Surface Science Division
Room Ballroom A - Session SS-TuP
Surface Science Poster Session

SS-TuP-1 Monolayer Functionalization of Semiconductor and Metal Oxide Surfaces with Boron-Containing Precursors*, Dhamelyz Silva Quinones*, *C. Byron, A. Teplyakov,* University of Delaware

The monolayer functionalization reactions of Si (100) single crystal with boron-containing compounds, including boron trichloride, boric acid, and 4-fluorophenylboronic acid were studied in order to understand the interactions of these molecules with hydrogen and chlorine terminated-Si (100) for designing possible silicon doping processes. This study was compared with the surface modification of TiO_2 and Al_2O_3 nanoparticles with 4-fluorophenylboronic acid in solution in order to understand the attachment chemistry and to develop spectroscopic labels for surface characterization.

The modification chemistry was followed by X-ray photoelectron spectroscopy (XPS), solid-state NMR (ss-NMR), and infrared spectroscopy to determine the binding modes of the attached compound. Density functional theory was utilized to supplement the analysis, interpret the results of spectroscopic measurements, and to interrogate the surface stability of possible surface species.

The results obtained in these studies confirm the attachment of the boron trichloride, boric acid, and 4-fluorophenylboronic acid showing selectivity for the Cl-terminated Si (100) surface compared to H-terminated Si (100).

The attachment chemistry of 4-fluorophenylboronic acid on the TiO_2 and Al_2O_3 nanoparticles was confirmed with a high coverage and the type of attachment on each metal oxide surface is described.

This work provides fundamental understanding and a new pathway to obtain functionalized flat and nanoparticulate surfaces with boron-containing molecules. In the case of flat surfaces, these reactions can be used for selective-area monolayer doping or as a deposition resist. For oxide nanomaterials, the same approach can be used for spectroscopic labeling or for further functionalization.

SS-TuP-2 Detection of Chemically-induced Hot Electron Flux Amplified by Plasmonic Effect on Pt/Ag/TiO_2 Nanodiodes*, Mincheol Kang*, *B. Jeon, J. Park,* Korea Advanced Institute of Science and Technology (KAIST) & Institute for Basic Science (IBS), Republic of Korea

Concern about the energy resource crisis has encouraged study of the conversion and utilization of solar energy to improve catalytic efficiency, and the design of the surface plasmon-based photocatalyst is attracting particular attention as a competitive catalyst system. In this work, catalytic devices based on Schottky nanodiodes (Pt/Ag/TiO_2) were fabricated for antenna-reactor plasmonic photocatalysis; hot electrons generated during the chemical reaction can be directly detected through the diodes. In this system, the surface temperature was measured using thermovision to distinguish contributions of the plasmonic effect and the photothermal heating effect. When the light of the particular wavelength region is incident on the diodes, the flow of reaction-induced hot electrons (chemicurrent) and the catalytic activity (turnover frequency) are amplified by the plasmonic effect. Plasmonic photocatalytic performance can be controlled with light wavelengths, light intensity, surface temperature, and structures of nanodiodes. Also, the plasmonic effect is exhibited visually, using the finite difference time domain simulations. These results elucidate the hot electron flow on antenna-reactor photocatalysis and offer improved strategies for efficient catalytic devices.

SS-TuP-3 Boosting Hot Electron Generation and Catalytic Performance by Engineering Metal-Oxide Interfaces*, Kyoungjae Song*, *J. Park,* Korea Advanced Institute of Science and Technology (KAIST) & Institute for Basic Science (IBS), Republic of Korea

The interface between catalytic metal and oxide support is an important factor that affects reaction performance. However, metal-oxide and oxide-oxide interface studies have been limited, because of the complex structure of metal-oxide-oxide interface. To investigate the influence of the complex interfaces on both catalytic performance and hot electron flux, we used an inverse oxide-metal Schottky diode from CeO_2/ $\text{Co-}_3\text{O}_4$ nanocubes (NCs) on Pt film, which measures hot electron flux and reaction rate under an exothermic methanol oxidation reaction. Turnover frequency (TOF), partial oxidation selectivity, and hot electron flux were obtained on CeO_2/ $\text{Co-}_3\text{O}_4$ NCs on Pt film; TOF was higher by a factor of 2,selectivity to methyl formate was higher by a factor of 1.5, and chemicurrent yield was higher by a factor of 7 compared to Co_3O_4 NCs on Pt film. Furthermore, the Co_3O_4 NCs half covered with CeO_2 showed higher values of both TOF and selectivity to methyl formate than CeO_2 NCs and Co_3O_4 NCs fully covered with CeO_2, indicating that the Co_3O_4/CeO_2 interface also affects the catalytic reaction. From ex situ XPS analysis, CeO_2-$\text{Co-}_3\text{O}_4$ on Pt film showed the highest proportion of Ce^{3+} ions compared to both CeO_2 NCs and Co_3O_4 NCs fully covered with CeO_2 nanoparticles. The result indicate that CeO_2 can not only prevent the reduction of Co_3O_4 by supplying oxygen, but also boosts the methanol oxidation reaction by supplying oxygen to Pt film, leading to enhanced hot electron flux.

