

## 2D Materials

### Room Central Exhibit Hall - Session 2D-ThP

#### 2D Materials Poster Session

##### **2D-ThP-1 Discretized Atomic Layer Deposition Recipe for Wafer-scale Synthesis of MoS<sub>2</sub>**, *S. Shendokar, Shyam Aravamudhan*, North Carolina A&T State University

Monolayer MoS<sub>2</sub>, a 2D material, holds enormous promise for transcending the fundamental limits of silicon-based electronics and continuing the downscaling of transistors and logic circuits for energy-efficient computing. However, major research efforts are needed to overcome many fabrication and integration challenges including wafer-scale growth control, doping, contacts, gate stack, and reliability. In this work, we attempt to address one of the challenges, namely wafer-scale synthesis of MoS<sub>2</sub>. Atomic Layer Deposition (ALD) is one of the most promising techniques for wafer-scale growth of MoS<sub>2</sub> due to its conformal, self-limiting, and low-temperature characteristics. We present here a novel discretized ALD recipe for wafer-scale deposition of uniformly thick MoO<sub>3</sub>, further, to sulfurized to stoichiometric MoS<sub>2</sub>. This is an alternative approach for ALD to determine temperature and time based on the Arrhenius equation and first-order reaction kinetics. Wafer-scale uniformity, film morphology, composition and crystallinity were measured using a comprehensive set of characterization techniques including ellipsometry, AFM, XPS, Raman, XRD and Photoluminescence measurements.

##### **2D-ThP-2 Topotactical Reaction of NiTe<sub>2</sub> Films with Excess Ni**, *Nirosha Rajapakse, M. Batzill, K. Lasek*, University of South Florida

Compositional control of layered materials has the potential for creating new 2D materials with desirable properties. Certain transition metal dichalcogenides (TMDs) may be modified by incorporating excess metals in between the 2D sheets and covalently linking them. Such an incorporation of metals may be achieved in a topotaxy approach. Topotaxy is a solid-state reaction in which the crystal structure of a starting material is modified by incorporation of elements into the existing crystal structure. Here this is explored for NiTe<sub>2</sub> by reacting it with excess Ni. In our study, NiTe<sub>2</sub> thin films were synthesized by molecular beam epitaxy. Subsequently, the composition of these films can be modified by two different approaches; (i) by thermal annealing inducing loss of Te and (ii) by reaction with excess Ni. In both cases the change in the Ni:Te ratio is monitored by XPS and a structural transformation of the film is observed by LEED and STM. With an increase in the Ni-content a ( $\sqrt{3} \times \sqrt{3}$ ) R30 superstructure is observed. In STM it can be shown that this new superstructure phase forms separate domains from the pure NiTe<sub>2</sub>, suggesting that it is compositional line phase in the Ni-Te phase diagram. The superstructure can be explained by Ni insertion in between NiTe<sub>2</sub> layers. From XPS measurements, the Ni-concentration in the intercalation layer is close to 2/3 of the Ni concentration of a NiTe<sub>2</sub> layer. The structural models for the intercalation are discussed based on DFT calculations. In STM nanoscale stripe like ripple networks are observed, which may indicate stacking faults in the intercalation layer due to lattice expansion. This study demonstrates a controlled approach to modify the composition of 2D NiTe<sub>2</sub>, which may help to control proposed properties of the layered Ni-telluride system, such as superconducting phases [1] or make it a more efficient electrocatalyst [2]. In general, the approach of modifying NiTe<sub>2</sub> by topotaxy may also allow to modify it with other transition metals than Ni and this will be studied in future work.

