

2D Materials Technical Group

Room Oregon Ballroom 203-204 - Session 2D-ThP

2D-Materials: Poster Session

2D-ThP-1 Multi-MOF-Based Chemical Gas Sensors with Enhanced Selectivity and Sensitivity via Quartz Crystal Microbalances, *Tzer-Rung Su, J. Dhas, C. Pan, M. Paul, C. Simon, C. Chang*, Oregon State University

Metal-organic frameworks (MOFs) have emerged as promising materials for gas sensing applications due to their high surface area, chemical stability, and absorbent selectivity. In this work, we study the combination of thin film MOFs, including Zeolitic Imidazolate Framework (ZIF)-4, ZIF-7, ZIF-8, and ZIF-71 on Quartz Crystal Microbalances (QCM) as chemical sensors. ZIF thin films with controllable thickness were deposited using chemical bath deposition. ZIF films' physical and chemical properties were characterized by X-ray diffraction, Scanning Electron Microscopy, Brunauer-Emmett-Teller analysis, Fourier-transform infrared spectroscopy, and X-ray Photon Spectroscopy. The sensing response of MOFs/QCM sensors depends strongly on the pore properties of sensing material and molecular chemical properties¹. The physical properties of each MOF, including its pore size, pore volume, and surface area, result in different uptake and release dynamic responses to various gas species, such as Ammonia, Carbon Dioxide, Water, and Volatile Organic Compounds. By simultaneously testing these MOFs/QCM sensors, we obtain different sensing responses to mixtures of gases; these data, combined with a data analytics tool, improve the overall selectivity of the sensing arrays.

Our results demonstrate that the MOF/QCM-based chemical sensing arrays can detect and distinguish a mixture of gas species, enabling the identification and quantification of different gas species.

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2D-ThP-2 Graphene/Noble Metal Nanoparticles Nanocomposites at the Biointerface with a Blood Brain Barrier Model to Scrutinize Brain Wound Healing, *A. Foti, L. Cali, A. Agafonova, A. Cosentino, C. Anfusio, G. Lupo, Cristina Satriano*, University of Catania, Italy

Graphene-based nanomaterials represent an emerging aspect of regenerative medicine, and graphene oxide (GO) has been especially exploited to overcome the blood-brain barrier (BBB). Noble metal nanoparticles (NPs), including gold (Au), silver (Ag), and palladium (Pd), have the properties of adjustable size, optical properties, flexible surface modification, and biocompatibility, which makes them very attractive for nanomedicine of brain diseases. NPs are able to cross the BBB, therefore can be used as drug delivery carriers or, given their intrinsic anti-inflammatory properties, as theranostic platforms.

In this work, we prepared Au, Ag, and Pd NPs, 20-100 nm in size, and their respective hybrid systems with GO (NP@GO), aiming to investigate wound healing, a complex process involving cell adhesion, migration, and proliferation processes. The wound healing is critically affected by hypoxia, which inhibits endothelial wound repair as a result of decreased migration and proliferation. A derangement of brain wound healing may cause some cases of Alzheimer's disease, leading to an impairment of BBB integrity and function.

The physicochemical characterization was assessed by UV-visible spectroscopy, AFM, DLS and zeta potential, to investigate the plasmonic response thus estimating the NP optical diameter, the morphology, the hydrodynamic size and the surface charge, respectively.

In order to mimic *in vitro* the condition of hypoxia related to pathological situations, we used human brain microvascular endothelial cells (BMECs), the principal components of the BBB together with pericytes and astrocytes, and human umbilical vein endothelial cells (HUVECs). The cytotoxicity and/or proliferation were inspected via MTT assay, and cell migration by the wound scratch assay, while the cellular uptake and the organelle perturbation were scrutinized by confocal microscopy. Moreover, the levels of inflammatory cytokines such as IL-1 β , IL-6, IL-8, TNF- α , and HIF1- α and VEGFA were detected at protein and mRNA levels, evaluating the reduction/increase of inflammatory cytokines/anti-inflammatory IL-10.