SS-TuP-4 Effect of Water Vapor on Oxidation Process of Cu(111) Surface and Sublayer; Ambient Pressure STM and XPS Studies*, Youngjae Kim*, *D. Kim, Y. Kim,* Korea Advanced Institute of Science and Technology (KAIST) & Institute for Basic Science (IBS), Republic of Korea*; Y. Jeong,* Institute for Basic Science (IBS), Republic of Korea*; B. Jeong,* Korea Basic Science Institute (KBSI), Republic of Korea*; J. Park,* Korea Advanced Institute of Science and Technology (KAIST) & Institute for Basic Science (IBS), Republic of Korea

Copper-based materials are used for heterogeneous catalytic reactions, including CO oxidation, low-temperature water gas shift reactions, and CO_2 hydrogenation. These applications could benefit from a better understanding of the transitions between copper-based oxidation states, metallic Cu, Cu_2O, and CuO. In this work, we directly observed different oxidation processes on a Cu(111) single crystal, using ambient pressure scanning tunneling microscopy (AP-STM) and X-ray photoelectron spectroscopy (AP-XPS). The Cu(111) surface started to be oxidized at 0.01 Torr of pure O_2 under dry oxidation conditions. Time-lapse AP-STM and AP-XPS results showed that dry oxidation started at the step-edges in the form of adsorbed oxygen atoms, $O_{(ad)}$, and progressed to the terrace in the Cu_2O phase. In addition, independent oxidations on the metallic Cu(111) terrace provided a more collapsed Cu_2O/Cu(111) surface structure. Under H_2O/O_2 mixed gas conditions, the humid oxidation of the Cu(111) surface occurred at 0.02 Torr. Time-lapse AP-STM images demonstrated that the oxidation also proceeded from the step-edges to the terrace, but there were no independent oxidations on the terrace, leading to fewer defect sites on the Cu_2O/Cu(111) surface. Time-lapse AP-XPS results showed that the appearances of $O_{(ad)}$ and Cu_2O peaks were similar to dry oxidation. Hydroxides were observed after the surface was completely saturated by the Cu_2O phase. Furthermore, by analyzing the relative intensity and peak area of XP spectra, we found that the depth of Cu_2O differed dramatically in the dry and humid oxidation processes. The Cu_2O thickness of the dry oxidation was greater than that of the humid oxidation under all similar pressures. Water molecules from the humid oxidation caused a different oxidation mechanism from the dry oxidation, with a different degree of oxidation.Specifically, the water vapor molecules inhibited sublayer oxidations, inducing less coverage of the step-edges on the Cu(111) surface than under the dry oxidation conditions.

SS-TuP-5 Phase-Dependence on the Friction of Exfoliated MoX_2 (X:S, Te) Layers*, Dooho Lee*, Korea Advanced Institute of Science and Technology (KAIST) & Institute for Basic Science (IBS), Republic of Korea*; H. Jeong,* Korea Advanced Institute of Science and Technology, Republic of Korea*; H. Lee,* Korea Advanced Institute of Science and Technology (KAIST) & Institute for Basic Science (IBS), Republic of Korea*; Y. Kim,* Korea Advanced Institute of Science and Technology, Republic of Korea*; J. Park,* Korea Advanced Institute of Science and Technology (KAIST) & Institute for Basic Science (IBS), Republic of Korea

Transition metal dichalcogenides (TMDs) 2-dimensional (2D) material is widely studied for its semiconducting nature, which makes it potentially suitable for applications in thin-film transistors.[1] Among TMDs, the molybdenum disulfide (MoS_2) monolayer is an atomically thin semiconductor with a bandgap of 1.8 eV. MoS_2 is also getting attention as an anode for Li-ion batteries, because of its Li intercalation mechanism. Electron donations from Li induce a MoS_2 phase transition from the stable semiconducting 2H phase to the metallic 1T phase. While MoS_2 chemically exfoliated with Li showed friction at a similar level with mica, mechanically exfoliated MoS_2 exhibits significantly lower friction than mica.[2]

We turned mechanically exfoliated 2H-MoS_2 into 1T-MoS_2 by a lithiation process and measured atomic-scale tribological and electrical properties of MoS_2, including friction, with atomic force microscopy (AFM). We report that the friction of MoS_2 increased significantly with the phase transition of 2H to 1T. The friction proportion of 2H-MoS_2 and 1T-MoS_2 is 0.12:1.07, with normalization to the value of mica. We also measured the friction of molybdenum ditelluride ($MoTe_2$), of which the pure 1T phase is commercially available, since it shows a stable 1T phase as well as a 2H phase. The friction proportion of exfoliated 1T-$MoTe_2$ and 2H-$MoTe_2$ is 0.18:1.09, normalized with the friction of mica. With density functional theory (DFT) calculation, we attribute the higher friction of 1T-MoX_2 to the increased overlap of phonon density of states (DOS) with mica substrate, as well as the higher energy barrier in the potential energy surface of 1T-MoX_2. The study suggests the intriguing possibility of tuning friction by a phase transition of 2D materials.

References

[1] G. Lee, et al. ACS Nano 2013, 7, 7931-7936.

[2] D. Lee, et al. The Journal of Physical Chemistry C 2020, 124, 16902-16907.

SS-TuP-6 Electron Dynamics at a Confined $Cu_{2-x}O$/Cu Interface*, J. Trey* ***Diulus****, J. Beckord, Z. Novotny, N. Comini, M. Hengsberger, J. Osterwalder,* University of Zurich, Switzerland

