2D Materials Technical Group
Room C123 - Session 2D-TuM

2D-Materials: Heterostructures and Functionalization

Moderators: Xiangfeng Duan, UCLA, **Kai Xiao**, Oak Ridge National Laboratory

8:00am **2D-TuM-1 A Wafer Scale Approach to Synthesize Targeted Metastable Heterostructures*, David Johnson,*** University of Oregon **INVITED**

Heterostructures consisting of two or more compounds with different crystal structures interleaved with targeted layer thicknesses and sequences of constituents have been the focus of intense interest due to the discovery of emergent properties of interest for a number of applications. My group has pioneered a synthesis approach to these materials based on repeated deposition of a sequence of elemental layers where the number of atoms in each layer correspond to the amount need to form each of the targeted constituent structures. These designed layered precursors self-assemble at low temperatures into the targeted heterostructures because phase segregation into separated bulk constituents is disfavored by low interdiffusion rates. Since this self-assembly is independent of the substrate structure, this synthesis approach is compatible with lithography. The ability to precisely control constituent layer thicknesses and layer sequences provides opportunities to systematically probe structure-function relationships. We discovered that monolayers of VSe_2 in $(MSe)_m(VSe_2)$ heterostructures have a charge density wave whose onset temperature depends on both the identity and the thickness of the MSe (*m*) constituent. We found that the chemical potential difference between constituent layers is compensated by charge donation, leading to systematic changes in electrical transport properties as the relative thickness of constituent layers are varied. We have also discovered that the interaction between constituent layers can stabilize constituent layer structures that are not known as isolated compounds. We have prepared magnetic Pb_2MnSe_3 layers in $(Pb_2MnSe_3)(VSe_2)_n$heterostructures and a new 1T structured transition metal dichalcogenide, $FeSe_2$, in $(PbSe)_1(FeSe_2)_n$. Since this synthesis approach is compatible with lithography, we have been able to develop an approach to measure both cross plane and in plane electrical properties on the same structure. The ability to prepare families of heterostructures with a variety of constituent layers from designed precursors creates a new "thin film metallurgy" where nanostructure, interfacial phenomena and interlayer interactions can be systematically exploited to manipulate physical properties.

8:40am **2D-TuM-3 Simple Approach to Demonstrate the Van Der Waals Heterostructure Composed of Different Kinds of MoS_2 Phase for Photodetector Application***, K. Aydin, T. Kim,* Sungkyunkwan University (SKKU), Republic of Korea*; **Chisung Ahn,*** Korea Institute of Industrial Technology, Republic of Korea

The 2D materials have considered as noticeable candidates to demonstrate photodetector because of their excellent optical and electronic properties. Especially, inherent phase dependent tunable optical band gap properties of 2D-MoS_2 (Molybdenum Disulfide) have significant advantages for versatile optoelectronic applications. Therefore, development the easy phase controlling methodology of 2D-MoS_2 could be considered as an important factor to figure out its applicability for photodetector. In this study, innovative procedure is suggested to synthesis the Van der Waals heterostructure by stacking the different phase of MoS_2 (1T and 2H) based on plasma assisted sulfurization process through only process temperature control under the optimized other variables. It allowed to prepare 4 kinds of different MoS_2 structures (1T/2H, 1T/1T, 2H/1T and 2H/2H) by stacking the homo or hetero phase, and photocurrents for each also measured to explore the relevant correlation.

9:00am **2D-TuM-4 TaS_x Prepared by Atomic Layer Deposition: Two-Dimensional Crystalline Films as Cu Diffusion Barrier***, **Sanne Deijkers**, H. Thepass,* Eindhoven University of Technology, The Netherlands*; H. Sprey, J. Maes,* ASM, Belgium*; E. Kessels, A. Mackus,* Eindhoven University of Technology, The Netherlands

As transistors in leading-edge nanoelectronics are becoming smaller and smaller, the challenge of scaling the interconnect becomes very prominent. In this scaling, we need a replacement for the Cu diffusion barrier in the back-end-of-line, since conventionally used TaN/Ta barriers fail if they are thinner than 3 nm [1]. Tantalum sulfide (TaS_x) is a versatile Ta-based two-dimensional transition metal dichalcogenide (2D-TMD) that can function as Cu diffusion barrier as has been recently shown for films prepared by chemical vapor deposition [2]. In this work we report on the diffusion barrier performance of TaS_x synthesized by atomic layer deposition (ALD). ALD offers the desired control and conformality required for thin layers in demanding structures. In our previous work, we have shown that 2D-TMD MoS_2 films synthesized by ALD can outperform MoS_2 films deposited by other techniques [3].