2D-ThP-4 Performance and Reliability Improvement of IGTO TFTs via Co-Sputtering, *Seung Jin Kim, B. Choi*, Sungkyunkwan University, Korea

In this study, highly improved positive bias stress (PBS) and negative bias stress (NBS) stability of IGTO (InGaSnO) thin film transistor is achieved by simultaneous co-sputtering of HfO₂ and IGTO target. Channel doping via co-sputtering has been extensively studied, and its effect on improving reliability under bias stress has been confirmed through several studies. However, side effects such as decrease in on/off ratio or mobility degradation have also been observed. In this study, we fabricated TFTs with a 2-layer structure, where the bulk channel material was deposited separately after thin co-sputtering deposition of HfO₂ and IGTO at the interface the gate oxide and channel material, instead of co-sputtering the entire channel material. The threshold voltage shift under positive bias and negative bias stress at a stress time of 3000s was improved from 11.5V to 5.8V, and 2.9V to 1.2V respectively. In result, this study suggests an ultimate device fabrication method that can improve the reliability issues due to stress, which is an inherent problems in oxide semiconductors.

2D-ThP-5 NanoFrazor Technology: Enabling Unique Nanowire and 2D Material Device Fabrication, *Nicholas Hendricks, A. Ubezio, M. Käppeli, J. Vergés, J. Chaaban, E. Çağın*, Heidelberg Instruments Nano, 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 [1-5]. 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 [6].

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-6 Synthesis of 2D-WS₂ on c-sapphire using H₂S gas-source CVD, *Kun-An Chiu, W. Chen, H. Chen, Y. Lin, C. Chen, H. Chen, F. Chen*, Taiwan Instrument Research Institute, National Applied Research Laboratories, Taiwan

Two-dimensional materials are considered one of the key materials for next-generation semiconductor devices and industrial applications. In recent years, semiconductor devices based on two-dimensional electronic channel materials have shown their feasibility in transistor applications, in order to continue Moore's law [1]. WS₂ is one of the representative materials in two-dimensional transistors. WS₂ exhibits excellent properties, such as high carrier mobility, large on/off ratio, high optical excitation intensity, low response time, and good compatibility with other two-dimensional materials such as graphene [2, 3]. The development of growth processes for rapid and large-scale production of 2D transition metal dichalcogenides (TMDs) are receiving increasing attention in the fields of nanophotonics, flexible electronics, and sensors. Chemical vapor deposition

(CVD) is the most promising method for obtaining high-quality large-area 2D-TMDs. However, current equipment and technology make it difficult to effectively produce large-area, high-quality two-dimensional materials. Most two-dimensional material processes use powder as a precursor. The vapor pressure of metal and sulfur powders is not easily and stably controlled. Although some studies use a mixed H₂S gas (Ar + H₂S), it is difficult to effectively control the H₂S concentration during the process due to the difference in gas density.

In this study, WS₂ was synthesized on a (0001) sapphire substrate using WO₃ powder and pure H₂S gas as precursors in a hot-wall CVD furnace. The experiment was carried out at a process temperature of 950°C, a pressure of 10-50 torr, and a H₂S/Ar flow ratio of 0.5-5%. The synthesized WS₂ flakes were characterized by using optical microscopy, Raman spectroscopy, in-plane X-ray diffraction, and transmission electron microscopy. The in-plane GIXRD results showed that the WS₂ flakes were heteroepitaxially grown on the (0001) sapphire substrate with two sets of orientation relationships: (100)_{WS2} // (110)_{Al2O3}, (110)_{WS2} // (100)_{Al2O3}, and (110)_{WS2} // (110)_{Al2O3}, (100)_{WS2} // (100)_{Al2O3}. This indicates that the WS₂ flakes have a consistent orientation. Furthermore, the TEM observation revealed that the WS₂ film thickness was ~ 7 Å, suggesting that the process can synthesize the WS₂ monolayer.

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2D-ThP-8 Polarization Sensitive Frequency Selective Metasurface for the Infrared Spectral Range, *Micheal McLamb, P. Stinson, N. Shuchi, D. Louisos, T. Hofmann*, University of North Carolina at Charlotte

Metasurfaces, in the form of perfect reflectors, have received attention for their sensing and filtering capabilities. Plasmonic metasurfaces allow for frequency filtering by controlling the input polarization. We demonstrate a frequency filtering metasurface composed of an array of subwavelength metallic pluses fabricated using two-photon polymerization.