Cuprous oxide (Cu_2O) is a promising photocathode material for the hydrogen evolution reaction (HER) due to its bandgap in the visible spectrum, relative abundance, and low cost. However, Cu_2O is unstable in aqueous solutions. To increase the corrosion resistance, a chemically stable capping layer, such as hexagonal boron nitride (*h*-BN), can be deposited on the Cu_2O surface. While the growth of *h*–BN on top of non-metallic oxides by chemical vapor deposition is difficult, one approach is to oxidize a Cu metal substrate underneath an *h*-BN monolayer via O_2 intercalation. This preparation method was implemented by exposing a Cu(111) single crystal with an h-BN monolayer to partial pressures of O_2 up to the millibar range at temperatures up to 200 °C. The atomic structure was unraveled with a combination of surface science techniques at the Swiss Light Source. The h-BN layer remains intact and the $Cu_{2-x}O$ oxide film has a thickness of a few atomic layers (3-4 Å) displaying structural motifs typical of the $Cu_2O(111)$ surface, comprising a chemisorbed O layer and a $Cu_{2-x}O$-like trilayer positioned in between the h-BN and the substrate. A well-ordered *h*–BN/$Cu_{2-x}O$/Cu(111) sample was prepared for characterizing the electronic structure and electron dynamics with ultraviolet and pump-probe photoemission spectroscopy. Angle-resolved photoelectron spectroscopy (ARPES) after oxidation shows the sharp σ and π bands of an intact *h*-BN monolayer and another narrow state 1.2 eV below the Fermi level, attributed to the valence band of Cu_2O that is shifted downwards due to the contact to a metallic copper substrate. Time-resolved two-photon photoemission (tr-2PPE) spectra show a short-lived state at 1.0 eV and a long-lived state at 0.1 eV above the Fermi level. The state at about 1 eV has a strong parabolic dispersion matching the conduction band of Cu_2O, whereas the low energy state has no dispersion, pointing towards a localized defect state of the $Cu_{2-x}O$ layer. Such defect states were also observed on the reconstructed bulk $Cu_2O(111)$ surface and were attributed to charged oxygen vacancy states with very high capture coefficients for trapping conduction electrons. The visible conduction band is promising, but the trapping is detrimental to the function as efficient photocatalyst. To render this system into a viable photocathode, the oxide film should be grown to a thickness adapted to the light absorption length of about 30 nm, and the defect concentration should be further reduced.

SS-TuP-7 Understanding Interfaces to Develop Advanced Materials for Industrial Applications*, **Pierluigi Bilotto Bilotto**, M. Ostermann, D. Miano,* Centre for Electrochemistry and Surface Technology (CEST GmbH), Austria*; M. Valtiner,* Centre for Electrochemistry and Surface Technology (CEST Gmbh), Vienna University of Technology (TUW), Austria

Industries eager for innovative solutions to strike against the climate crisis. For instance, that translates into developing innovative composites material expressing multifunctionalities, reduce the energy produced because of wearing via green solid lubricant, or for instance optimizing yield and efficiency of industrial processes.

The poster will summarize the projects and results obtained at the Centre for Electrochemistry and Surface Technology (CEST, Austria) in the *material and interfaces* research areas for application in aeronautical, aviation and semiconductor industries. Specifically, we propose a clean and upscalable process for the production of graphene oxide, [1] which will be used for advanced coatings expressing de-icing, lightning strike protection and corrosion functionalities. Moreover, for the *interface* area we will show our strategies to elucidate the tribological mechanisms of MXenes based solid lubricant, and the utilization of nanobubbles to optimize wafer cleaning processes.

(1) Ostermann M. *et al* – (submitted in May 2022)

SS-TuP-8 Investigation of CO Oxidation on Rh(111) with IRRAS*, **Faith Lewis**, D. Killelea,* Loyola University Chicago

Fourier-transform Infrared (FTIR) spectroscopy is widely applied to identify small molecules adsorbed to metal surfaces. Here, FTIR was coupled to an ultra-high vacuum (UHV) system where the sample environment was carefully controlled to eliminate interference from atmospheric species. IR reflection measurements from a metal surface were performed under UHV conditions and the catalytic oxidation of carbon monoxide (CO) to carbon dioxide (CO2) over Rh(111) was investigated. This reaction was used as a probe reaction to determine the relative reactivity of various oxidic species. We determined the binding sites on different oxygenaceous phase and determined their chemical significance towards heterogeneously catalyzed oxidation of CO. This provided atomic level information regarding oxidation reactions, and advanced our understanding of the different surface phases relevant to many Rh catalyzed processes.

SS-TuP-9 Modifications of Surface Optoelectronics in ZnO Nano- and Microcrystals Following Exposure to *Staphylococcus Aureus* and Bacterial Growth Media*, **Dustin Johnson**,* Texas Christian University*; J. Reeks,* INSTITUTE OF LOW TEMPERATURE AND STRUCTURE RESEARCH - POLISH ACADEMY OF SCIENCES, Poland*; A. Caron,* Texas Christian University*; I. Tzoka,* University of Texas at Arlington*; O. Castillo, K. Nguyen,* Paschal High School*; M. Hattarki,* Rice University*; S. McGillivray, Y. Strzhemechny,* Texas Christian University

A combination of useful optoelectronic properties and high biocompatibility rendered ZnO a versatile material with budding applications at the nano- and microscale, among which are pharmaceutics, bioengineering and medical diagnostics, specifically employing ZnO as an antibacterial agent. With bacterial growth inhibition observed for both gram-positive and gram-negative bacteria as well as antibiotic strains, the antimicrobial action of ZnO is both promising and well documented. Yet application is significantly hindered due to uncertainty regarding fundamental mechanisms underlying such properties. Presently, discussion centers on several proposed mechanisms, such as generation of various reactive oxygen species, Zn ion release and surface-surface interactions between the bacterial cell wall and free crystalline surface. Here we investigate surface and near-surface modifications of optoelectronic properties in ZnO microcrystals following exposure to bacterial environments to elucidate those specific mechanisms. Microscale ZnO crystals are well-suited to serve as a platform to investigate the role played by crystalline surfaces as they exhibit comparable antibacterial action to nanoscale forms while minimizing effects of internalization. A bottom-up hydrothermal growth method allows for controlled synthesis of high-quality ZnO microcrystals with tunable morphology and controllable relative abundance of polar vs. non-polar surfaces. The quality of crystalline lattice and free surface as well as the predominant morphology of these samples are confirmed by FE-SEM, EDXS, and surface photovoltage (SPV) studies. The antimicrobial efficacy of these particles is characterized by minimum inhibitory concentration assays, utilizing wild type *s. aureus* in Mueller Hinton broth media. A series of optoelectronic experiments including temperature-dependent PL spectroscopy as well as spectroscopic and transient SPV are performed to probe changes occurring at ZnO surfaces during such assays. These comparative studies reveal that antibacterial action of ZnO microparticles is primarily rooted in interactions between crystalline surfaces and extracellular material of the bacteria. This is supported by observed degradation of the crystal surface and significant spectral changes due to surface interactions with bacteria and growth media. We show that interaction with *s. aureus* results in considerable change to the excitonic structure of the ZnO microcrystals. We also demonstrate dependence of such interactions on growth media, specifically those containing aqueous phosphates, finding not only changes in bactericidal efficacy but also the nature of these interactions.

