficacy for corneal epithelial tissue regeneration.

UN-ThP-6 Exploring the Capabilities of Oxygen-Release Coatings on Collagen Films*, **Haylee McFall**, M. Hawker,* California State University, Fresno

Common resective and regenerative periodontal surgeries leave tissues exposed during postoperative healing. These sites are hypoxic, prolonging tissue regeneration. An ideal postoperative patch would provide a sustained barrier to protect against infection and deliver oxygen for expedited healing. Collagen has recently been applied in postoperative healing due to its hemostatic advantages and physical barrier capabilities. However, collagen alone does not alleviate hypoxia through localized oxygen delivery. Oxygen release coatings through plasma-enhanced chemical vapor deposition (PECVD) have been used to control the release of drugs and other species from polymer surfaces. Although literature precedent reports the use of a 1,7-octadiene precursor for PECVD to encapsulate oxygen release coatings on polydimethylsiloxane, this strategy has yet to be applied to collagen for oral postoperative healing. We seek to extend this previously published approach to fabricate an oxygen-releasing collagen substrate.

In this work, collagen films were prepared as model substrates. Calcium peroxide powder was sieved to <37µm and applied to a collagen film. A hydrocarbon film was then deposited over the peroxide layer using PECVD with 1,7-octadiene as the plasma precursor. By manipulating exposure time, the plasma-deposited film thickness was altered. PECVD rate was measured using ellipsometry. A dissolved oxygen probe determined the flow of oxygen released from the prepared constructs in an aqueous environment, which was compared to exposure time. The relationship between film thickness and oxygen delivery was elucidated. With newly incorporated oxygen delivery capabilities, these plasma modified collagen films positively contribute to postoperative healing.

UN-ThP-7 A Precise Measurement of Atomic Spacings in Rotated Hexagonal Mn Adatom Structures on a MnGaN-2D FM Substrate*, **Cherie D'Mello**,* Ohio University*; Y. Ma,* Ohio University, China*; D. Hunt, M. Barral, V. Ferrari,* CAC-CNEA, Argentina*; A. Smith,* Ohio University

We precisely measured the atomic spacings between Mn adatoms composing two rotated hexagonal structures on a Mn/MnGaN-2D aFM/FM surface. The purpose of our study is to help verify possible theoretical structures proposed for the system.

The MnGaN-2D substrate used is ferromagnetic[1]. As measured using SQUID magnetometry, adding more Mn atoms on top results in a reduction of the overall surface magnetization, and this can potentially be understood as a partially compensated ferrimagnetic structure. But the precise nature of such a structure is in this case not yet understood. However, the Mn/MnGaN-2D structure was atomically resolved by *in-situ* scanning tunneling microscopy (STM). The images revealed two hexagonal Mn adatom structures (type A and type B) which differed in rotation by approximately 20 degrees. This was surprising given that the 2D MnGaN substrate used has a very regular hexagonal-like lattice structure. Three possible theoretical models of the rotated Mn hexagonal structures have been proposed, but none of them so far has been verified to be correct. What is needed is more precise and verified measurements of the spacings between the adatoms and the location of their precise geometrical positions. If this was done carefully, it would be important for ultimately being able to determine a successful model.

Therefore, we measured the spacings of the hexagonal structures seen in the STM images of the surface of the Mn/MnGaN-2D structure by first determining the STM image calibration using the well-known structure of the substrate and the known spacings between the substrate lattice sites as measured in the STM images. We performed first the drift corrections and after that the scanner asymmetry/scale corrections. After calibration, the results reveal the corrected spacings between the adatoms composing the two rotated hexagonal regions. Even the 20° rotation between the type A and B hexagons cannot easily be explained by a standard theoretical model involving adatoms resting in ideal surface substrate sites. The correct explanation will require additional theoretical modeling, possibly going beyond the standard methods.

Acknowledgements:

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[1] Y. Ma *et al.*, "A Two-Dimensional Manganese Gallium Nitride Surface Structure Showing Ferromagnetism at Room Temperature," Nano Letters **18**, 158 (2018).

UN-ThP-8 In-situ Spectroscopy Investigations of Methane Pyrolysis in Catalytic Molten Media*, **Phineas Lehan**, O. Polonskyi, E. McFarland, M. Gordon,* University of California at Santa Barbara

The extensive use of fossil fuels as energy sources has raised serious concerns related to their limited supply as well as harmful greenhouse gas emissions. It is thus apparent that new, sustainable energy sources are needed, such as hydrogen. Current industrial approaches to produce hydrogen, e.g., steam and/or autothermal reforming of methane, are undesirable due to high CO_2 emissions. An interesting alternative to these processes is direct decomposition of methane to H_2 and solid carbon; moreover, this process can be made CO_2-free by recycling part of the H_2 product for heating.

There has been recent strong interest in using molten media (metals or salts) both as thermochemical reaction media and for heat transfer to efficiently carry out methane pyrolysis. In this process, CH_4 is typically bubbled through the molten media, reacting to form H_2 and low-density carbon that rises to the surface where it can be easily separated. However, traditional methods for analyzing gaseous products of methane decomposition involve ex-situ sampling, which cannot measure short-lived intermediates and potentially introduces discrepancies in results. Therefore, in-situ experiments are preferred to make time-resolved measurements to understand such processes.