2D-ThP-9 *In-situ* X-ray Absorption Spectroscopy Study of Monodispersed Cobalt Phthalocyanine on Carbon Nanotubes as Electrocatalyst for Carbon Dioxide Reduction to Methanol, *Mason Lyons*, Oregon State University; *C. Rooney, H. Wang*, Yale University; *Z. Feng*, Oregon State University

Carbon dioxide (CO₂) is accumulating in the atmosphere, causing entrapment of thermal energy and more chaotic weather. To sustainably decumulate the atmospheric CO₂ and sequester future emissions, it must be utilized in a circular economy. Upcycling of CO₂ to value added products such as hydrocarbons and alcohols requires the use of catalysts, among which molecular catalysts are the most promising due to their product selectivity and high utilization of metals. Unlike many other catalysts which primarily produce the undesired carbon monoxide (CO) intermediate, cobalt phthalocyanine (CoPc) non-covalently anchored on carbon nanotubes (CNTs) exhibits preferential formation of methanol (MeOH) from CO₂ due to a modified Co electronic structure. To investigate the electronic and geometric arrangements of CoPc-CNTs during CO₂ reduction, *in-situ* X-ray absorption spectroscopy (XAS) was employed. The pre-edge peaks at 7710 eV related to orbital mixing increased while the 7715 eV peak related to bonding centro-symmetry decreased, when scanning from open circuit voltage to -1.1 V vs Reference Hydrogen Electrode (RHE) indicating a higher density of states in Co 3d² and axial coordination from CNT as well as C adsorbate, respectively. An absorption edge shift associated with Co reduction to Co(I) was also observed and persisted at MeOH producing conditions, previously only reported for CO producing systems. Fitting of the extended X-ray absorption fine structure (EXAFS) spectra confirmed the CoPc coordination and bond lengths with theoretical calculations as well as the presence of a carbon adsorbate at potentials more negative than -0.5 V vs RHE, enabling further CO reduction to MeOH. The rich information from *in-situ* XAS elucidated the structure-property relationship of this catalyst to explain the superior performance of CoPc dispersed on CNTs for CO₂ upgrade.

2D-ThP-10 A Method for creating Single Atom Catalysts through Vapor-phase Synthesis of Covalent Organic Frameworks, *Siamak Nejati*, University of Nebraska–Lincoln; *S. Gnani Peer Mohamed*, University of Nebraska - Lincoln

The process of synthesizing thin films of covalent organic frameworks (COFs) in situ, without the use of solvents, is an attractive route for the

creation of single-atom catalysts (SACs) based on metal-N₄ motifs. This one-step synthesis and integration approach makes it suitable for incorporating the materials into the architecture of electrode devices. Compared to traditional SACs preparation methods, this approach allows for an increase in the number of active sites and improved synthetic precision, resulting in highly desirable electrocatalytic performance. In this study, we employed porphyrins as precursors and demonstrated the feasibility of using vapor phase deposition to create COFs with metal-porphyrins. In recent decades, the improved electrocatalytic properties of porphyrin-based COFs with two or three dimensions have garnered significant attention. However, their covalent networks and organic nature make solution-based COF synthesis challenging for creating thin films, which limits their widespread use in various applications. We demonstrate a solvent-free vapor phase synthesis of crystalline and porous porphyrin-based COFs (POR-COFs) using 5,10,15,20-tetra(4-aminophenyl)porphyrin (TAPP) and its transition metal complex (MTAPP, M = Cu²⁺, Co²⁺) through pulse-assisted oxidative chemical vapor deposition (oCVD). Pyridine, a co-crystallizing agent, is used to enhance the crystallinity and structure of the MPOR-COF. We observed varying electrocatalytic activity towards different reactions depending on the occupancy of the porphyrin center. The synthesized MPOR-COFs exhibit excellent electrochemical performance for nitrate electroreduction to ammonia (Faradaic efficiency of ~86% at 1.7 V vs Ag/AgCl), oxygen reduction and evolution reaction in aprotic media, and as a cathode material for Li-Oxygen battery. This synthetic approach offers a sustainable and scalable method for thin film COF production and opens up new opportunities for their application in energy storage and conversion systems. The measured electrocatalytic activities proved that our approach to synthesizing catalysts from COFs is a viable path to realize the next generation of SACs catalysts.