SS-TuP-10 A Potential Model for Investigating the Edge Properties of FeO by Taking Advantage of Different Metal Affinities*, **Dairong Liu**, L. Li, S. Mahapatra, N. Jiang,* University of Illinois - Chicago

As a series of catalysts with wide catalysis applications and high economic efficiency, iron oxide has caught extensive attraction in the past several decades. During the various types of iron oxide, the FeO, well known as Ferrous oxide, has been proved to have high catalysis reactivities in catalysis reaction, e.g. CO catalysis oxidation. To obtain a throughout understanding of the catalysis mechanism, it is vital to investigate the surface and edge properties of FeO. In the past decade, various techniques have been applied the reach the surface properties of FeO, the researchers found that the edge of FeO plays an important role in the initial CO oxidation. However, due to the limit of the characteristic technique, the specific edge properties of FeO are still under debate. Here, we established a model, to selectively expose the distinguished type of edges on FeO. By taking advantage of the different metal affinities of the O-edge and Fe-edge in FeO, the Pd and Pt are introduced and found to selectively block the distinguished edge. The blocked edges are expected to be excluded from the catalysis reaction, which means that in the reaction, only the unblocked type of edge will be involved. By further comparison of the different performances of Fe-edge and O-edge selective exposed samples, the roles of different types of edge in the catalysis reaction can be studied, which can give an insight into the edge properties of the FeO and contribute to the design of high-efficiency FeO catalyst.

SS-TuP-11 Effects of Thermal Atomic Layer Etching on the Magnetic Properties of CoFeB*, **Marissa Pina**, M. Konh, Y. Wang, J. Xiao, A. Teplyakov,* University of Delaware

Atomic layer etching (ALE) is emerging as a major approach to control feature size of modern devices at the atomic scale. Thermal approaches are especially important for expanding the capabilities into the 3rd dimension and approaching more-than-Moore technology. However, for complex materials that are used in spintronics and magnonics, developing thermal ALE methods is difficult because the materials often contain several elements, some of the elements have not been investigated for ALE, little control over the surface properties of the resulting films is established, and their effect on the physical properties of the device (such as magnetic properties) has not been investigated. This work will interrogate the chemistry of thermal ALE of CoFeB alloys used in the magnetic tunnel junction and present an investigation of the effect of this chemistry on the magnetic properties of thin films. The effect of a half-cycle of chlorination and a full cycle of exposure to chlorine and acetyl acetone will be compared for films of comparable thickness produced by multiple ALE cycles and by ion milling. The effect of chemistry and surface smoothing will be evaluated based on a comparison of surface characterization by atomic force microscopy and XPS with the outcomes of ferromagnetic resonance measurements. Further pathways for controlling the effects of ALE on the physical properties of thin films prepared from different materials will be proposed.

SS-TuP-12 The Diamond (111) Surface Reconstruction and Epitaxial Graphene Interface*, **Benjamen Reed,*** National Physical Laboratory, UK*; M. Bathen,* ETH Zurich, Switzerland*; J. Ash,* Aberystwyth University, UK*; C. Meara,* Newcastle University, UK*; A. Zakharov,* Max IV Laboratory, Sweden*; J. Goss,* Newcastle University, UK*; J. Wells,* University of Oslo, Norway*; D. Evans,* Aberystwyth University, UK*; S. Cooil,* University of Oslo, Norway

There is rejuvenated interest in (111)-orientated diamond as a state-of-the-art electronic material, especially for quantum information and sensing applications, and its nanoscale properties for the production of diamond-graphene interfaces. However fundamental studies of the diamond (111) surface remain incomplete and there is an unresolved controversy surrounding the electronic nature of the C(111)-(2×1) surface. Density functional theory (DFT) calculations predict symmetrically π-bonded surface chains that exhibit a metallic surface state that intersects the Fermi level (E_F),[1,2] but experimental angle-resolved photoemission spectroscopy (ARPES) studies have shown a semiconducting surface (ΔE = 0.5 eV) that corresponds to a dimerized π-bonded surface chain model.[3,4]

Our combined ARPES and DFT results show that the C(111)-(2×1) surface is metallic as it has electronic states that intersect E_F. This is in strong agreement with a symmetrically π-bonded chain model and should contribute to resolving the controversies that exist in the literature surrounding the electronic nature of this surface. Above 1000°C in vacuo, the reconstructed surface atoms are liberated into a free-standing monolayer of epitaxial graphene which exists above a newly formed C(111)-(2×1) surface and appears to have little substrate interaction as the Dirac-point is observed at E_F. We also demonstrate that is possible to hydrogen terminate the underlying diamond surface by means of plasma processing without removing the graphene layer, forming a graphene-semiconductor interface.[5]

[1] W.G. Schmidt, A. Scholze, F. Bechstedt, *Surf. Sci.* **351**, 183 (1996).

[2] F. Bechstedt, A. A. Stekolnikov, J. Furthmüller, and P. Käckell, *Phys. Rev. Lett.* **87**, 016103 (2001).

