Nanometer-scale Science and Technology Division
Room A222 - Session NS-TuA

Recent Advances in Nanoscale Probing and Fabrication

Moderator: Jay Mody, GLOBALFOUNDRIES Inc.

4:20pm **NS-TuA-7 Electrical, Photovoltaic, and Nano-Optical Characterization of TMD Lateral Heterostructures***, **Marudachalam Shanmugasundaram,*** HORIBA Scientific*; A Elias, M Terrones,* The Pennsylvania State University*; H Terrones,* Rensselaer Polytechnic Institute

The growth of lateral heterostructures of transition metal dichalcogenides (TMDs) was recently demonstrated, which has created the potential for fabricating semiconductor devices with novel electronic properties. Specifically, it would combine distinct properties of materials derived from different sources into one device. It has been shown that under well-controlled growth conditions, MoS_2-WS_2 lateral heterostructures with atomically sharp interfaces can be synthesized. While the growth of such materials can be challenging, the development of analytical methods with the capability of providing chemical information, in addition to morphological information, with nanometer-scale spatial resolution is equally challenging.

Raman spectroscopy is used to study chemical composition of materials with high specificity, but it lacks sensitivity due to the inherent weakness of the Raman scattering phenomenon. Besides, its spatial resolution is diffraction-limited to ~0.5 λ. These drawbacks can be overcome by combining Raman spectroscopy with Scanning Probe Microscopy (SPM) in which certain metal particles placed at the end of the SPM tip act as plasmonic substrate. This technique is referred to as tip-enhanced Raman spectroscopy (TERS). This combination provides not only the benefits of both SPM and Raman microscopy at the same time, but also enables Raman mapping with spatial resolution proportional to the size of the coated SPM tip (well below the diffraction limit) due to plasmonic enhancement of Raman signal.

In this work, we present characterization of MoS_2-WS_2 lateral heterostructures based on morphology, electrical properties, photovoltaic properties, and chemical composition, using a single platform. Scanning Kelvin imaging was used to map the surface potential as well as electro-mechanical contrast proportional to capacitance from the heterostructures. Their surface potential and capacitance change dramatically in a reversible manner when the heterostructures are illuminated by a laser, highlighting their photovoltaic properties. Raman and photoluminescence (PL) maps were recorded with 532 nm excitation, which enabled collection of Raman and PL bands from both materials simultaneously with reasonable separation. In addition, tip-enhanced Raman and PL maps were collected across the interface, with sub-diffraction limited spatial resolution. In summary, a unique collection of characterization techniques were used based on AFM-Raman instrumentation to study morphological, electrical, photovoltaic properties, and chemical composition of MoS_2–WS_2 lateral heterostructures.

4:40pm **NS-TuA-8 Development of Near-Field Electrospinning for 3D Nanofabrication for tissue engineering applications***, **Alex Nagle,*** University of Wollongong, Australia

The major goal in this work was to mimic the nanofibrous proteins found in the neural extracellular matrix (nECM). NFES is a versatile nanofiber patterning technique, utilising additive layer-by-layer deposition to create nanofibrous microstructures. However, high volume can be a difficult to achieve due to inhibition of the ejection process by polymer build-up. To mimic the 3D nECM, led to the development of a new technique: Suspension Near-Field Electrospinning (SNFES).

Suspended, aligned fibres can be printed across void space between electrodes and so a strategy of using free standing electrode pillars to support distributed PEO fibres within space was investigated. This strategy relied on a high accuracy, software integrated NFES system as well as 3D printed pillar electrodes, fabricated by Selective laser melt (SLM). Interpillar motion of the emitter, drew fibers between four-pillar electrodes, demonstrating SNFES.

The process parameters, working distance, maximum stage speed, voltage, PEO solution concentration, and pattern iteration effects of SNFES through orthogonal experiments. The need for more complex structures in TE, led to the development of further pattern types, working around the simple four-pillar structure, to produce crossing arrays. Alignment of the arrays was accurate to ± 5°; diameter was modulated by the process parameters; while density exponentially decayed at high iteration by the electrostatic inhibitory effects.