2D-ThP-11 Real-Time Machine Learning Enhanced Defect Engineering in Ceria Nanostructures, *U. Kumar*, University of Central Florida; *A. Arunachalam*, University of Texas at Dallas; *C. Feit, N. Berriel*, University of Central Florida; *K. Basu*, University of Texas at Dallas; *P. Banerjee, S. Seal*, University of Central Florida; *Yifei Fu*, University of Central Florida, Orlando

Ceria nanostructures have been employed in diverse applications due to their distinctive defect structure, which grants them regenerative oxidative properties. The redox activity of ceria depends on its surface defect structure and is generally determined by its Ce³⁺/Ce⁴⁺ oxidation state ratio, often measured by ex-situ X-ray photoelectron microscopy (XPS). Numerous studies have demonstrated that defect engineering strategies, such as size and morphology manipulation or introduction of doping, are effective in altering ceria nanostructures for various applications. However, despite the success achieved by these methods, it is still challenging to have precise and reversible control over ceria defect structures. To address this challenge, we propose the use of Machine Learning (ML) techniques to enhance defect engineering in ceria nanofilms.

Deposition conditions, such as temperature, pressure, and the number of cycles, play an important role in the ALD process. Our previous work¹ has demonstrated that well-optimized ALD processes can be achieved with the help of *in-situ* spectroscopic ellipsometry (SE). Therefore, the desired thickness of ceria thin film can be rapidly developed without the ex-situ characterization usually required by conventional approaches. In the current work, data collected through *in-situ* SE and ex-situ XPS has been correlated using ML algorithms. Two approaches have been studied to exert better control over the defective structure of ceria thin film. The first method involves an indirect approach of thickness prediction using an ML algorithm, followed by Ce³⁺/Ce⁴⁺ estimation using an experimental calibration curve. The second method, with a more direct approach, involves Ce³⁺/Ce⁴⁺ prediction using real-time ellipsometry data (amplitude ratio ψ and phase difference Δ) using Gradient Boost and Random Forest Regressor. Overall, in the present work, an ML algorithm trained by *in-situ* ES data was shown to be an effective approach to control the thickness and defect level of Ceria ALD films.

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2D-ThP-12 Investigating the Fate of Nanoplastics in Aquatic Environments, *Tycho Roorda, I. Groot*, Leiden University, The Netherlands

Plastic particles in the ocean have become a contaminant of emerging concern due to their damage to humans and marine life[1,2]. Of all plastic production, which is increasing still, it has been shown that more than 99% of plastic waste which ends up in the oceans can not be accounted for[2,3]. The belief is that part of all this missing plastic degrades to a micro-

and nano-sized scale which had not yet been detected[4,5]. Nanoplastics have also been shown to promote the spreading of toxins, such as heavy metals, which would otherwise sink to the ocean floor at their source[6,7]. In order to understand the fate of nanoplastics in aquatic environments, we must have a better understanding of the degradation mechanisms at an atomic and chemical level. In this project, we have successfully deposited nanoplastics onto a substrate in UHV by physical vapor deposition for degradation studies and to investigate their binding mechanism to other toxins in the ocean. The deposition of nanoplastics is confirmed by mass spectrometry, Auger electron spectroscopy and X-ray photoelectron spectroscopy. The degradation mechanisms which will be studied are oxygenation, hydrogenation, UV exposure and thermal annealing which will be investigated in ultra-high vacuum with atomic force microscopy and combined scanning tunneling microscopy. This combination allows for the identification of individual particles by conductivity making it possible to study the binding mechanism between nanoplastics and certain toxins. In this project, we aim to investigate the binding mechanism between nanoplastic particles and heavy metals as well as the nanoplastics' degradation by operando dosing of gases and heating to real world conditions.