In this study, we present results of in-situ infrared (IR) spectroscopy investigations of methane pyrolysis in molten media at temperatures between 800-1200°C. The primary focus is on melts composed of molten salts and their mixtures with catalytic, transition metal additives. We utilize an L-shaped quartz reactor configuration that allows analysis of an individual gas bubble as an isothermal batch reactor. In this configuration, conversion and reaction intermediates can be studied in real time and the molten salt environment wets the quartz reactor walls, preventing coking.

Methane conversion, obtained from the methane IR peak intensity as a function of time, temperature, and melt composition, was investigated. Results show that decomposition of methane in molten KBr has an activation energy of 333 kJ/mol, compared to 413 kJ/mol for gas phase thermal decomposition. Measurements with 3 wt % Fe in an $FeCl_3$ / KBr mixture suggest lower activation energies, and the presence of catalysis. Specifically, 90% conversion was achieved within 10 minutes at 850°C, which is comparable to conversion obtained in KBr melt at 1100°C under the same conditions. Additionally, multiple hydrocarbon intermediates within the infrared spectral range of 2800 cm^{-1} to 3400 cm^{-1} have been observed during early stages of pyrolysis at higher temperatures (~1200°C), which could provide additional insight into methane pyrolysis mechanisms.

UN-ThP-9 Ultraviolet Photoelectron Spectroscopy as a Powerful Technique to Investigate the Synthesis - Electronic Properties - Optical Behavior Correlation of a $Cu_2O||TiO_2$ Z-Scheme*, **Beatriz de la Fuente**, T. Hauffman,* Vrije Universiteit Brussel, Belgium

Among the electronic properties, the positions of the electronic band edges and the work function are essential parameters for determining the potential of a photocatalyst and its ability to function in a solar conversion system. Oxidation and reduction reactions are greatly affected by the electrical characteristics of the material. In this concern, ultraviolet photoelectron spectroscopy (UPS), a highly surface-sensitive technique allowing the determination of work functions, ionization energies, and examination of valence levels, provided new synthesis – electronic property links of $Cu_2O||TiO_2$ direct Z-schemes systems in combination with other surface characterization techniques such as field emission scanning electron microscopy (FE-SEM), energy-dispersive X-ray spectroscopy (EDX) and X-ray photoelectron spectroscopy (XPS). This study reveals that TiO_2 nanotubes modified with Cu_2O nanoparticles exhibited a reduction in the value of the work function (WF = 3.67 ± 0.01 eV) and ionization potential (IP = 6.01 ± 0.04 eV) with respect to the TiO_2 substrate (WF = 4.29 ± 0.02 eV and IP = 7.65 ± 0.05 eV). By varying the deposition time, an optimized amount of Cu_2O nanoparticles deposited led to a significant reduction in the WF and IP to facilitate the excitation of electrons, which later translated into a maximum absorbance in the visible wavelength range. This work provides a tool to tune the mentioned electronic parameters based on the electrodeposition time of Cu_2O, which is beneficial for the improvement of $TiO_2||Cu_2O$ catalyst design and fabrication.

UN-ThP-10 Reduced Microbial Attachment with Increased Oil Infusion in Liquid-Infused Silicone Material*, **Emma Kunesh**, C. Fong, C. Howell,* University of Maine

Silicone polymers infused with free liquid silicone are of interest in the biomedical materials community due to their ability to significantly reduce both protein and bacterial adhesion. However, the potential for free liquid on the surface to be lost into the environment is of concern. To enhance the safety of liquid-infused silicone in medical applications, we examined how reducing free liquid via partial infusion of the solid affected the adhesion of three different species of clinically important bacteria. To create the partially infused samples, controlled infusion duration was used, resulting in samples with infusion volumes ranging from 10–100% of maximum. The partially infused samples were then exposed to *Enterococcus faecalis*, *Escherichia coli* and *Pseudomonas aeruginosa* for 24 h. For all bacteria, increasing infusion levels correlated with progressive reductions in attachment and biofilm formation. Samples infused to 80% of their maximum value were able to resist *E. coli* and *E. faecalis* adhesion at levels statistically similar to fully infused controls. However, below this infusion percentage *E.coli* and *E. faecalis* adhesion increased significantly. In contrast, samples infused to only 40% of their maximum values were able to resist adhesion by *P. aeruginosa* at levels similar to controls. Further tests with *P. aeruginosa* showed that significant differences were visible after only 4h of incubation. Together, our results demonstrate that partially infused silicone material can still effectively reduce microbial attachment, providing a potential avenue for enhancing the safety of liquid-infused silicone materials in medical applications.

UN-ThP-12 Exploring Thresholding Methods in Textured Surface UV-Vis Detection of Chemical and Biological Contamination in Liquids*, **Anna Folley**, L. White, C. Howell,* University of Maine

Current commercial assessment of chemical and biological pollutants in liquids frequently requires labor-intensive manual collection and measurement, typically employing costly UV-Visible spectrometers. We have recently shown that a low-cost surface texture that functions as a diffraction grating can be used to get comparable results to a spectrometer; however, the system's sensitivity could be improved. Here, we describe how optimizing thresholding methods could increase the sensitivity and decrease the limit of detection of contaminants in liquid. We designed a method to image and capture changes in the diffraction pattern as a liquid containing biological and chemical pollutants passes over the diffraction surface. Various image thresholding methods were evaluated to determine their influence of overall detection sensitivity. The efficacy of distinct thresholding techniques for analyzing contaminants which scatter light as opposed to simply absorb light was also explored. The findings from our study demonstrate that thresholding plays a pivotal role in identifying liquid contaminants and suggest the potential for refining thresholding methods to enhance sensor sensitivity.