[3] F. J. Himpsel, D. E. Eastman, P. Heimann, and J. F. van der Veen, *Phys. Rev. B* **24**, 7270 (1981).

[4] R. Graupner, M. Hollering, A. Ziegler, J. Ristein, L Ley, and A Stampfl, *Phys. Rev. B* **55**, 10841 (1997).

[5] B. P. Reed, M. E. Bathen, J. W. R. Ash, C. J. Meara, A. A. Zakharov, J. P. Goss, J. W. Wells, D. A. Evans, and S. P. Cooil, *Phys. Rev. B* **105**, 205304 (2022).

SS-TuP-13 The Nature of Electrical Double Layer Near Graphene and Anatase*, **Xiao Zhao**, S. Yang, M. Salmeron,* LBNL

Structure and profiles of electrical double layer (EDL) govern many electrochemical reactions. Fundamental knowledge of EDL is based on simplified Gouy-Chapman and Stern model, in which solvation and specific interactions of the electrolyte ions with the electrode are neglected. Here we present our recent progress determining the EDL structure near substrate-free graphene and near thin anatase films using Raman, Sum Frequency Vibrational Spectroscopy (SFVS), Kelvin Probe Force Microscopy (KPFM) and Near Edge X-ray Absorption Fine Spectroscopy (NEXAFS). Near suspended graphene SO_4^{2-} anions were found to preferentially accumulate near the interface at open circuit potential (OCP), creating an electrical field that orients water molecules below the interface while no such increase was observed with Cl^-. The degree of orientation of the water molecules as well as the electrical double layer strength increased further when positive voltages are applied. Negative voltages on the other hand produce smaller changes in the intensity of the H-bonded water peaks, but affect the intensity and frequency of the dangling O-H bond peaks. Near anatase ice-like water layer has been observed using SFVS and NEXAFS, and different segregation behavior has been observed for Na^+ and Cl^- under both OCP and applied bias. Our findings demonstrate the effect of solvation n and electrode-ion interactions on EDL structure and call for theoretical insight in this direction.

SS-TuP-14 Reactions of Tetrakis(Dimethylamido)Titanium on Halogenated, Hydrogenated, and Oxidized Silicon Monolayer Resists for Atomic Layer Deposition*, **Tyler Parke**, D. Silva-Quinones, A. Teplyakov,* University of Delaware

In atomic layer deposition (ALD) of TiO_2 with titanium tetrachloride ($TiCl_4$) and water, silicon (100) substrates with atomic chlorine (Cl-Si) or hydrogen (H-Si) terminations have previously been shown to be non-growth surfaces, resisting adsorption of and reaction with $TiCl_4$, as opposed to reactive oxidized silicon (HO-Si) growth surfaces, upon which $TiCl_4$ readily deposits. However, Cl-Si(100) degrades and loses selectivity rapidly under ALD conditions, leading to $TiCl_4$ nucleation on oxidized surface sites. In contrast, tetrakis(dimethylamido)titanium (TDMAT) follows a different reaction pathway on Si(100) surfaces, implying a difference in TDMAT's surface selectivity on silicon terminated with chlorine or perhaps other halogens, as well as a difference in the mechanism and extent of the selectivity loss. Here, the reactivity of TDMAT was studied under ALD conditions with oxidized, halogenated, and hydrogenated Si(100) surfaces. TiO_2 deposition was monitored on each surface using *ex situ* X-ray photoelectron spectroscopy (XPS). The initial nucleation behavior in the first few ALD cycles was compared between each surface using atomic force microscopy (AFM). Details of the bonding of TDMAT to the surface were elucidated using spectroscopic data in conjunction with density functional theory (DFT) observables on models of local surface geometry to propose surface reaction pathways.

SS-TuP-15 A 2D Bismuth-induced Honeycomb Surface Structure on GaAs(111)*, **Yi Liu**, S. Benter,* Lund University, Sweden*; C. Ong, R. Maciel, O. Eriksson,* Uppsala University, Sweden*; A. Mikkelsen, R. Timm,* Lund University, Sweden

Bi-containing III-V semiconductors are of significant interest due to their superior charge carrier mobility, tunable direct band gap, large spin-orbit splitting, and predicted non-trivial topological behavior. This is relevant for realizing quantum information technology due to a large flexibility in material combinations and a potential for room-temperature operation. However, the realization of ordered, crystalline alloys with high Bi content remains a challenge. Epitaxial growth of III-V films only allowed dilute compounds with very low Bi atom incorporation, while surface evaporation has typically demonstrated Bi metallic films on top of the semiconductor surfaces. Instead, formation of ordered 2D semiconducting III-V:Bi films remains a desired alternative.

Here, we present the successful Bi incorporation into a clean GaAs(111)B surface, based on Bi deposition under optimized growth conditions. Atomically resolved low-temperature scanning tunneling microscopy and spectroscopy (LT-STM/S) shows a well-ordered large-scale honeycomb structure, consisting of Bi atoms in a √3×√3 30° reconstruction on GaAs(111). An almost defect-free, large-scale honeycomb structure is obtained after short anneal. X-ray photoelectron spectroscopy proves the successful incorporation of Bi atoms in the GaAs surface and shows that the Bi atoms of the honeycomb structure only bond to the underlying As atoms. This is supported by density functional theory calculations which confirm the honeycomb structure, including a preferential formation of Bi-As bonds, and predict Bi-induced electronic bands within the GaAs band gap that open up a gap of non-trivial topological nature. STS results support the existence of Bi-induced states within the GaAs band gap.

The ordered Bi-induced 2D layer with a high Bi content of up to 67% surface coverage, covalently bonded to the GaAs substrate, and indications for non-trivial topological behavior is a great step towards realizing III-V semiconductor heterostructures with high Bi content that make use of the large spin-orbit coupling of Bi for enabling novel electronic properties. Furthermore, this result is a successful example for Bi-introduced low-dimensional structures with unique electronic states in III-V semiconductor systems.