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##### **2D-ThP-3 Compositional Phase Control of Mote<sub>2-x</sub> via Growth Temperature, Post-Growth Annealing, and Post-Growth Metal Incorporation**, *Onyedikachi Alanwoko, M. Batzill*, University of South Florida

The ability to control and create different phases of two-dimensional(2D) materials like 2D transition metal dichalcogenides (TMDs) is a promising way of realizing new electronic and chemical properties of 2D materials. MoTe<sub>2</sub> has a small formation energy difference (~0.04eV) between its two competing 1H and 1T' phases. In MBE growth it has been shown that low

growth temperatures favor the 1T' phase while at higher growth temperatures the 1H phase is preferentially obtained. However, the 1H phase is generally tellurium deficient resulting in the formation of Mo-rich mirror twin grain boundaries (MTBs). This tellurium deficiency at higher growth temperatures may be related to the preferential formation of the 1H phase. Here we show through scanning tunneling microscopy (STM) that the Te-deficiency in the monolayer film can be tuned and a new ordered 2D Mo-telluride phase is obtained. With increasing Te-deficiency the structures change from a disordered MTB network to superstructures with  $2(\sqrt{7} \times \sqrt{7})R19.1$  and  $2(\sqrt{3} \times \sqrt{3})R30$  periodicity. Some of these phases can be assigned to periodic MTB networks. However, the different phases require different synthesis procedures, and once formed these phases appear thermally stable in vacuum to 500°C when they all transform into a tubular Mo<sub>6</sub>Te<sub>6</sub> phase. In this study, we systematically investigate the preparation conditions (which include the variation of the growth temperature, Te-desorption by post-growth vacuum annealing, and vapor deposition of Mo) enabling the controlled synthesis of these new phases. Particularly promising is the observation that we can react MoTe<sub>2</sub> with vapor-deposited Mo to obtain new ordered Te-deficient phase, this opens the possibility in future studies to react MoTe<sub>2</sub> with dissimilar TM to create new doped or alloyed 2D materials with potentially desirable properties.

##### **2D-ThP-4 Influence of Fluorination and Oxygenation Sources on the Thermal Atomic Layer Etching of MoS<sub>2</sub>**, *Jacob Tenorio*, Boise State University

Atomic layer etching (ALE) has emerged as a pivotal technique in the precise fabrication of two-dimensional (2D) materials, particularly molybdenum disulfide (MoS<sub>2</sub>), which holds promise in the semiconductor industry due to its high mobility in monolayer form. The ability to precisely etch amorphous and crystalline MoS<sub>2</sub> films provides a pathway for controlling thickness, which is critical to achieving desired electrical and optical properties. Previous studies used MoF<sub>6</sub> and H<sub>2</sub>O in thermal ALE of MoS<sub>2</sub>. Here, we report studies of alternate sources of fluorination and oxygenation and evaluate their impact on thermal ALE of MoS<sub>2</sub>. Oxygen sources include water and ozone and fluorine sources include HF/Pyridine and MoF<sub>6</sub>. Etch rates, uniformity, and surface chemistry post ALE were characterized using spectroscopic ellipsometry, atomic force microscopy, and X-ray photoelectron spectroscopy. Preliminary results indicate etch per cycle values of 0.5 Å/cycle for MoF<sub>6</sub>+H<sub>2</sub>O at 200 C, 0.32 Å/cycle for HF+H<sub>2</sub>O at 250 C, and 0.26 Å/cycle for HF+O<sub>3</sub> at 250 C. Additionally, ALE processes were combined with ALD to demonstrate thickness control for achieving few-layer MoS<sub>2</sub>.

##### **2D-ThP-5 SCTD Through Ultraviolet Ozone Treatment for 2D Semiconductor Based Field Effect Transistors**, *J. Park, Juwon Lee*, Sungkyunkwan University (SKKU), Republic of Korea

The semiconductor industry is increasingly demanding high-performance, highly integrated circuits and the downscaling of conventional cell size has reached its limits. However, using silicon-based technology into downscaled technology has faced diverse challenges in ensuring high cell transistor performance. Therefore, many researchers are exploring the application of next generation semiconductor materials, such as two-dimensional(2D) metal dichalcogenides (TMDs). TMDs have received significant attention as a novel alternative to silicon in the semiconductor industry because of their excellent electrical, mechanical properties.

To achieve the performance of TMD-based devices, it is very important and essential to have good ohmic contact with Schottky barrier (SB) control. The SB is typically controlled by doping such as ion implantation and thermal diffusion. However, these conventional doping methods are impossible to TMDs because they can damage the crystal lattice or cause defects. This is due to the characteristics of TMDs having a thin layer structure.