UN-ThP-13 Analyzing Diffraction Pattern Colors in Textured Surface UV-Vis Detection of Chemical and Biological Contamination in Liquids*, **Lindsay Pierce**, L. White, C. Howell,* University of Maine

Conventional evaluation of chemical and biological pollutants within liquids entails manual collection and measurement procedures. We have developed an alternative approach to contaminant analysis that uses a textured surface as continuous, in-line diffraction grating sensor; however, systematic shifts in the color of the diffraction pattern as contaminant levels rise and fall have not yet been analyzed. Here, we explore the prospect of tracking systematic color shifts within the diffraction pattern to enhance the detection of liquid contaminants. Using images of the diffraction pattern under both static and continuous flow conditions, we investigated different hue thresholding methodologies. The colors exhibited clear, systematic shifts in the presence of contaminants within the liquid, demonstrating the potential to extract color information from the diffraction grating sensors to provide additional information about contaminants in liquid.

UN-ThP-14 A Density Functional Theory Analysis of an Acetone-Acetone Aldol Condensation on an Pt-Doped Fe_3O_4 Surface*, **Jack Gordon**, H. Nguyen, L. Árnadóttir,* Oregon State University

Aldol condensation reactions provide an efficient way to form carbon-carbon bonds, making them pivotal for processes in synthesis and polymerization. An Fe_3O_4 surface acts to catalyze the process, but experimental data shows that an addition of Pt in small concentrations enhances the reaction rate, suggesting alterations in the reaction mechanism and/or a decrease in the activation energy. Due to the surface's promise in facilitating aldol condensations, a greater understanding of the mechanism is desired. Density Functional Theory (DFT) as implemented in VASP 6.2 was used to calculate and compare changes in energies and the activation barriers of elementary reaction steps of different reaction pathways. The calculations indicate that the platinum-doped surface does act as a more efficient catalyst than the non-platinum-doped alternative. Furthermore, the data suggests a plausible mechanism in which both an octahedral iron and platinum act as adsorption sites for acetone, while a surface oxygen acts as a recipient for hydrogen during enolate formation. Of the two co-adsorbed acetones, the acetone bound to the iron demonstrates a preference toward enolate formation.

UN-ThP-15 An STM Investigation of the Ambient Adsorption of L-Isoleucine on the Surface of Au(111)*, **Dillon Dodge**,* University of Tulsa*; R. Dirks,* Columbia University*; L. Hornbrook, E. Iski,* University of Tulsa

The role of surfaces in the molecular interaction between 2D layers of amino acids has become a recent topic of investigation concerning questions like homochirality and, by extension, the origin of life on Earth. Previous research has examined how metallic islands are formed on the surfaces of Cu(111) and Au(111) due to the immobilization of diffusing metal adatoms in ultra-high vacuum (UHV) and electro-chemical (EC) liquid cells respectively, showing that the biological molecules drastically interact with the surface indicating that metallic surfaces do not act as static hosts during these molecular interactions.

This research used scanning tunneling microscopy (STM) to observe the interactions of L-Isoleucine on the surface of Au(111) scanning completely in air at room temperature following drop cast deposition of the amino acid. Similar to past research, we observed interactions with the surface including step edge deformations and the formation of metallic islands, though in notably different scales and frequencies. This indicates that results found from experiments in UHV and EC cells are at least partially analogous to those done in air, which is a potentially more realistic representation of conditions of early earth.

However, not all behaviors seen in our experiments done in air were perfectly correlated to ones in prior investigations. For example, whereas the metallic islands caused by the deposition of 0.55 mM L-isoleucine in UHV and EC cells were frozen in place regardless of active observation by the tip, the deformations that we observed in air were quickly reconstructed as a result of tip-assisted reconstruction regardless of isoleucine concentration. Additionally, we imaged herringbones present next to sites of molecular interaction after hours of unprotected exposure to air following deposition. These findings indicate the need to study molecular adsorption at a wide variety of conditions in an effort to truly understand the interaction between biological molecules and model surfaces, like Au(111).

UN-ThP-16 Towards Plasma Enhanced Atomic Layer Deposition*, **Sivagya Kc**, W. Jen, S. Hues, E. Graugnard,* Boise State University

The fabrication of microelectronics relies on thin film technologies. As the demand for improved performance of microchips continues to escalate, atomic layer deposition (ALD) has emerged as a crucial technique in enabling precise and controlled thin film deposition. Plasma-enhanced ALD in particular is an energy-enhanced method for synthesizing thin films with mono-layer resolution. Unlike conventional thermal ALD processes where chemical precursors react with a heated substrate to deposit the thin film, forming a plasma of the ALD precursors allows for alternate reaction paths, potentially leading to improved film density, crystallinity, and mechanical properties at lower deposition temperatures. Plasma exposure during ALD can also assist in the removal of surface contaminants during the deposition process.