SS-TuP-16 Hydrochloride Production from Dichlorosilane Decomposition and Its Impact on Atomic Layer Deposition of Silicon Nitride,

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Plasma-enhanced atomic layer deposition (PEALD) has been demonstrated to be a promising technique for the controlled growth of silicon nitride (SiN) thin films. The advantages of PEALD include excellent conformality, precise thickness control, and high quality at relatively low temperatures. In this talk, we will present molecular mechanisms underlying the PEALD of SiN thin films using dichlorosilane (DCS) as the Si source and N_2/NH_3 plasma as the N source. The adsorption and decomposition of DCS have been found to be sensitive to the surface functional groups; especially, the presence of primary amines plays a critical role in the silicon deposition half cycle. According to our recent studies, the by-products of DCS decomposition, H^+/Cl^- pairs, may have a significant effect on the film quality and deposition temperature. First-principles calculations predict that H^+/Cl^- pairs are strongly bound to the H-terminated N-rich surface by forming –NH_3^+/Cl^- ionic complexes. Because of the sizable binding energy (~ 1 eV), it would be difficult to remove H^+/Cl^- pairs from the surface unless the PEALD temperature is substantially high. This implies that the reaction of DCS with surface primary amines, and in turn SiN ALD, can be significantly suppressed by the presence of H^+/Cl^- pairs at relatively low temperatures. The existence of H^+/Cl^- has been confirmed by FTIR measurements which shows two distinctive peaks at 1420 and 2800 cm^{-1}.

SS-TuP-18 Enhancing Fiber-Coupled Thermal Emission Collection Using IR Plasmonic Coating,

***Aman Patel**, R. Kayastha, K. Agyepong, B. Birmingham, Z. Zhang,* Baylor University

Current thermal emission measurement devices have made significant strides in the past few decades but with the current progress of technology towards smaller scale systems, the spatial resolution capabilities of current devices have become inadequate as they utilize the far field emission. The near field emission has orders of magnitude larger signal intensity compared to the far field emission. Current techniques like near field scanning optical microscopy (NSOM) collect the near field emission to improve spatial resolution but remain susceptible to low signal-to-noise ratio. In this experiment, we use titanium nitride (TiN) as an IR-plasmonic coating to enhance the near-field thermal emission collection. Optical fibers were etched to produce different tip geometries, coated with TiN using directed thermal vapor deposition, and put into a furnace to conduct thermal measurements at various temperatures. The collected thermal emissions using the fiber probes before and after TiN coating were compared to analyze the collection of the near field emission. The performance of the plasmonic TiN thin film was compared with a traditional plasmonic metal Au, at temperatures below 600ºC. An increase in signal intensity of the collected thermal emission was observed for fiber tips coated with TiN and with Au. Probes with different TiN coating thicknesses and different tip geometries have been tested to develop a thermal probe with an improved signal-to-noise ratio. The thermal probe is integrated into an NSOM setup, for nanoscale thermal measurements for samples.

SS-TuP-19 The Effects of Surface Treatments on the Nucleation and Growth of Ruthenium on Tantalum Nitride,

*C. Feit, U. Kumar, N. Berriel, **Luis Tomar**, S. Seal, P. Banerjee,* University of Central Florida

Ruthenium (Ru) has emerged as an alternative to copper interconnects acting as a diffusion barrier, leading to improved electromigration. Atomic layer deposition is widely used for high-quality, ultra-thin film deposition. However, the deposition of ultra-thin Ru films is challenging. Current Ru ALD processes exhibit island-like grow and long nucleation delays, driven by the surface reactions among sterically bulky precursors, oxidation state of the metal center, and wettability of the substrate. Due to poor nucleation of ruthenium on industrially relevant tantalum nitride (TaN) surfaces, surface engineering is required to reduce Ru liners to competitive widths.

This work examines the effects Ru nucleation and growth, using ruthenium dimethyl butadiene tri-carbonyl (Ru(DMBD)(CO)3) and H2O on ultra-violet ozone treatment of TaN. The film nucleation and surface roughness is measured using atomic force microscopy (AFM). The Ru film thickness is measured by spectroscopic ellipsometry. The surface chemistry is investigated using X-ray photoelectron spectroscopy (XPS) and water contact angle measurements. Furthermore, the thermal conductance and electrical conductance confirm enhance film coalescence. Continuous Ru films can be achieved at ~ 2 nm on UV-ozone treated TaN compared to ~5 nm on untreated TaN.

SS-TuP-20 Laser Assisted Thermal Reactivity of Alkanes on Pt(111),

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A molecular-level understanding of heterogeneous reactions on catalytic surfaces remains to be achieved leading to limitations in improved catalyst design. Alkane dissociative chemisorption on transition metal catalyst surfaces (e.g. Pt, Rh, Cu, etc.) is a key elementary step in alkane reforming providing an important model system to understand surface reaction kinetics and dynamics. The reactivity of a gas phase molecule striking a surface can be described by the molecule’s Dissociative Sticking Coefficient (DSC). A DSC describes the probability of a molecule to dissociate on a surface [$RH_{(g)} \leftrightarrow R_{(c)}+H_{(c)}$]. DSCs can be resolved in detail by specifications of temperature (T), energy (E_t, E_v, E_r), and angle (ϑ) of the incident molecules providing enhanced details about the system's kinetics and dynamics. In some instances, DSCs are too small (<10-6) to measure by conventional elemental analysis (Auger Electron Spectroscopy). Instead, it is desirable to study the reactions that produce alkanes in the reverse direction, [$R_{(c)}+H_{(c)} \leftrightarrow RH_{(g)}$]. Laser-assisted thermal associative desorption/Laser activated dissociative desorption (LAAD/LADD) using a 10ns pulsed laser allows for the measurement of the alkane product time-of-flight spectra to a quadrupole mass spectrometer.[1,2] The translational energy distribution, $Pt(E_t)$, of the desorbing alkanes should be identical to the energy distribution of the successfully reacting alkane molecules in the reverse reaction, at the reaction temperature, via the principle of detailed balance.