Several doping schemes have been investigated to reduce contact resistance in TMD-based devices, including edge contact, interlayer depinning, and surface charge transfer doping (SCTD). Among them, SCTD is an effective doping technique for 2D semiconductors due to its non-destructiveness and simplicity. The SCTD mechanism follows an alignment of Fermi level at the semiconductor and dopant material interface. The difference in work function (WF) between semiconductors and metal oxides is the main factor in charge transfer. When the WF of the metal oxide is larger than that of the semiconductor, the electrons in the semiconductor spontaneously move to the metal oxide, the holes accumulate in the semiconductor, and the energy band at the interface bends upward, eventually the semiconductor is doped p-type. In this study, we introduce a method to oxidize WSe<sub>2</sub> to WO<sub>x</sub> using ultraviolet (UV) ozone treatment. By this method, the surface of WSe<sub>2</sub> is changed to WO<sub>x</sub>, and WO<sub>x</sub> is a

substance having a larger WF than WSe<sub>2</sub>, and acts as a dopant material to perform p-type doping of WSe<sub>2</sub>. As a result, we confirmed that the device characteristics of 2D WSe<sub>2</sub>-based field effect transistor (FET) were improved.

The SB formed at the interface between the 2D semiconductors and the metals obstructs carrier injection and causes contact resistance to increase. Regardless of metals, an unintended high SB exists due to the Fermi level pinning effect. SCTD can selectively dope 2D semiconductors around metal contacts. Contact doping using SCTD is an effective way to lower the SB and improve the contact characteristics of 2D FETs.

**2D-ThP-6 Plasma Assisted Etching of MoS<sub>2</sub>: An Ab-Initio Molecular Dynamics(AIMD) Study, Shoab Khalid, Y. Barsukov, S. Ethier, I. Kaganovich, Princeton University Plasma Physics Lab**

Molybdenum disulfide (MoS<sub>2</sub>) in its two-dimensional form represents a leading contender for the fabrication of advanced semiconductors. A critical attribute of MoS<sub>2</sub> is its adjustable bandgap, which varies with material thickness. This characteristic is vital for the tailored production of nanoelectronics devices, aligning with industry requirements for precision and flexibility. In this study, we employ ab initio molecular dynamics (AIMD) to investigate the etching mechanisms of Molybdenum disulfide (MoS<sub>2</sub>). Our results provide a basic understanding of plasma assisted etching process. By simulating the interaction of plasma with MoS<sub>2</sub> surfaces, we identify the critical factors that can influence the etching rates and patterns. Our calculations indicate that fluorinating the MoS<sub>2</sub> surface before subjecting it to Ar plasma bombardment can enhance etching yield and improve surface roughness. The presence of fluorine (F) at the surface forms a stronger F-S bond compared to the Mo-S bond, facilitating etching of the surface sulfur (S) atoms without significant damage to the underlying layers. This process is crucial for reducing the surface roughness of the unetched layers. Furthermore, the effect of Ar ion energy on etching yield and surface roughness is also addressed.

**2D-ThP-7 The Relationship between the Adhesion Strength and the Anodization Time for the Formation of Titanium Oxide Nanotubes on Ti-6Al-4V, ITZEL PAMELA TORRES AVILA, M. VARGAS LÓPEZ, A. CHINO ULLOA, J. CASTREJÓN FLORES, Unidad Profesional Interdisciplinaria de Biotecnología, Mexico**

In this work, an anodic oxidation process was applied to the surface of Ti-6Al-4V in order to form titanium oxide nanotubes (TONs). This titanium alloy is the most studied due to its  $\alpha/\beta$  microstructure, which provides different mechanical properties. The anodic oxidation was carried out at a constant voltage of 60 V using an electrolyte based on ethylene glycol (EG), 0.5 wt.% ammonium fluoride, and 1 wt.% distilled water. The established anodization time were 10, 20, 30, 40, 50, and 60 min. The adhesion strength of the different TONs layers to the Ti-6Al-4V surface was evaluated by nanoscratch test and the critical load was determined from the analysis of the groove of the nanoindenter path. It ranged from 0 mN for 10 min samples to 47 $\pm$  3 mN for 50 min samples. The results showed that the TONS formed at 50 min presented the best adhesion strength to the titanium alloy sample.