In this project, a capacitively coupled plasma is generated by applying a direct current (DC) bias between the powered and grounded electrodes in a quartz chamber, inducing an electric field. This couples with the precursor gas to create a high-energy plasma that produces energetic reactive species, which can then be directed to the substrate, providing novel reaction pathways having a more desired thermal budget to achieve the desired film properties. This chamber will be integrated into an ALD system to enable plasma-enhanced ALD. The chemical, physical, and electrical properties of the resulting films will be characterized.

UN-ThP-17 Role of Post-Deposition Annealing on Defectivity in 2d Materials*, **Icelene Leong**, W. Jen, A. Rode, J. Wilson, R. Clouse, D. Tenne, S. Hues,* Boise State University*; E. Graugnard,* Boise State University and Center for Advanced Energy Studies

With the increasing complexity of microelectronics, the development of new forward-looking materials and processes has become imperative to enable their functionality. Among the potential pathways to further miniaturize devices, two-dimensional (2D) materials offer great promise due to their outstanding electrical properties even at the atomic level. Molybdenum disulfide (MoS2) is a notable example of a 2D material that exhibits these desirable characteristics and can be synthesized through chemical vapor deposition (CVD) at elevated temperatures. For deposition temperatures below 300°C, atomic layer deposition (ALD) shows promise for synthesis of MoS2 films, but film quality is generally lower than CVD films, and ALD films often employ post-deposition annealing (PDA) to improve their quality.

Ultimately, electrical performance of 2D materials is of primary interest, yet device fabrication can be time consuming and expensive. Thus, there arises a need for the ability to rapidly evaluate the quality of ALD thin films prior to test device fabrication. Raman spectroscopy, a powerful analytical technique widely employed for the characterization of 2D thin films, presents itself as a promising approach for efficient metrology. Variations in the crystallinity and defect density of MoS2 can induce peak shifts or broadening in the corresponding Raman spectra. Establishing a quantitative correlation between these changes and the film properties would enable a swift and non-destructive method for characterizing thin films to evaluate which processing conditions produce films of sufficient quality for device fabrication. To establish this approach, ALD MoS2 films will be deposited on a variety of substrates and subsequently subjected to various annealing conditions, including different temperatures, durations, and environments. The Raman spectra of the annealed samples will be evaluated using deconvolution of the phonon modes giving rise to the peaks in the spectra. These data, along with processing conditions, will be correlated with defect densities acquired through transmission electron and scanning probe microscopies and film conductivity. This approach will establish a quantitative relationship between Raman spectral features and film mobilities, which will enable high-throughput metrology for ALD process development of high quality 2D materials.

UN-ThP-18 Plasma-Excited Nitrogen for Stabilization of GaN During High Temperature Annealing*, Reilly Shanahan*, *E. Thimsen, D. Mohr,* Washington University in St. Louis

Gallium nitride (GaN) is a wide bandgap semiconductor material that can outperform silicon in power electronics applications. Activation of p-type Mg dopants embedded by ion implantation requires extreme annealing temperatures, at which elemental decomposition becomes a challenge. High N_2 pressures are usually required to prevent the decomposition of GaN during high temperature annealing, which leads to exorbitant production costs. In this work, we explore the hypothesis that the annealing process can be run at low pressure conditions (decreasing costs) by using N_2 plasma to provide the chemical potential required to stabilize GaN. Previous research has demonstrated that the presence of plasma results in the growth of GaN from Ga melt at unexpectedly high temperatures without high pressure. In this work, a comparative approach is used wherein thin film GaN samples deposited on sapphire substrates are annealed at high temperature with and without N_2 plasma. The samples are characterized specifically by looking for pits on the GaN surface. These pits are a hallmark of the early stage of decomposition. The results suggest that N_2 plasma improves stability of GaN during low-pressure, high-temperature annealing.

UN-ThP-19 C_3 Oxidation Chemistry over CuO_x/Cu(111)*, John Yoo*, *E. Schell, J. Loiselet, A. Baber,* James Madison University

The oxidation of C_3 compounds, propylene and 1-propanol (1-PrOH), yield important products including propylene oxide and hydrogen over copper-based catalysts. Gaining a better insight into the activity of the C_3 compounds over Cu and CuO_x will help improve the understanding of which surface preparations are most reactive. The adsorption and reaction of propylene and 1-PrOH were studied over Cu(111), sputtered Cu(111), oxidized Cu_2O/Cu(111), and partially oxidized CuO_x/Cu(111) using temperature programmed desorption (TPD). TPD results showed the oxidized Cu(111) catalyzed the reaction of 1-PrOH but not propylene. Cu(111) was sputtered with Ar^+ ions to further identify and analyze the C_3 adsorption on defect sites. Sputtered Cu(111) introduced more adsorption sites compared to the clean and oxidized Cu(111) surfaces. These experiments help provide a fundamental understanding of the interactions that occur between C_3 compounds and the differently prepared Cu(111) surfaces. This will set the groundwork for future Cu-based model catalyst research.