Finally, ultrafine polycaprolactone (PCL) fiber arrays prepared using SNFES, then encapsulated into a biocompatible gellan gum methacrylate (GGMA) hydrogel matrix, to mimic the nanofibrous proteins of the nECM. Parametric studies varying fiber diameter, as well as electrode pillar design and pattern iteration; elucidated the encapsulated array effects. It was found that fiber encapsulation led to dramatic improvements in the constructs mechanical properties, raising the storage modulus from 0.17 up to 1.28 kPa, (native tissue 0.5 -1kPa) upon minimising the fiber diameter below 1 micron.

The findings of this research are significant as it creates for the first time a suspended polymer nanoarray, in a directed manner, which can be extended across multiple working 3D planes in situ. The hybrid fiber-gel systems can be mechanically tailored based on the findings of the parametric experiments. The increase in nanoarray volume and density achieved here is expected to address challenges of producing hierarchical tissue constructs in 3D.

Acknowledgements

The authors acknowledge the Australian Research Council financial support of the Australian Research Council (ARC) Centre of Excellence Scheme (Project CE 140100012).

5:00pm **NS-TuA-9 The Fundamentals of Silica Nanoparticle-based Hydrophilic Antifouling Coating***, **Dan Yang,*** University of wollongong, Australia*; P Molino,* University of Wollongong, Australia*; M Higgins,* University of Wollongong

Biological fouling of artificial surfaces has led to enormous problems for many industries including biomedical devices and maritime shipping. One of the strategies is using environmentally benign antifouling coatings, in particular, hydrophilic coating to prevent the adhesion of microbes. From an industry perspective, the silica nanoparticles (SiNP) synthesis can be easily scaled up and applied by different fabrication techniques, making the use of hydrophilic SiNPs a promising strategy to address the challenges of biofouling.

A commercially available Glycidoxypropyltrimethoxysilane (GPS) modified SiNPs hydrophilic coating system was firstly discovered to have an excellent antifouling performance by our research group, after tests against protein, bacteria and fungal spore. To elucidate the underlying antifouling mechanisms of GPS-SiNPs coating, static AFM force measurements were undertaken to compare the nanoscale surface forces of Unmodified versus GPS modified SiNPs coatings in liquid as a function of salt concentration and pH, and 3D Scanning Force Microscopy (3D-SFM) was employed to visualize the interfacial structures at the molecular and atomic level above single nanoparticles. These studies showed that the presence of a GPS/hydration layer on the GPS-SiNPs surface was attributed to the antifouling properties and suggested to arise from the presence of hydration/steric forces.

In the current work, Single Cell Force Spectroscopy (SCFS) was employed to reveal the biological interactions between the above antifouling coatings and single live fungal spores of *Epicoccum nigrum*. A main finding is that the GPS-SiNPs surfaces can prevent the fungal spore adhesion through both the long-range EDL repulsion, as well as the short-range hydration/steric repulsion. Furthermore, the latter short-range hydration/steric effect upon spore contact is stable at all salt concentrations, and hence shows remarkable ability of the GPS/hydration layer to prevent the spore adhesion given the known sophisticated surface structures and diversity of biomolecules of these microbial organisms. This study reveals the fungal spore interactions on surfaces at the molecular level upon approach to and during the detachment process by using a single-cell method to quantify the antifouling performance of coatings against biofoulants, i.e. fungal spore, and give insights about future coating design.

5:20pm **NS-TuA-10 The Effects of Atomic-Scale Strain Relaxation on the Electronic Properties of Monolayer MoS_2***, **Daniel Trainer**, Y Zhang,* Argonne National Laboratory*; F Bobba,* University of Salerno, Italy*; X Xi,* Temple University*; S Hla,* Argonne National Laboratory*; M Iavarone,* Temple University

The ability to control nanoscale electronic properties by introducing macroscopic strain is of critical importance for the implementation of two-dimensional (2D) materials into flexible electronics and next-generation strain engineering devices. In this work, we correlate the atomic-scale lattice deformation with a systematic macroscopic bending of monolayer molybdenum disulfide films by using scanning tunneling microscopy and spectroscopy implemented with a custom-built sample holder to control the strain. Using this technique, we are able to induce strains of up to 3% before slipping effects take place and relaxation mechanisms prevail. We find a reduction of the quasiparticle bandgap of about 400 meV per percent local strain measured with a minimum gap of 1.2 eV. Furthermore, unintentional nanoscale strain relaxation of van der Waals monolayer sheets can negatively impact strain engineered device performance. Here we investigate such strain relaxation mechanisms that include one-dimensional ripples and 2D wrinkles which alter the spatial electronic density of states and strain distribution on the atomic scale.