TaS_x films were deposited using a plasma-enhanced ALD process using tert-butyliminotrisdimethylaminotantalum (TBTDMT) as Ta precursor and an H_2S / Ar / H_2 plasma mixture as co-reactant at 300 °C. It is demonstrated that the crystallinity and stoichiometry can be altered by changing the plasma composition. Addition of H_2 to the Ar and H_2S plasma mixture leads to crystalline TaS_2 films, instead of amorphous TaS_3 films, as measured by x-ray diffraction and x-ray photoelectron spectroscopy.

The barrier performance of the TaS_x films against Cu diffusion was characterized by time-dependent dielectric breakdown (TDDB) tests. Amorphous TaS_3 films do not function as Cu diffusion barrier, while the crystalline TaS_2 films show a median time to failure ($TTF_{50\%}$) of 530 ± 14 s, where the longest observed breakdown time is 93 hours. This is a substantial improvement compared to barrierless structures ($TTF_{50\%}$ = 201 ± 5 s), which reveals the potential of ALD-grown TaS_x as Cu diffusion barrier.

[1] Li *et al., Materials* **13**, 5049 (2020)

[2] Lo *et al., J. Appl. Phys.* **128**, 080903 (2020)

[3] Deijkers *et al., Adv. Mater. Interfaces***10**, 2202426(2023)

9:20am **2D-TuM-5 Hybrid Epitaxial Heterostructures for Topological Spintronics***, **Nitin Samarth**,* Pennsylvania State University **INVITED**

The confluence of fundamental symmetries and spin-orbit coupling is known to produce emergent electronic states in crystalline solids that are accurately described using the language of topology [1]. This talk describes how recent developments in the synthesis and study of epitaxially grown topological quantum materials and their heterostructures yield new insights into the interplay between spin and charge transport, providing an attractive path toward topological spintronic technologies that work under ambient conditions [2-9].

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1. Nitin Samarth, "Quantum materials discovery from a synthesis perspective," *Nature Mater,* **16**, 1068-1076 (2017).
2. A. R. Mellnik, *et al.*, "Spin-transfer torque generated by a topological insulator," *Nature* **511,** 449 (2014).
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4. Hailong Wang *et al.*, "Fermi level dependent spin pumping from a magnetic insulator into a topological insulator," *Phys. Rev. Res.* **1**, 012014 (R) (2019).
5. W. Yanez *et al*., "Spin and charge interconversion in Dirac semimetal thin films," *Phys. Rev. Appl.* **16**, 054031 (2021).
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7. W. Yanez *et al*., "Giant dampinglike-torque efficiency in naturally oxidized polycrystalline TaAs thin films," *Phys. Rev. Appl.* **18**, 054004 (2022).
8. W. Yanez *et al*., "Thin film growth of the Weyl semimetal NbAs," arXiv:2304.13959
9. A. Vera, W. Yanez, et al., "Emergent spin phenomena in air-stable, atomically thin lead," arXiv:2205.06859

11:00am **2D-TuM-10 Designer Quantum Matter in Van Der Waals Heterostructures***, **Peter Liljeroth**,* Aalto University, Finland **INVITED**

Van der Waals (vdW) heterostructures have emerged as a playground for realizing and engineering exotic quantum states not found in naturally occurring materials. Materials with very different physical properties can be combined essentially at will. As the layers interact only through weak vdW forces, the individual layers retain their intrinsic properties. However, proximity effects cause properties to "leak" between the adjacent layers and allow creating exotic quantum mechanical phases that arise from the interactions between the layers. These key features have recently made it possible to realize exotic quantum phases by design.

I will highlight these concepts through our results on realizing topological superconductivity and heavy-fermion physics in vdW heterostructures [1-3]. We use molecular-beam epitaxy (MBE) in ultra-high vacuum for the sample growth and characterize the resulting samples using low-temperature scanning tunneling microscopy (STM). Topological superconductivity requires combining out of plane ferromagnetism, Rashba-type spin-orbit interactions and s-wave superconductivity, and we use monolayer ferromagnet $CrBr_3$ on a superconducting $NbSe_2$ substrate to realize this [1,2]. I will discuss how the moiré pattern due to the lattice mismatch between $CrBr_3$ and $NbSe_2$ is an essential ingredient in this system as it profoundly modifies the topological phase diagram and enables the realization of a topological superconducting state that would not be accessible in the absence of the moiré. As another example of a designer system, I will introduce 1T–TaS_2 / 1H-TaS_2 heterostructures as a platform for realizing heavy fermion physics in a vdW heterostructure [3]. These results highlight the versatility of vdW heterostructures in realizing quantum states that are difficult to find and control in naturally occurring materials.