UN-ThP-20 Computationally Enhanced Experimental Investigation of Reactivity of Isomeric Butanolon TiO_2/Au(111)*, Haley Frankovich*, *L. Garber, A. Galgano, E. Schell, K. Letchworth Weaver, A. Baber,* James Madison University

Biofuels can be used to reduce global dependence on fossil fuels while contributing to a carbon-neutral cycle. Biobutanol has low volatility and multiple transportation options which make it an attractive alternative fuel. Understanding the fundamental thermal catalysis processes of butanol over heterogeneous model catalysts can aid in the design of more efficient catalysts. To better understand the processes in play, temperature-programmed desorption (TPD), atomic force microscopy (AFM), density functional theory (DFT), and high-performance computing are used to investigate its reaction. This study aimed to examine the reactivity of different isomers of butanol, namely 1-butanol, 2-butanol, and isobutanol, when exposed to a TiO2/Au(111) surface. TPD was used to detect products, with 1-butanol showing little reactivity and elimination products, 2-butanol showing oxidation and elimination, and isobutanol yielding all products. The selectivity of the reaction was not altered during successive desorption experiments, indicating that the model catalyst was stable without reoxidation between experiments. AFM highlighted the morphology of the surface and shows the Au(111) crystal has ~0.13ML and 0.27ML of TiO_2 with predominantly 1D wire like nanoparticles. Higher coverages of TiO_2 result in more particles distributed across the surface indicating that the reactivity was influenced by butanol proximity to TiO_2 nanoparticles rather than differences in size or shape. DFT calculations to investigate energetic trends and provide an atomic-scale understanding of the structure of butanol adsorbed on the surface are ongoing.

UN-ThP-21 Effect of Thermal Annealing and Sputtering by Ion Bombardment on WSe_2 Adsorption Sites*, Ava Galgano*, *E. Schell,* James Madison University*; J. St. Martin,* University of Virginia*; A. Baber,* James Madison University*; P. Reinke,* University of Virginia

Transition metal dichalcogenides (TMDs) are two dimensional materials gaining attention as catalysts for CO_2 hydrogenation and the hydrogen evolution reaction due to their unique properties at low dimensions. Defects, or surface irregularities, of the atomic structure of TMDs are suggested active sites; however, the link between defects, electronic structure, and activity is unknown, which limits the ability to control reactivity. To better understand the fundamental nature of defects on TMDs, WSe_2 was studied using temperature programmed desorption (TPD). The surface of WSe_2 was cleaved via mechanical exfoliation and the sample was mounted on a tantalum (Ta) sample holder. The WSe_2/Ta sample was gently annealed and sputtered under ultrahigh vacuum (UHV) conditions to increase the defect inventory. Results shown here will highlight the reactivity of methanol as a probe molecule using UHV-TPD on WSe_2/Ta. Methanol/Ta control experiments showed a shift to higher desorption temperature (192 to 237 K) after the sample anneal temperature was increased from 473 to 673 K. Similarly, on WSe_2/Ta after annealing, methanol desorption temperatures increased from 168 to 200 K, indicating a potential alloying of WSe_2 with Ta. The WSe_2 surface was gently sputtered via Ar^+ bombardment and the desorption temperature of the methanol/WSe_2 peak (120-140 K) increased as sputter energy increased for similar methanol coverages. These results indicate that ion bombardment increased the defect inventory of WSe_2 without alloying. Future microscopy studies will link the geometric changes induced by sputtering WSe_2 to the shift in methanol binding energies, lending insight into the structure/stability relationships of TMD defects.

UN-ThP-22 Enhancing the Selectivity of Acetaldehyde Formation Using a Copper-based Model Catalyst*, Joseph Loiselet*, *E. Schell, A. Galgano, A. Baber,* James Madison University

Acetaldehyde is a common intermediate in many industrial chemical syntheses. Current methods of acetaldehyde formation are inefficient and wasteful, leading to low product yields and unwanted by-products. In order to improve acetaldehyde yield and minimize other products, the dry dehydrogenation and dehydration of ethanol was observed using temperature programmed desorption (TPD). These reactions occurred on flat, roughened, and oxidized Cu(111) surfaces under ultrahigh vacuum (UHV) conditions. The reaction of ethanol over each surface was studied, and the oxidized Cu(111) most readily formed acetaldehyde and hydrogen at 350 K. A second reaction pathway formed ethylene and water at 350 K. The selectivity for acetaldehyde production was maintained over 80% throughout consecutive TPDs, yet the yield decreased continuously as the surface became less oxidized. Future experiments will study the reactivity of a partially oxidized Cu(111) sample using UHV-TPD.