Keywords: nanotubes adhesion strength, titanium

**2D-ThP-8 Characteristics of Composites of Expanded Graphite and Silver Nanoparticles Prepared by Thermal Decomposition, Won Gyu Lee, Kangwon National University, Republic of Korea**

The dispersibility of the metallic Ag nanomaterial on the surface of the graphite carbon material was significantly reduced, and depending on the process conditions, it aggregated on the surface of the specific carbon material, making it difficult to construct the carbon/nanometal composite with the expected uniform structure. It was concluded that this result was based on the poor dispersibility of nanometals in solvents. In addition, the adhesion between the synthesized carbon/metal nanocomposite materials was poor, making it difficult to produce sheets for sample characterization. In particular, in the case of expanded graphite, it was judged to be due to interlayer shrinkage due to capillary force during the material drying process after composite synthesis in aqueous solution. Therefore, it can be seen that a synthesis method with the low surface tension of nanometal dispersion solvent is essential.

Therefore, in this study, a process environment that excludes surface tension was required to increase dispersibility by using the supercritical properties to improve the dispersibility of nano metals and to increase processability due to the shrinkage of the material. Supercritical carbon dioxide uses supercritical carbon dioxide, in which the surface tension of the fluid disappears at temperatures above 31.0°C and pressures above

73.8 bar, and nanometals are evenly dispersed and evenly attached to the surface of carbon materials from which hydrophobic properties have been removed. The research focuses on synthesizing carbon composites to improve the physical properties of a single material and realize high functionality through networking between materials. Therefore, it is expected that synthesizing a carbon/nanometal composite under supercritical process conditions will enable the synthesis of a homogeneous and highly processable composite material. Carbon materials such as graphene, which have high thermal conductivity and excellent mechanical properties, do not change their thermal conductivity characteristics even when bent, thereby overcoming the physical and functional limitations of existing heat dissipation materials and providing high-performance, lightweight, and environmentally friendly properties. In addition, it is attracting attention as a new material with optimal characteristics as a high heat dissipation material that can achieve energy savings.

**2D-ThP-9 Momentum Dependent Charge Density Wave Gap in an Antiferromagnetic Metal, Nathan Valadez, University of Central Florida; S. Regmi, Idaho National Laboratory; I. Bin Elias, A. Pradhan Sakhya, D. Jeff, M. Sprague, M. Islam Mondal, D. Jarret, A. Agosto, University of Central Florida; T. Romanova, Polish Academy of Sciences, Poland; J. Chu, University of Washington; S. Khondaker, University of Central Florida; A. Ptok, D. Kaczorowski, Polish Academy of Sciences, Poland; M. Neupane, University of Central Florida**

Charge density wave (CDW) ordering has been an important topic of study for a long time owing to its connection with other exotic phases such as superconductivity and magnetism. The RTe<sub>3</sub> (R = rare-earth elements) family of materials provides a fertile ground to study the dynamics of CDW in van der Waals layered materials, and the presence of magnetism in these materials allows to explore the interplay among CDW and long range magnetic ordering. Here, we have carried out a high-resolution angle-resolved photoemission spectroscopy (ARPES) study of a CDW material GdTe<sub>3</sub>, which is antiferromagnetic below  $\sim$  12 K, along with thermodynamic, electrical transport, magnetic, and Raman measurements. Our ARPES data show a two-fold symmetric Fermi surface with both gapped and ungapped regions indicative of the partial nesting. The gap is momentum dependent, maximum along  $\Gamma$ -Z and gradually decreases going towards  $\Gamma$ -X. Our study provides a platform to study the dynamics of CDW and its interaction with other physical orders in two- and three-dimensions.