2D-ThP-13 Plasma-Induced Energy Band Evolution for Two-Dimensional Heterogeneous Junctions, A. Ahmed, A. Cabanillas, A. Chakravarty, F. Yao, Huamin Li, University at Buffalo

With the rise of two-dimensional (2D) materials and nanoelectronics, compatible processes based on existing Si technologies are highly demanded to enable new and superior device functions. In this work, we exploit the CMOS-compatible O_2 plasma treatment as an effective anionic substitution doping approach for 2D WSe_2 , and demonstrate a heterogeneous WSe_2/MoS_2 junction as an anti-ambipolar field-effect transistor (FET) with outstanding performance. Specifically, novel plasma-induced oxidation and doping were performed to achieve a controllable enhancement of hole transport in WSe_2 through moderate or even degenerate doping. By incorporating with 2D MoS_2 dominated by electron transport as well as the applied in-plane and out-of-plane electric fields, an evolution of the energy band structure of the 2D heterogeneous junction can be obtained, and the corresponding charge transport, dominated by the Fowler-Nordheim (FN) tunneling, is comprehensively elucidated. As an anti-ambipolar FET, our prototype device exhibits outstanding and balanced performance including a superior peak-valley ratio (PVR, 2.4×10^5) and a high current density (55 nA/ μm). This work demonstrates the great potential of 2D materials and their doping engineering to feasibly integrate with the existing CMOS technology and eventually improve the efficiency of future nanoelectronics.

2D-ThP-14 in-situ Electronic structure monitoring of 2D TMDC-field effect transistor by operando-XPS, Seungwook Choi, Korea Research Institute of Standards and Science (KRISS), Republic of Korea; G. Oh, T. Kim, Jeonbuk National University, Republic of Korea; A. Kim, Korea Research Institute of Standards and Science (KRISS), Republic of Korea

Two-dimensional transition metal dichalcogenide material-based field effect transistor (2D TMDC-FET) could be one of next-generation transistors because they have novel material properties including high on-off ratio above 10^6 , subthreshold swing of 140 mV/dec, Hall mobility around 10 cm^2/Vs , and tunable bandgap depending on the number of layers. "Operando", which means under working conditions, analysis method has been proposed to investigate the correlation between devices and materials and observe intermediate state of material while the device is working. To examine chemical and electrical properties at the channel interface of thin film FET under working condition, operando X-ray photoelectron spectroscopy (XPS) should be studied due to its surface-sensitive performance.

In this study, we will introduce a lab-source operando XPS system specially for commercial XPS system including a transistor probe stage and a special sample holder. Here, we present the change of electronic structure of TMDC-FET depending on a gate voltage using our lab-source operando-XPS system. The results reveal that the quantitative band bending of the FET channel can be observed during operating FET (switching on/off). Furthermore, the quality of active channel/insulator interface can be monitored during FET operation. We provide the strategy to minimize beam-damage attributed by the use of micro-focused x-ray beam during operando analysis. Furthermore, this operando-XPS analysis results enable to provide the optimized material and device structure of 2D TMDC-FET.

2D-ThP-15 Atomic Layer Deposition of Al_2O_3 on Monolayer MoS_2 with Mild NF_3 Remote Plasma Treatment, Kwangwuk Park, J. Kang, H. Lee, M. Leem, G. Yeom, H. Kim, Sungkyunkwan University (SKKU), Republic of Korea
Keywords: Plasma treatment, atomic layer deposition, two-dimensional crystals, molybdenum disulfide, surface functionalization.

Abstract. Considering the expected superior immunity to short-channel effects while maintaining high electron mobility even at a few monolayer thicknesses [1, 2], molybdenum disulfide (MoS_2), with a two-dimensional structure, is emerging as a promising alternative to ultrathin Si channels in future sub-nanometer transistors. Nevertheless, from a device integration standpoint, there remains a critical challenge: forming continuous dielectric films with a thickness of less than a few nanometers on MoS_2 via atomic layer deposition (ALD) due to the limited number of active sites on the MoS_2 surface [3]. Although various approaches have been explored to activate the MoS_2 surface for facile chemical interaction with ALD precursors [4], several challenges remain unresolved. These include achieving thickness scalability of MoS_2 down to a monolayer, ensuring thickness scalability of the gate dielectric, and adapting the process to three-dimensional device structures.

In this presentation, we introduce the use of NF_3 remote plasma treatment on the MoS_2 surface prior to ALD of an Al_2O_3 film at 200 °C. Without treatment, direct thermal ALD of Al_2O_3 on MoS_2 results in island-like growth characterized by numerous incomplete boundaries. In contrast, MoS_2 treated with NF_3 remote plasma facilitates the deposition of continuous and pinhole-free Al_2O_3 films, even at a thickness of 2 nm. We confirmed the minimal physical damage of the pretreatment to the monolayer MoS_2 through Raman and photoluminescence spectroscopy. Finally, we will discuss the electrical characteristics of MoS_2 field-effect transistors incorporating NF_3 remote plasma pretreatment.