UN-ThP-23 Understanding CO Binding Trends for CO2 Reduction Catalyst Optimization*, Erin Schell*, *J. Loiselet, A. Galgano, A. Baber,* James Madison University

In the past century, there has been a drastic increase of anthropogenic carbon dioxide in the Earth's atmosphere. The excess of this greenhouse gas has dramatic negative effects on the environment such as extreme weather patterns, poorer air quality, and a rise in global temperatures. Studying the thermodynamics of the formation of carbon dioxide (CO2) is a crucial component to combat this obstacle. Cu-based catalysts are the industrial standard for the reduction of CO2. One mechanism for CO2 reduction first produces CO as an intermediate, however the binding of CO to metal sites inhibits further CO2 reduction. Therefore CO binding must be minimized to promote the efficient reduction of CO2. This is a detailed study of the adsorption and reaction of CO on a Cu(111) surface. A clean Cu(111) sample was prepared under ultrahigh vacuum (UHV) conditions and exposed to varying pressures of carbon monoxide as well as a sputtered Cu(111) sample, and an oxidized Cu2O/Cu(111) sample. Temperature programmed desorption experiments were done on each of the prepared samples. Defects imposed by sputtering formed higher energy CO adsorption sites, whereas oxidized surfaces decrease the stability of CO binding. Therefore the oxidized Cu(111) surfaces play an important role in minimizing CO poisoning on Cu catalysts.

UN-ThP-24 Comparatively Testing CO Oxidation on Rh-Doped and Pt-Doped Copper-Based Catalysts, ***Maggie Rickman***, *G. Miller,* Washington State University; *V. Çinar,* Tufts University; *I. Waluyo,* Brookhaven National Laboratory; *E. Sykes,* Tufts University; *J. McEwen,* Washington State University

The production of carbon monoxide (CO) at low temperatures, from incomplete combustion, is a prominent issue due to its effects of acting as a poison. One way to counteract this is through single-site catalyst that aids in its conversion at low temperatures. Previous work in the literature has extensively investigated the use of precious metals for this reaction, but this becomes increasingly costly. The use of precious metal nanoclusters also binds CO too strongly at low temperatures, which causes the catalyst to deactivate. An alternative is to design a catalyst in which the precious metal is atomically dispersed. Such a catalyst has been shown to have low temperature catalytic performance when Pt is atomically dispersed and deposited on a Cu surface oxide support [1]. We have compared the mechanistic pathways of such a single-site catalyst to when Pt is incorporated into the underlying Cu(111) surface to form a single atom alloy [2]. The oxidation of CO is also tested where a cluster of Rh atoms forms an alloy with the underlying Cu(111) surface for which a Cu oxide layer is grown over it. We further test the activation of H_2 on such systems, where Rh is placed at its most energetically favorable position on the oxide layer. We compare the energetic pathways when Rh is adsorbed next to an oxygen adatom in the oxide layer to determine its effect on the dissociative adsorption of H_2. The optimized versions of these structures were calculated via Density Functional Theory (DFT) calculations using the Vienna ab initio Simulation Package (VASP). We then used Nudged Elastic Band (NEB) calculations to model the kinetic barriers. Once the initial test of the Pt/Cu surface completes, we will be able to compare and contrast how it acts as a catalyst relative to Rh. We have been able to produce the kinetic pathways for Rh single atom alloys as well as Rh clusters to see which is more favorable for CO oxidation. This will allow us to move forward for the rational design of catalysts for the activation of CO in the presence of H_2.

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UN-ThP-25 Deconvoluting information-rich Ga(I) X-ray adsorption near-edge spectroscopy features from first principles, ***Grace Miller***, Washington State University; *C. Huang,* Carleton College; *S. Scott,* University of California at Santa Barbara; *J. McEwen,* Washington State University, Pacific Northwest National Labratory

Due to the high demand of propylene, it is appealing to look at replacing Pt- and Cu-based catalysts for propane dehydrogenation. In this regard, an attractive alternative are Ga-based compounds. X-ray Adsorption Near-Edge Spectroscopy (XANES) contains information about the coordination environment and the oxidation state of Ga under reaction conditions. In our previous work, we deconvoluted the experimental features of Ga(III) compounds [1]. Since Ga(I) and Ga(III) compounds are both involved in propane dehydrogenation, we benchmark the spectral features of Ga(I) compounds in this work. We compare the calculations derived from structures based on *Li et al.* [2] to three additional Ga(I) structures ($Ga(Si(SiMe_3)_3)_4$), ($Ga(C(SiMe_3)_3)_4$), (($Ga_8Br_8)_6NEt$) to further deconvolute the XANES features. Based on the literature, the XANES features with higher intensities correspond to Ga(I) oxidation states while the XANES features with lower intensities correspond to Ga(III) oxidation states. Using the CASTEP code with a Perdew-Berkman Erzenhoff (PBE) functional, we simulate the XANES from first principles. We further compare the Ga(III) features of our compounds to what has been identified previously in the literature [1]. Interestingly, two bulk Ga(I) structures did not have the high-intensity feature as was identified in the other Ga(I) compounds. The study is ongoing where we are quantifying interaction energy between Ga(I) cations within these structures, where our initial results indicate that the interaction energy between them is attractive.