Implementing this experimental technique required an understanding of the laser’s interaction with a Pt single crystal surface. Theoretical laser induced surface temperature jump calculations were used to predict the surface temperature (T_s) rise caused by the laser at a specific pulse energy and beam size.[3] For a thermal reaction, with an Arrhenius rate constant, under fast laser heating a majority of reactivity occurs at the peak surface temperature such that a quasi-isothermal reactivity at the peak temperature (T_s) is achieved. Theoretical work from the Harrison Group has successfully simulated LAAD experiments for [$CH_{3(c)}+H_{(c)} \leftrightarrow CH_{4(g)}$] on Pt(111)[4] and Ru(0001)[2]. Here we present experimental limits for Nd:YAG laser to avoid surface damage or induce alteration to the desorbing flux. The first implementation of the LAAD/LADD experimental technique in our lab has been to look at the laser assisted thermal desorption of methane [$CH_{4(ad)} \rightarrow CH_{4(g)}$] by measuring the methane $Pt(E_t)$, which is expected to roughly be a flux-weighted Maxwell-Boltzmann distribution at the desorption temperature.

SS-TuP-21 ID31 - High-Energy Beamline at ESRF for Buried Interface Structure and Materials Processing,

***Andrea Sartori**, J. Drnec,* ESRF, France

Complex heterogeneous materials, and their interfaces, inside operating devices can only be studied adequately by combining experimental methods to reveal the interplay between the microscopic material/interface properties and the macroscopic device performances. The need for combining techniques is instrumental in the development of hard x-ray synchrotron methods applied in situ and operando for studying both real devices under operating conditions and idealized model systems under precisely controlled environments.
The high energy beamline ID31 of ESRF, dedicated for studies of buried surfaces and interfaces, enables a portfolio of hard x-ray characterization techniques, including reflectivity, wide angle diffraction both in

transmission and grazing incidence geometry, small angle x-ray scattering, and imaging methods coupled with great versatility in choosing beam sizes (minimum: horizontal 20.0 x vertical 3.0 μm^2, maximum horizontal: 2.0 x vertical 1.0 mm^2), energy range (21.0 – 150 keV) and detectors optimized for high energy x-rays. The design enables many different studies with remarkable potential. More details about the beamline are reported in the supplemental file.

In this contribution we will discuss the design and the capability of the beamline, together with example of in situ experiment in the field of liquid organic hydrogen carrier (LOHC). By using high energy X-Ray diffraction to study the dehydrogenation reaction of benzyltoluene. We investigated, at atomic resolution, a catalyst of single crystal Al_2O_3 sample supporting Pt nanoparticles. The experiments were performed in a custom-made reactor in operando under realistic conditions (260 °C, 1.5 bar). The first results show an increase of the full width half maximum and the shift of the Pt (111) peak suggesting possible formation of a carbide in the nanoparticles surface, extended more than just one monolayer. Further characterization and experiments are in progress.

SS-TuP-22 Modeling Surface Interactions: Methods and Select Applications*, **Sierra Jubin**,* Princeton University*; Y. Barsukov,* Princeton Plasma Physics Laboratory*; I. Kaganovich,* Princeton Plasma Physcis Laboratory

Though molecular dynamics (MD) is a powerful tool for investigating materials properties, one must take great care that the MD potentials properly represent the system of interest. The modeling of surface interactions presents a particularly difficult challenge. MD potentials which reproduce bulk properties may fail to predict energies and geometries related to the adsorption and reaction of atoms and molecules on the surface. For example, our MD simulations showed that bond order MD potentials which have been used to describe amorphous boronized graphite yield highly unrealistic models of boron adsorption on a graphene sheet [1].

For systems where suitable MD potentials are not available or lead to questionable results, the DFTB MD (density functional tight binding molecular dynamics) method might be used. Note that DFTB is a semi-empirical parameterized method, and parameter sets exist for a limited number of chemical systems. Moreover, there is no guarantee that DFTB parameters for a set of elements give the correct structures of all possible compounds consisting of this set of elements. For example, available DFTB parameter sets can describe the geometry of stable NH_3 and HF molecules, but do not predict the existence of salts with an ammonium cation, such as $NH_4^+F^-$ and $NH_4^+HF_2^-$. For such complex systems, the Car-Parrinello MD method can be used rather than DFTB. Another issue with MD methods can occur in chemical reactions proceeding via a significant barrier, because the simulation time required to overcome the barrier may be prohibitively long. Nonetheless, our group has used DFTB MD to successfully explore the formation of BN chains and fulborenes by self-assembly [2].

A powerful method for the study of chemical reactions with large energy barriers is the use of DFT (density functional theory) in conjunction with transition state theory, which can predict the probabilities of elementary steps in surface reactions. Often, the rate of a whole reactions is limited by the rate of the slowest elementary step within that reaction. For example, using DFT modeling we showed that F_2 dissociative adsorption on a fluorinated Si surface leads to Si-Si bond breaking, following a reaction pathway that proceeds over a barrier. Thus, the rate of Si etching by F_2 can be calculated as a function of F_2 partial pressure and temperature. This modeling also demonstrated that the rates of F_2 dissociative adsorption on (111), (110) and (100) oriented Si surfaces are significantly different at room temperature.