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2D-ThP-16 AgNFs Supported on Graphene Based Materials as Multi-Wavelength SERS Active Platforms, A. Brancato, M. Condorelli, S. Sciacca, C. Bonaccorso, M. Barcellona, M. Fragalà, C. Satriano, G. Compagnini, Luisa D'Urso, University of Catania, Italy

Surface Enhanced Raman Spectroscopy (SERS) has been successfully employed in several fields of interest such as plasmonic sensing and biosensing, in-situ photocatalysis studies, single molecule detection, and many others real-world applications. Usually, the greatest contribution to the Raman enhancement is explained by an electromagnetic mechanism. To further potentiate the SERS effect, several research studies reported the employ of peculiar plasmonic nanostructures that allow the creation of hot-spots on characterized by strong electromagnetic fields. Moreover, the possibility to amplify Raman signals is strongly linked to the excitation wavelength of the employed laser interacting with the SER active substrate. In order to explore novel functional nanomaterials with a high enhancement in a wide range of excitation wavelengths, in this work we propose Silver Nanoflowers (AgNFs), anchored to reduced thiolated graphene oxide (r-GOSH) nanosheets. The success of the coupling preparation procedure was verified by comparing the Raman and IR spectra of the materials, before and after coupling metal nanostructures with the 2D layers, and by UV-vis spectroscopy analyses. Furthermore, a morphological characterization of the new materials was carried out using scanning electron and atomic force microscopies. Thanks to the NFs morphology and to the extended surface of 2D materials is possible create numberless hot spot regions between silver petals and in the nanogaps area of the 2D material, exhibiting significant plasmonic effects as well as unique optical feature in the overall visible range. The SERS properties of the 2D hybrid material were studied using a standard molecule 4-mercaptobenzoic acid (4-MBA) as probe analyte at the nanomolar concentration. As the AgNFs extinction spectra cover the entire visible range, we were able to study the enhancement in a laser wavelength range between 532 and 785 nm, finding very high enhancement factors. This suggests that AgNF could be an excellent SERS substrate on the entire visible and near infrared spectral region and demonstrates that such nanomaterial can be easily used to study analytes at low concentrations with any exciting wavelength, opening the possibility to investigate several biological and medical interest analytes without the interference of not desired optical phenomena such as luminescence.

Thursday Evening, November 9, 2023

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2D-ThP-17 Angiogenin-Tailored Graphene Oxide Nanosheets to Target Prostate Cancer, Diego La Mendola, T. Marzo, University of Pisa, Italy; O. Hansson, University of Goteborg, Sweden; C. Satriano, University of Catania, Italy

Angiogenin (ANG), an ubiquitous protein with a potent angiogenic power, is able to stimulate new vessel growth and cell self-renewal under both physiological and pathological conditions, including neuroprotection, inflammation and immune response. Anovel platform for modulating angiogenic processes in cancer therapies was developed based on graphene oxide (GO) functionalized with ANG. The new GO@ANG nanocomposite was characterized by means of UV-visible and fluorescence spectroscopies. The GO@ANG nanotoxicity was assessed by *in vitro* cellular experiments on human prostatic cancer cells (PC-3 line). Laser confocal microscopy (LSM) cell imaging evidenced an enhanced internationalization of the 2D nanomaterial functionalized with the protein rather than the bare nanosheets. Furthermore, significant changes in cell cytoskeleton organization compared to the cell treatments with free protein in different environmental conditions were detected. These results pointed to the modulating capability by the hybrid nanocomposite for different cellular biochemical response.