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UN-ThP-26 A Computational Investigation of the Urea Oxidation Reaction Mechanism Using Density Functional Theory: Promoting the NiOOH Active Phase by Introducing Effective Metal-Dopants, ***Matteo Garcia-Ortiz***, *Q. Jin, L. Árnadóttir,* Oregon State University

Urea electrochemical oxidation is of general interest for water treatment in agriculture, but also a possible fuel for urea fuel cells. Urea oxidation is also of fundamental interest for amide chemistry. The urea oxidation reaction (UOR) in alkaline medium neutralizes urea into relatively benign products including H_2, N_2, and CO_2, rather than harmful NO_x compounds. Previous studies have suggested direct and indirect reaction routes for this full oxidation. The presence of metallic ions such as Fe, Co, and Cu in the nickel hydroxide surface may improve selectivity towards the indirect pathway where the $Ni(OH)_2$/NiOOH redox couple plays an important role. Since NiOOH is the active phase for UOR, the first step of transferring $Ni(OH)_2$ to NiOOH is crucial. In this work, we investigate the effect of Fe dopant on the Ni hydroxide transformation. Performing DFT calculations, as implemented in the Vienna Ab initio Simulation Package, the thermodynamics of the nickel dihydroxide to nickel oxyhydroxide mechanism was calculated. We found that doping the β-$Ni(OH)_2$ surface with Fe significantly reduces the free energy change for sequential surface dehydrogenation to β-NiOOH, from 2.27 eV to 0.93 eV, favoring the creation of UOR active sites. This indicates promising potential for the improvement of urea oxidation performance with Fe doping.

UN-ThP-27 Advanced Scanning Probe Microscopy and Infrared Nanospectroscopy Characterization of Atomic Layer Deposited and Etched Thin Films, ***Benjamin Bailey***, *P. Davis,* Boise State University

Scanning probe microscopies are routinely employed for nanoscale materials characterization. In particular, atomic force microscopy (AFM) and associated advanced scanning probe microscopy (SPM) techniques can map nanoscale surface topography and morphology as well as provide insight into electrical, magnetic, and mechanical properties. More recently, with the development of AFM-IR, AFM can be combined with infrared (IR) spectroscopy to provide chemical identification with <10 nm resolution. Here, we report AFM characterization of atomically thin films created through metal-organic chemical vapor deposition (MOCVD), atomic layer deposition (ALD) of layered two-dimensional (2D) semiconductors such as MoS_2 and WSe-$_2$. High resolution AFM is used to characterize ALD film quality and morphology, while advanced SPM modes are employed to measure electrical properties of interest. Additionally, AFM-IR is brought to bear to provide insight into the use of atomic layer etching (ALE) for these materials. These results hold promise for advancing the characterization and integration of novel 2D materials into semiconductor device manufacturing.

UN-ThP-28 Towards in-Situ Transmission Ftir of ALD Systems, ***Anthony Donegan***, *S. Hues, E. Graugnard,* Boise State University

An apparatus was constructed which allowed a Nicolet Magna 550 Fourier Transform Infrared Spectrometer (FTIR) to interface with an industrial Atomic Layer Deposition (ALD) furnace. Aluminum Zinc Oxide films were grown using ALD. The resulting films were characterized through in-situ FTIR. Significant noise was introduced by the method of interfacing the FTIR with the ALD furnace. The film produced little to no absorbance and the resulting signal showed no indication of chemical changes which could not be attributed to random noise. Guidelines to reduce noise and signal loss in future similar experiments were provided.

UN-ThP-29 Gas-Phase Analysis of Plasma-Enhanced Modification of Silk Films, ***Mollie Corbett***, *B. Yashkus, J. Blechle,* Wilkes University

Silk fibroin's range of mechanical properties make it a viable option for use in tailored medical devices, but its uncontrolled biological lifespan poses a significant challenge in creating these various types of devices. To combat this issue, the wettability can be altered to promote or inhibit enzymatic interactions, resulting in predictable material degradation. Plasma-enhanced chemical vapor deposition (PECVD) has been shown to be an effective method in altering the wettability of silk films via water contact angle goniometry results. Because little is known about the chemical mechanisms which make these modifications possible, an improved understanding of gas phase interactions can aid in ensuring reproducible surface modifications.

One way to combat this issue is utilizing optical emission spectroscopy (OES), which is an effective way to monitor the plasma during the treatment process. Mechanistic information is gleaned by analyzing the gas phase species with and without the presence of silk. Specifically, density and temperature measurements can be determined from plasma emission and are used to provide better insight into the gas-surface interface.

Acrylic acid and pentane precursors are used, as they have been shown to successfully deposit hydrophobic or hydrophilic films on silk materials. For ease of comparison, all treatments lasted 30 s at 65 W with a total system pressure of 75 mTorr, utilizing a 10% (by pressure) argon addition to serve as both a carrier gas and actinometer.

Molecular nitrogen emission was observed in all plasmas containing silk, indicating possible etching of the surface. Additionally, molecular H_2 bands were observed in both pentane and acrylic acid spectra. Acrylic acid plasmas also contained molecular bands for CO, CO_2^+, and OH. Excluding argon and hydrogen, all other expected atomic transitions (such as carbon and oxygen) remained absent through all pentane and acrylic acid plasmas. Density measurements indicate a slight increase in the concentrations of all observed species upon the addition of silk. The concentrations of all species, excluding nitrogen, were calculated to have increased by a factor of ~1.5 to 2.0. Vibrational temperature measurements of CO were determined to be 943 ± 13 K, while the temperature of H_2 increases by an order of magnitude.

Using gas phase measurements, we can gain insights to better understand the success demonstrated by PECVD in silk film modification. Recognizing the mechanisms of the changing surface chemistry can assist in making fine procedural adjustments, helping to achieve more consistent results in altering silk to control its lifetime without impacting its bulk properties.