References

[1] S. Kezilebieke, M.N. Huda, V. Vaňo, M. Aapro, S.C. Ganguli, O.J. Silveira, S. Głodzik, A.S. Foster, T. Ojanen, P. Liljeroth, Topological superconductivity in a van der Waals heterostructure, Nature 588, 424 (2020).

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[3] V. Vaňo, M. Amini, S.C. Ganguli, G. Chen, J.L. Lado, S. Kezilebieke, P. Liljeroth, Artificial heavy fermions in a van der Waals heterostructure, Nature 599, 582 (2021).

11:40am **2D-TuM-12 2D Hybrids Based on Graphene Oxide and Palladium Nanozymes for Multimodal Theranostics***, A. Foti, L. Calì, S. Petralia, A. Fraix, G. Forte, R. Fiorenza, S. Scirè, L. D'Urso, C. Bonaccorso, C. Fortuna,* ***Cristina Satriano,*** University of Catania, Italy

Graphene oxide (GO)/palladium (Pd) nanocomposites have shown a great potential asmultifunctional nanoparticles with plasmonic, photothermal and enzyme-like behavior for multimodal theranostics.

In this work, different types of hybrid 2D GO/Pd nanosystems were synthesized, with the size of the 2D nanomaterials being controlled by the precursor concentrations as well as different chemical functionalities, including GO vs. reduced-thiolated GO (rGOSH), N-doped reduced GO (rGO-N_X),mixed organic/inorganic matrix. The physicochemical properties were scrutinized by using UV-visible and Raman spectroscopies, atomic force microscopy, zeta-potential and hydrodynamic light scattering. Theoretical DFT calculations paralleled the experimental studies. The GO/Pd hybrids were tested in terms of photocatalysis experiments of H_2 evolutionand photothermal response.

The assessment of nanozyme features for theGO/Pd nanoplatforms unveiled a strong enhancement of hydrogen evolution and broad antioxidant activities, as scrutinized respectively by photocatalysis experiments and MitoSOX and SOD-like activity, respectively.The bio-interface response of systems was evaluated on both tumor cells and healthy cells. Proof-of-work in vitro cell experiments on human prostate cancer cells (PC-3 line) and mouse embryonic fibroblast cells (3T3 line) cells were carried out in terms of cytotoxicity (MTT assay), inhibition of cell migration (wound scratch test) and organelle perturbation (colocalization studies by confocal microscopy). The MTT assay and wound scratch test confirmed the antitumor efficiency of all Pd-based samples in inhibiting tumor growth and monitoring cell migration, respectively. In particular, cells treated with GO-PdNP hybrids with larger sizes showed higher cell viability and migration rate in healthy cells (3T3 line). This makes them promising candidates as nanozyme-theranostic platforms for cancer treatment.The results pointed to a significant reduction of tumor growth and thus the promising potential of the developed GO/Pd hybrid nanozymes in cancer therapy.

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12:00pm **2D-TuM-13 Hybrid Molecule/Quantum Material van Der Waals Heterostructures***,* ***Emanuele Orgiu,*** Institut national de la recherche scientifique (INRS), Canada

2D materials are held together by weak interplanar van der Waals (vdW) interactions. The incorporation of molecules in such materials holds an immense potential to understand and modify the fundamental physical properties of the pristine materials while creatin new *artificial materials*. Whilst nature offers a finite number of 2D materials, an almost unlimited variety of molecules can be designed and synthesized with predictable functionalities. The possibilities offered by systems in which continuous molecular layers are interfaced with inorganic 2D materials to form hybrid organic/inorganic van der Waals heterostructures (H-vdWH) are emphasized. Similar to their inorganic counterpart, the hybrid structures have been exploited to suggest novel device architectures. Moreover, specific molecular groups can be employed to modify intrinsic properties and confer new capabilities to 2D materials. In particular, I will highlight how molecular self-assembly at the surface of 2D materials can be mastered to achieve precise control over position and density of (molecular) functional groups, paving the way for a new class of hybrid functional materials.

In particular, within such vdW heterostructures, currently assembled by mechanical superposition of different layers, *periodic potentials* naturally occur at the interface between the 2D materials. These potentials significantly modify the electronic structure of the individual 2D components within the stack and their alignment, thus offering the possibility to build up hybrid and novel materials with unique properties.

Also, I will show how the presence of ordered supramolecular assemblies bearing different functional groups can *modify the pristine Shubnikov-De Haas oscillations* occurring in graphene.

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