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**2D-ThP-10 Investigating the Electronic Structure of Bilayer Graphene/RuCl<sub>3</sub> Heterostructure, Aalok Tiwari, S. Sasmal, I. Kao, Carnegie Mellon University, USA; C. Jozwiak, E. Rotenberg, Advanced Light Source, Lawrence Berkeley National Laboratory; A. Bostwick, advanced light Source, Lawrence Berkeley National Laboratory; S. Singh, J. Katoch, Carnegie Mellon University, USA**

The stacking of two-dimensional materials to form van der Waals (vdW) heterostructures provides an unprecedented ability to tune electronic structure and engineer interfaces. RuCl<sub>3</sub> has recently attracted significant attention as it is a Mott insulator, Kitaev material, and interfacing with graphene results in massive charge transfer, modifying their electronic properties. This can be exploited to create low-power devices for novel optoelectronic applications. In this talk, I will present a comparison of the electronic structure of bilayer graphene on interfacing with  $\alpha$ -RuCl<sub>3</sub> and hBN, using angle-resolved photoemission spectroscopy with nanoscale spatial resolution (nanoARPES). We can directly explore the charge transfer at the interface due to different work function of the bilayer graphene and RuCl<sub>3</sub>. I will discuss tuning the electronic structure in bilayer graphene/RuCl<sub>3</sub> using electron doping via potassium atom deposition.

**2D-ThP-11 2D Materials for Energy-Efficient Nanoelectronics, F. Yao, Huamin Li, University at Buffalo - SUNY**

With the rise of graphene (Gr) since 2004, two-dimensional (2D) have been extensively explored for energy-efficient nanoelectronics due to their novel charge transport properties compared to conventional three-dimensional (3D) bulk materials. However, there are still challenges and issues for practical implementation of 2D materials. Here we take 2D semiconducting MoS<sub>2</sub> as an example to review our recent research of energy-efficient nanoelectronics, ranging from materials synthesis to structure engineering and device demonstration. First, by functionalizing the growth substrate, we can achieve on-demand selective-growth of 2D MoS<sub>2</sub> using chemical vapor deposition (CVD) and the electron mobility can be up to 20 cm<sup>2</sup>/Vs at

room temperature. At the interface between MoS<sub>2</sub> and SiO<sub>2</sub> substrates, an interfacial tension can be induced due to a mismatch of thermal expansion coefficients, which creates an anisotropy of in-plane charge transport [1, 2] as well as a self-formed nanoscroll structure [3]. Second, at the interface between MoS<sub>2</sub> and metal contact, a monolayer h-BN decoration can enable novel manipulation of charge transport through quantum tunneling, in contrast with conventional thermionic emission [3]. The contact resistance can be suppressed by both localized and generalized doping using transition metals [4]. Third, at the interface between MoS<sub>2</sub> and other 2D materials, band-to-band Zener tunneling and cold-source charge injection can be enabled, giving rise to a superior transport factor (<60 meV/decade) in field-effect transistor (FET) configurations. These novel charge transport can be utilized to overcome the fundamental limit of “Boltzmann tyranny”, and realize tunnel FETs and cold-source FETs with sub-60-mV/decade subthreshold swings [5-7] or novel anti-ambipolar FETs [8]. Fourth, at the interface between MoS<sub>2</sub> and ferroelectric or ionic dielectrics, excellent electrostatic gating leads to a superior body factor (<1), and also improves the energy efficiency for transistor operation [9].

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## **2D-ThP-12 Unique Nanowire and 2D Material Device Fabrication by Nanofrazor Technology, Nicholas Hendricks, F. Yang, E. Clerc, J. Chaaban, E. Çağın, Heidelberg Instruments Nano AG, Switzerland**

Thermal scanning probe lithography (t-SPL), enabled by the NanoFrazor technology, is a nanolithography technique particularly suitable for patterning, contacting, and modifying 2D materials and nanowires [1-6]. t-SPL generates patterns by scanning a heated ultrasharp tip over a sample surface to induce local changes. By using thermal energy as a stimulus, it is possible to perform various modifications to the sample via removal, conversion, or addition of/to the sample surface. Along with an ultrasharp tip, the t-SPL cantilever contains several other important functions such as an integrated thermal height sensor and an integrated heating element both of which are advantageous for generating devices from nanowires and 2D materials.