2D-ThP-18 Defect Inventory of CVT Grown TaS₂ Crystals, Dejia Kong, R. Peckham, University of Virginia; Z. Mao, S. Lee, Pennsylvania State University; K. Burns, I. Harrison, P. Reinke, University of Virginia

Defects are critical to the use and function of transition metal dichalcogenides (TMD), necessitating the study of the defect inventory from point defects to dislocations. The defect inventory sensitively modulates device performance metrics such as electron and phonon conductivity and exciton lifetimes. TMD layers exfoliated from bulk TMD crystals continue to serve as the main vehicle for experiments, and prototype devices. In this work, we present a scanning tunneling microscopy (STM) study at 293 K of the defect inventory in metallic 2H-TaS₂ which is a candidate for contacts in TMD devices. The 2H-TaS₂ bulk crystal was grown by chemical vapor transport (CVT) with an iodine transport agent and high crystalline quality is confirmed with XRD. We capture different groups of defects formed during the CVT process across length scales from point defects to screw dislocation. One of the most prominent surface defects are line vacancies that resemble drainage system patterns in geomorphology maps (Figure 1) and are interpreted as remnants of the flux agent reaction at the growth surface. These line defects are closed and overgrown. The subsurface line defects can be resolved in STM as they imprint electronic and structural inhomogeneities on the subsequent layers. TEM analysis will elucidate the structure and composition across the buried line defects. We will include a discussion of recent electrical measurements.

In addition to mapping the defect inventory, we studied tip-induced nanolithography which affords nanoscale control of vacancy island formation in 2H-TaS₂ and is initiated at point defects. A tip-induced reaction allows selective removal of the top layer (Figure 2) with nanometer precision creating well-defined and faceted "holes", respectively vacancy islands (v-island). The selective area removal of 2H-TaS₂ initiated by SPM probes has been reported previously, but the mechanism of such degradation is still discussed. We propose that it is related to the presence of traces of water at the tip or surface and present a detailed kinetic analysis of the etching process.¹⁻³ We studied the v-island growth over extended times and will discuss the feasibility of targeted etching of structures within the 2H-TaS₂ as a highly selective and high-resolution lithography process.

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2D-ThP-19 Advance in Momentum Microscopy with NanoESCA MARIS, Marten Patt, N. Weber, M. Escher, T. Kuehn, FOCUS GmbH, Germany

Since its introduction in 2005, the energy-filtered photoelectron microscope NanoESCA [1,2] has been used for various application including work-function mapping, imaging XPS and in the last years more prominently for imaging the reciprocal space, i.e., momentum microscopy or orbital tomography (e.g., at the NanoESCA at synchrotron Elettra, Trieste [3]).

The latest revision of the analyzer, called NanoESCA MARIS, has a new

microscope lens. It was designed to achieve a better angular / momentum resolution while keeping the same good real space resolution < 35 nm from its predecessor. In momentum space mode, the instrument achieves a resolution of 0.005 Å⁻¹. We will show the performance on the Rashba split surface state of a Au (111) single crystal (Fig. 1,b). In addition, new working modes, like off-axis zoom, double dispersive imaging mode and an energy dispersion snapshot mode were introduced with the new analyzer and will be presented. Developments in the Imaging Spin Filter for NanoESCA [4] will be discussed.

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2D-ThP-20 A Novel Method to Measure Cross-plane Resistivity of Ultra-Thin Films, S. Weng, University of Southern California; Y. Wang, Stanford University; Celsey Price, H. Blackwood, M. Choffel, A. Miller, University of Oregon; R. Li, M. Chen, University of Southern California; D. Johnson, University of Oregon; A. Majumdar, Stanford University; S. Cronin, University of Southern California

Two-dimensional van der Waals heterostructures are of great interest because they are ideal for fundamental studies and diverse device applications. By vertically stacking 2D materials, you introduce the ability to control, manipulate, and generate the transport and confinement of charge carriers, excitons, phonons, and photons. Understanding and characterizing charge carrier transport across van der Waals interfaces is critical to the fundamental understanding and application of 2D van der Waals heterostructures. Measuring the cross-plane properties of a heterostructure is difficult, however, due to the measurements being intrinsically 2-probe, with the measured total cross-plane resistance including the lead and contact-sample interface resistances in addition to the resistance of the sample. Here we present a novel method to determine the bottom and top sample-contact and lead resistances through in-plane measurements, modeling the extent of current crowding in the end voltage as a function of contact width. The cross-plane sample resistance is obtained by subtracting these resistances from the measured total cross-plane resistance. This opens a unique opportunity to investigate the nature of charge transport across van der Waals interfaces. Temperature-dependent data for the PbSe(VSe₂) heterostructure is used to demonstrate this approach. The dominant contributor to in-plane transport is the metallic VSe₂ layers. The cross-plane carrier transport is expected to be dominated by the semiconducting PbSe layers. A several order of magnitude difference between cross-plane and in-plane resistivities over the 5.5 – 300 K temperature range has been measured.