UN-ThP-30 Quantifying Oxygen Diffusion in Epitaxial $SrTiO_3$ Thin Films*, **Sihang Hui**,* University of Florida, Gainesville

Emerging technologies such as magneto-ionic memory devices, fuel cells, and resistive switches rely heavily on the oxygen migration through thin films [1,2]. Such a device's performance requires precise control and understanding of oxygen diffusion [3]. These diffusion mechanisms and oxygen barriers are imposed in part by the design of strain and interface symmetry of the heterostructures. However, due to the difficulty of measuring small concentrations of oxygen ions (~1 at%) moving through nanoscale distances, the diffusion rates of oxygen ions in these heterostructures are not well characterized. This project focuses on developing a method to better measure and understand the migration rates and barriers of oxygen ions in oxide thin films using X-ray reflectometry (XRR). While XRR methods for measuring diffusion exist for superlattice structures [4], the focus here is on enabling such measurements in single layer epitaxial films, which would greatly expand the utility and accessibility of the method.

Our approach uses a nanoscale diffusion couple composed of an epitaxial layer of perovskite SrTiO3 (STO) thin film using the pulsed laser deposition (PLD) process and capped with a metal gettering layer (e.g., Ta) and an atmospheric protection layer (e.g., Pt). In-situ annealing experiments were conducted to promote diffusion. To quantify the diffusion at the interface, XRR measurements were collected and fit to one-dimensional chemical depth-profile models before and after the anneal. From there, a diffusion coefficient for each annealing condition can be calculated from a fit to the oxygen profile shape [5]. Figure 1a shows an example of an X-ray reflectivity (XRR) scan before and after an annealing procedure near our low-temperature-time bound. Post-annealing, there are changes in the reflectivity curve for Q ≥ 0.15 Å-1 that can be fit to a small change in the Ta/STO interface roughness.

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UN-ThP-31 Understanding the Role of the Interface in Thermoelectric Materials*, **Eli Robinson**, Z. Irving-Singh, J. Sanders, R. Brown, W. Kim, P. Hall, N. Coates,* University of Portland*; J. Heath,* Reed College

A thermoelectric material is able to convert waste heat into usable electricity. A typical thermoelectric consists of inorganic semiconductors. Newer classes of thermoelectrics are instead composed of organic-inorganic composites, which offer the advantage of being solution-processable for greater ease and lower cost of fabrication. Here, we studied how the interface of a composite thermoelectric comprising gold nanoparticles and PEDOT:PSS influences its thermoelectric figure of merit. In order to better understand this interfacial component, samples of Au nanoparticles were mixed with PEDOT:PSS in varying volume fractions. These samples were then prepared for various analytical methods, with emphasis on SEM imaging and TGA analysis.

UN-ThP-32 Ex-Situ Synthesis and Characterization of PEDOT:PSS-Au NP Composite Thermoelectrics*, **Won Sung Kim**, J. Sanders, E. Robinson, Z. Irving-Singh, R. Brown, P. Hall, N. Coates,* University of Portland*; J. Heath,* Reed College

Thermoelectrics offer significant promise in addressing society's demand for advancements in energy conversion and storage technologies. The interface between hybrid organic/inorganic films comprising poly(3,4-ethylenedioxythiophene):polystyrene sulfonate(PEDOT:PSS) and PSS-coated gold nanoparticles (AuNPs) plays a critical factor in thermoelectric properties. We hypothesize that the size, shape, and surface chemistry of the AuNPs influence the total interfacial area, energy, and thickness. To fine-tune these interfacial properties, we used an ex-situ approach to precisely control the shape (prisms, rods, spheres) and volume fraction of AuNPs in PEDOT:PSS@AuNP films. SEM images revealed that this method enables reproducible control over the volume fraction of AuNPS, and surface enhanced Raman spectroscopy (SERS) provided additional details about the chemical composition of the interface.

UN-ThP-33 Stabilization of Amidines and Imidoyl Amidine Ligands*, A. Peoble, **Michaela Martinez**, R. Castañeda,* New Mexico Highlands University

Imodylamidines are prospective nitrogen-based ligand frameworks with the opportunity to adopt two chelate coordination modes, bidentate and tridentate. These coordination modes are advantageous for binding to various metal ions, by which multiple applications can be derived. Among such possible applications, imodylamidines can be used as a starting material in Magnetic Resonance Imaging (MRI) contrasting agents. Our research focuses specifically on the synthesis of N-2-pyridylimodyl-2-pyridylamidine (Py_2ImAm), and N-2-pyrimidylimodyl-2-pyrimidylamidine (Pm_2ImAm) and its metastable form N-2-pyrimidylamidine (Pm_2Am). All three ligands have been successfully synthesized, however, only Py_2ImAm is a stable compound. Pm_2ImAm and Pm_2Am decompose over time, which hinders the possibilities of large-scale production, long-term storage, and overall utilization. As such, we are currently investigating stabilization procedures for Pm_2ImAm and Pm_2Am, one of which is transforming the ligands into stable salts. Thus far, we have been successful in synthesizing a stable discrete-hydrogen bond dimer with trifluoroacetic acid and Pm_2Am. Currently, we are attempting other possible anions for the stabilization of these ligands as salts, while also testing their solubility and stability.

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