5:40pm **NS-TuA-11 Understanding Tip-induced Nanoscale Wear for Tomographic Atomic Force Microscopy*, Umberto Celano,*** IMEC, Belgium*; X Hu,* University of California-Merced*; L Wouters, K Paredis, T Hatschel, P van der Heide,* IMEC, Belgium*; A Martini,* University of California-Merced

The ability of contact-mode atomic force microscopy (AFM) to remove material while scanning has repeatedly been used for surface modification and small-scale tip-induced nanofabrication.[1] In the simplest form, the physical removal of material can be achieved by scanning the nanosized probe against the surface at high enough pressure.[2] More recently, tomographic capability has been explored for various electrical AFM modes by leveraging the same concept and alternating tip-induced removal and probing, in what is often referred to as Scalpel AFM.[3] Here, high-pressure AFM scans (i.e., high load force) are used for a controlled material removal and alternated with conventional contact-mode scans (i.e., standard load force). The alternation of scanning conditions delivers a slice-and-view methodology that generates three-dimensional (3D) datasets, with nm-precision in depth. This method has found wide application in the analysis of ultra-scaled nanoelectronics, where 3D architectures are currently dominating and the probing of confined volumes is mandatory.[4] However, for complex nanostructures such as integrated electronic devices, a detailed comprehension of the tip-sample interaction it's required for the precise control of the removal process in heterogenous materials. In this work, we combine experimental AFM data with molecular dynamics (MD) simulations that study the fundamentals of high-pressure tip-induced material removal for heterogenous nanostructures. Metal-oxide nanopillars (80 -120 nm diameter) embedded in SiO_2 are experimentally probed using high pressure sliding contacts (i.e., diamond probes). We select a regime whereby tens of nm^3 are removed targeting a controllable removal rate below 3 nm/scan. The impact of the tip-sample interaction inside the worn regions is investigated in order to generate understanding on the physical wear mechanisms. The experimental results are compared with MD simulations that allow us to study the removal processes as a function of different parameters of the AFM scan, including removal rate and the quality of the machined area. As such, this work paves the way for the development of accurate models to improve the quality of tip-induced material removal in complex nanostructures, with great scientific and technological interest for tomographic probing using AFM.

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6:00pm **NS-TuA-12 Probing the Viscoelastic Properties of Polymer Composites with AFM-based Dynamic Mechanical Analysis*, Bede Pittenger,*** *S Osechinskiy, J Thornton, S Loire, T Mueller,* Bruker Corporation

The mechanical performance and function of polymer composites and thin films are controlled by the properties of the components as well as the microstructure of the material. As confinement effects and interphase formation can alter properties of the microphases, only measurements performed directly on the composite can provide the needed local property distribution. Mechanical properties of polymers are generally time dependent, so a full understanding requires measurements over a range of frequencies and temperatures. Ideally, one would like to observe the mechanical behavior of these microscopic domains while they pass through their glass transitions to appreciate the influence of size effects and confinement on time dependent mechanical properties.

With its proven ability to map mechanical properties at the nanometer level [1], Atomic Force Microscopy (AFM) has the resolution and mechanical sensitivity needed to investigate these domains. Unfortunately, established AFM measurement modes do not yield results that allow direct comparison to established rheological techniques like Dynamic Mechanical Analysis (DMA). Contact resonance [2] provides mechanical property maps at well-defined frequencies, but cantilever resonances are many orders of magnitude higher than DMA, making comparisons indirect at best. Intermittent contact methods like TappingMode [3], force volume, and PeakForce Tapping [4] face challenges in calculating intrinsic mechanical properties like storage and loss modulus (or tan delta) due to the non-linear process of making and breaking contact [5].

AFM based nano-DMA (AFM-nDMA) provides viscoelastic results that can be directly compared with bulk DMA. Like bulk DMA, it provides spectra of storage and loss modulus across frequency and temperature allowing construction of master curves through Time Temperature Superposition (TTS) [6]. In addition, it allows high resolution measurements localized to the microscopic structures within heterogeneous samples. This presentation will examine the capabilities of this new mode with examples in a wide range of polymers and composites.

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