2D-ThP-21 Evaluating the Impact of Defects, Interfaces and Boundaries on Thermal Transport in 2D Materials Using a Novel Opto-Thermal Metrology Technique with Sub-Micron Resolution, John Gaskins, A. Jones, P. Hopkins, B. Foley, Laser Thermal

Two-dimensional materials offer unprecedented, often record setting thermal properties with seemingly robust potential to structurally and chemically manipulate phonon scattering and thermal transport. These phonon scattering events in 2D systems arise from the plethora of defects and interfaces that arise from both growth and post processing that also are routinely used to manipulate the 2D materials functionalities. The thermal transport properties of 2D materials at and around these defect phonon scattering sites, which often have length scales and spacings on the order of nanometers to 10's of nanometers, are difficult to isolate and measure individually with thermal measurement techniques. For example, optical based techniques for measuring thermal properties of 2D materials (e.g., Raman, TDTR) are ultimately diffraction limited and thus restricted to areal spatial resolution on the order of single micrometers. Techniques using lasers coupled with AFM-tips (e.g., Nano-FTIR) have shown promise in achieving sub-diffraction limited areal resolution to qualitatively interrogate optically excited surfaces, but lack the opto-thermal transduction power afforded by thermoreflectance-based methods to ensure accurate measurement of local temperature and thermal wave modulation.

Here, we introduce a new platform capable of characterizing the thermal properties of 2D materials with ~10 nm areal spatial resolution. Thermal maps of CVD-grown molybdenum disulfide (MoS₂) and exfoliated hexagonal boron nitride (hBN) flakes (both on SiO₂/Si supporting substrates) are presented, highlighting both (a) the higher in-plane thermal conductivity of the hBN compared to MoS₂, as expected per the literature,

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but more importantly (b) the direct visualization of how the thermal resistance increases near wrinkle defects, adlayer nucleation sites, and flake boundaries. These local increases in resistance are attributed to the impact of the defect on phonon transport. As a result, this new capability enables the direct visualization and estimation of the length scales over which various defect structures exert influence over phonon transport in these 2D materials.

2D-ThP-22 Site-Specific Synthesis of Molybdenum Dichalcogenide Using Chemical Vapor Deposition Technique, *Chu Te Chen, A. Butler, Y. Fu, A. Cabanillas, A. Ahmed, A. Chakravarty, S. Jadeja, H. Hui, L. Samson, H. Zeng, A. Yadav, H. Li*, The State University of New York, Buffalo; *K. Wong*, Applied Materials; *F. Yao*, The State University of New York, Buffalo

Two-dimensional (2D) semiconducting transition metal dichalcogenides (TMDs) have been extensively explored for their potential as channel materials in electronic devices. The device performance has been significantly improved over the years due to the advancements in understanding of TMD materials, device design, and fabrication process. Despite the early success in demonstrating proof-of-concept devices, scalable and single-crystal growth of TMD films on suitable substrates remains a formidable roadblock to the development of commercially viable TMD-based nanoelectronics. To mitigate this problem, there is a pressing need for the precise growth of high-quality TMD layers at desired locations in the device architecture with consistent layer characteristics.

In this study, we introduce a novel approach for the direct and site-selective synthesis of MoS₂ flakes, a representative type of TMD materials, on silicon substrates using the chemical vapor deposition (CVD) technique. This achievement is enabled through seed layer patterning using E-beam lithography, facilitating site-specific nucleation and growth. By systematically exploring the CVD synthesis parameter space, critical process parameters that govern the sublimation and diffusion processes of the Mo-containing intermediates have been identified. To validate the success of the selective growth of MoS₂ and unveil the structure-property-performance relationship, a series of microscopic and spectroscopic characterizations coupled with electrical measurements are employed to determine the microstructural and transport properties of the obtained flakes. Our results represent technological innovation for direct, scalable synthesis of TMDs in a location-selective manner which has potential to advance the development of next-generation nanoelectronics based on TMD materials.

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