[1] S Jubin *et al* 2022 *Frontiers in Physics***10** DOI: 10.3389/fphy.2022.908694

[2] Y Barsukov *et al* 2021 *Nanotechnology***32** 475604 DOI: 10.1088/1361-6528/ac1c20

SS-TuP-24 Deterministic Switching Using Unconventional Spin-Orbit Torques in Atomically Clean WTe_2/FGT Heterostructures*, **Sean Yuan**, I. Kao, R. Muzzio,* Carnegie Mellon University*; J. Edgar,* Kansas State University*; J. Goldberger,* Ohio State University*; J. Yan,* Oak Ridge National Laboratory*; J. Hwang,* Ohio State University*; J. Katoch, S. Singh,* Carnegie Mellon University

Layered materials with low-symmetry crystal structure, such as WTe_2 and $MoTe_2$, are energy efficient spin source materials for spintronics-based memory and logic devices. We will present results showing the fabrication of spin-orbit torque (SOT) switching devices constructed out of vdW based heterostructures with atomically clean interfaces. The sharpness of the interface is essential to suppress interfacial spin dephasing, and thus enhance SOT efficiency for spintronics applications. Here, we present results showing the fabrication of SOT switching devices with atomically sharp interfaces, which we construct to enable SOT-driven deterministic control of a magnet with out-of-plane polarization[1]. This is challenging because deterministic field-free switching of a perpendicularly polarized ferromagnet requires an out-of-plane anti-damping torque, which is typically prohibited due to in-plane crystal symmetries within conventional spin sources. In order to achieve this unconventional SOT form, we exploit the low in-plane crystal symmetries of WTe_2, enabling an out-of-plane SOT component[2,3]. This work is the first step towards realizing all-vdW based spintronic devices that are ultra-thin and have ultra-low power consumption for their operation.

1. Kao, IH., *et al*., *Nat. Mater.* 21, 1029–1034 (2022).
2. D. MacNeill *et al.,Nat. Phys.* 13, 300 (2017)
3. F. Xue *et al.,Phys. Rev. B* 102, 01440 (2020)

SS-TuP-25 Preparing and Characterizing Thin Hexagonal Boron Nitride Flakes for Creating Spin Defects*, **Seth Eisenberger**, I. Kao, R. Muzzio, J. Katoch, S. Singh,* Carnegie Mellon University

Spin defects in layered van der Waals systems, such as hexagonal boron nitride (h-BN), is an appealing platform for quantum sensing. In this work, we will discuss the preparation and characterization of atomically thin flakes of h-BN using different experimental methods including Raman spectroscopy and atomic force microscopy. We have successfully coupled h-BN flakes to on-chip micro coplanar waveguides and have created atomic defects in h-BN using high energy ion implantation. We will also discuss methods for transferring h-BN flakes onto scanning transmission electron microscopy grids for characterizing these defects.

SS-TuP-26 Visualizing the Electronic Structure of Multiple Twisted Bilayer Graphene Domains*, **Indra Periwal**, R. Muzzio,* Carnegie Mellon University*; C. Jozwiak, A. Bostwick, E. Rotenberg,* Lawrence Berkeley National Laboratory*; S. Singh, J. Katoch,* Carnegie Mellon University

Twisted two dimensional (2D) heterostructures have emerged as a novel way to modulate the physical properties of matter, the most famous of which is the unconventional superconductivity in twisted bilayer graphene (twBG). It is therefore essential to determine the evolution of twisted bilayers as we vary the twist angle. In this study, we employ nano-focused angle resolved photoemission spectroscopy (ARPES) to investigate twBG over a wide range of twist angles. We will discuss the heterostructure fabrication, momentum-resolved measurement, and 4-dimensional analysis of our sample which contains various twBG domains. Each domain contains a different twist angle and we will discuss the implications of the change in the electronic structure.

SS-TuP-27 Angle-Resolved XPS Analysis of the Oxidation of Ru Thin Films*, **Shivan Antar**, A. Valenti, R. Wheeler, C. Ventrice,* SUNY Polytechnic Institute*; M. Strohmayer, J. Brewer, C. Nassar, C. Keimel,* Menlo Micro

Ruthenium is often used as an electrical contact material because of its resistance to oxidation at elevated temperatures. In addition, the most stable stoichiometry of ruthenium oxide under ambient conditions is RuO_2, which is an electrically conductive oxide. The goal of this study is to determine the stoichiometry and measured thickness of the surface oxide on Ru formed by various and typical semiconductor fabrication processing techniques such as reactive ion etch, plasma ashing processes, silicon dioxide depositions, and annealing in various environments. The primary analysis technique used for this study is X-ray photoelectron spectroscopy (XPS). The Ru thin films were deposited on SiO_2/Si(100) substrates. Angle-resolved XPS data were collected at takeoff angles of 10°, 20°, 30°, 40°, 50°, and 60°, where the takeoff angle is measured from the plane of the surface. The acceptance angle of each of the angle-resolved measurements was 10°. Angle-integrated XPS data were collected at a takeoff angle of 45° and acceptance angle of 40°. Analysis of the Ru-3d XPS spectrum of the as-grown Ru film indicates that the native oxide is in a 2+ state and is less than a nm thick. Annealing at atmosphereic pressure results in the formation of Ru in a 4+ state (RuO_2) at the surface that is ~2 nm thick. In addition, the presence of higher order oxides and surface carbon is detected after the anneal. Performing either a RIE or ash process on the as-deposited Ru film also results in the formation of RuO_2 but with a thickness of ~1 nm. Higher order oxides (RuO_x) and carbon are also present in the surface region after these processing techniques have been performed but at a lower surface concentration than the sample annealed in air. Analysis of the O-1s XPS spectra of the samples indicates the presence of an ~1 nm thick water layer on top of each sample during the measurements.

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