Nanowires and 2D materials have been the focus of intense academic and industrial research as these materials provide great promise as next generation electronic devices. However, when patterning electrical contacts to nanowires and 2D materials with conventional fabrication techniques (photolithography, electron beam lithography), the fabrication process becomes challenging and time consuming due to overlay requirements. These techniques can also lead to less than desired device performance due to damage from charged particles or ultraviolet irradiation, as well as contamination from residual resist. The issue of time intensive processing comes from the random positioning of nanowires and 2D material flakes on substrates which makes overlay challenging. This point of overlay is addressed with t-SPL by having an integrated thermal height sensor that allows for a non-invasive, in-situ measurement technique to detect buried nanowires or 2D materials prior to patterning. Such capabilities allow for real-time imaging and markerless overlay with high precision.

Within this presentation, the background and workings of t-SPL will be briefly introduced, nanostructuring on nanowires and 2D materials will be discussed along with electrical and optical device performance for nanowire and 2D material-based devices fabricated using t-SPL.

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## **2D-ThP-13 Engineering Surface Termination of Ti<sub>2</sub>C<sub>3</sub>T<sub>x</sub> MXene for Enhanced Soft Actuator Performance, Dhamelyz Silva Quinones, H. Wang, Duke University**

Ti<sub>2</sub>C<sub>3</sub>T<sub>x</sub>, the pioneer MXene, has attracted attention for its unique properties such as adjustable electrical conductivity, high mechanical stability, and versatile responsiveness, thus holding immense potential for advancing soft robotics and sensing applications. However, the performance of the MXene-based soft actuator is limited by uncontrollable surface terminations (-OH, -F, etc) induced in the synthesis process. Modifying these surface functional groups allows for customizing Ti<sub>2</sub>C<sub>3</sub>T<sub>x</sub> to possess desired properties.

This study introduces an innovative methodology to manipulate the surface termination of Ti<sub>2</sub>C<sub>3</sub>T<sub>x</sub> through plasma treatment. Various plasma conditions were applied to Ti<sub>2</sub>C<sub>3</sub>T<sub>x</sub> flakes, with resultant alterations in surface termination analyzed via X-ray Photoelectron Spectroscopy (XPS). Additionally, changes in structure were evaluated using X-ray Diffraction (XRD) and Raman Spectroscopy. Furthermore, Ti<sub>2</sub>C<sub>3</sub>T<sub>x</sub>/cellulose actuators were fabricated utilizing Ti<sub>2</sub>C<sub>3</sub>T<sub>x</sub> with controlled surface terminations. Nanocrystal and nanofiber phases of cellulose were employed and compared to optimize actuation performance. Remarkably, the Ti<sub>2</sub>C<sub>3</sub>T<sub>x</sub>/cellulose actuator exhibited robust responses to Near-Infrared (NIR) light, showcasing potential applications in soft robotics and sensing. The mechanism of controlled surface terminations contributing to the multi-responsive actuator will also be discussed.

## **2D-ThP-14 Graphene-Based Hybrid Nanoparticle for the Chemotherapy Treatment of Prostate Cancer, Diego La Mendola, L. Chiaverini, R. Di Leo, C. Giorgieri, University of Pisa, Italy; C. Satriano, University of Catania, Italy; T. Marzo, University of Pisa, Italy**

Prostate cancer (PC) is a frequent malignancy in men with a poor prognosis in the case of relapse or disease detected at the advanced stage with metastasis. It is ascertained as the levels of angiogenin (Ang) a potent angiogenic factor involved in cancer cells spreading- dramatically increase in PC patients, positively correlating with the disease progression and prognosis. Accordingly, Ang and angiogenesis-related processes represent a promising target. On the other hand, though taxanes represent the standard chemotherapy, their combinations with platinum anticancer drugs show advantages. Based on these premises we aim to improve the combination chemotherapy for PC developing PLGA-PEG fluorescent biocompatible nanovectors (NVs) for drugs loading decorated with angiogenin-mimicking peptides, and deposited onto reduced form of graphene oxide (rGO).

These new graphene-based hybrid nanoparticle have been characterized by means of UV-visible spectroscopy, Zeta potential, Atomic Force Microscopy. Biological tests showed that the synthesized systems are able to carry out taxanes, platinum complexes into specific target leading to impairment of cancer cells angiogenesis.

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