

Tuesday Morning, October 22, 2019

2D Materials

Room A216 - Session 2D+AS+MI+NS-TuM

2D Materials Characterization including Microscopy and Spectroscopy

Moderator: David Geohegan, Oak Ridge National Laboratory

8:00am **2D+AS+MI+NS-TuM-1 Near-field Infrared Spectroscopy of Single Layer MnPS₃**, *Sabine Neal*, University of Tennessee Knoxville; *H Kim*, Rutgers University; *K Smith*, *A Haglund*, *D Mandrus*, University of Tennessee Knoxville; *H Bechtel*, Advanced Light Source, Lawrence Berkeley National Laboratory; *L Carr*, National Synchrotron Light Source II, Brookhaven National Lab; *K Haule*, *D Vanderbilt*, Rutgers University; *J Musfeldt*, University of Tennessee Knoxville

In order to explore the properties of a complex van der Waals material under confinement, we measured the near-field infrared response of the magnetic chalcogenide MnPS₃ in bulk, few-, and single-layer form and compared the results with traditional far field vibrational spectroscopy and complementary lattice dynamics calculations. Trends in the activated B_u mode near 450 cm⁻¹ are particularly striking, with the disappearance of this structure in the thinnest sheets. Combined with the amplified response of the A_g mode and analysis of the $A_u + B_u$ features, we find that the symmetry is unexpectedly *increased* in single-sheet MnPS₃. The monoclinicity of this system is therefore a consequence of the long-range stacking pattern rather than local structure.

8:20am **2D+AS+MI+NS-TuM-2 Multi-parameter Analysis of Genesis and Evolution of Secondary Electrons produced in the Low Energy Regime**, *Alessandra Bellissimo*, ETH Zürich, Switzerland; *G Pierantozzi*, CNR - Istituto Officine Materiali, Italy; *A Ruocco*, *G Stefani*, Università degli Studi Roma Tre, Italy; *O Ridzel*, *V Astašauskas*, *W Werner*, Technische Universität Wien, Austria; *M Taborelli*, CERN, Switzerland; *G Bertolini*, *U Ramsperger*, ETH Zürich, Switzerland; *O Gürlü*, ETH Zürich, Switzerland, Turkey; *D Pescia*, ETH Zürich, Switzerland

The mechanisms responsible for electron-induced Secondary Electron Emission (SEE) generation of these ubiquitous Secondary Electrons (SEs) in a solid surface is not yet fully understood. In particular, the question *how many* "true secondary" electrons are generated and emitted from the target per incident primary electron awaits resolution and is of great fundamental as well as technological importance. The present work reports on a study of these and related questions by means of a variety of spectroscopic tools of increasing finesse. The interaction of Low-Energy Electrons with surfaces exhibiting different long-range order, was investigated by combining measurements of the Total Electron Yield in absolute units, single-electron as well as (e,2e)-coincidence spectroscopy. This investigation has led to the disentanglement of the elementary processes that need to be considered and comprehended for the understanding of the SE-generation probability, fully taking into account both energy and momentum conservation in the collision and the band structure of the solid. Single ionising scattering events, assisted by collective excitations, i.e. *plasmons*, constitute one of the fundamental ingredients leading to SEE. In the Low-Energy-regime the electron yield of a material is constituted by the interplay of reflectivity and SEE, both strongly dictated by the target band structure. The gathered information is further used in an attempt to interpret the signal generation mechanisms relevant in Scanning Field-Emission Microscopy (SFEM) [1].

Reference:

[1] A. Bellissimo, PhD Thesis, "Multiparameter Analysis of Genesis and Evolution of Secondary Electrons produced in the Low Energy Regime", URL: https://www.researchgate.net/publication/332684398_Multiparameter_Analysis_of_Genesis_and_Evolution_of_Secondary_Electrons_produced_in_the_Low_Energy_regime

8:40am **2D+AS+MI+NS-TuM-3 Probing Point Defects, Folds and Interfaces in 2D Material Heterostructures using Scanning Transmission Electron Microscopy**, *Sarah Haigh*, University of Manchester, UK **INVITED**

Scanning Transmission Electron Microscopy (STEM) is one of the few techniques able to probe the structure and chemistry of 2D materials when these are stacked to form vertical heterostructures. By combining STEM with electron energy loss spectroscopy and energy dispersive X-ray spectroscopy it is possible to characterise individual point defects,[1] to measure interlayer distances for dissimilar materials [2] and to investigate the microstructure of mechanically deformed structures at the atomic scale [3]. We have extensively employed plan view and cross sectional STEM imaging to investigate complex 2D heterostructures. For example, we have

shown that protruding defects prevent the realisation of pristine interfaces between transition metal selenides (MoSe₂, WSe₂, NbSe₂) and boron nitride, unless exfoliation is performed in an inert environment.[2]

We have analysed microstructures produced when 2D van der Waals materials (graphite, boron nitride, MoSe₂) are subjected to mechanical deformation and find that the types of defect can be predicted from just the bend angle and thickness of the materials.[3] In particular we find that above a critical thickness the materials exhibit numerous twin boundaries and for large bend angles these can contain nanoscale regions of local delamination. Such features are proposed to be important in determining how easily the material can be thinned by mechanical or liquid exfoliation.[3]

2D material heterostructures are also enabling new STEM imaging capabilities. We show they can be used as a platform to study real time reactions in liquid environments with unprecedented spatial resolution and spectroscopic capabilities [4]. We further demonstrate that graphene encapsulation allows imaging of point defect dynamics, structural degradation and mechanically induced stacking faults in 2D monochalcogenides, GaSe and InSe [1].

References

- [1] D G Hopkinson et al, ACS Nano, (2019) 10.1021/acsnano.8b08253
- [2] A P Rooney et al. Nano Letters, (2017) 17, 5222.
- [3] A P Rooney et al. Nature Communications (2018) 9, 3597
- [4] D J Kelly et al Nano Letters, (2018) 18, 2, 1168

9:20am **2D+AS+MI+NS-TuM-5 Low-Energy Electron Induced Disorder and Decomposition of Self-assembled Monolayers on Au(111)**, *Jodi Grzeskowiak*¹, University at Albany - SUNY; *C Ventrice, Jr.*, SUNY Polytechnic Institute

To study the interaction of low energy electrons with thin organic films, measurements have been performed on electron induced disordering and decomposition of 1-decanethiol molecules grown via vapor phase deposition on Au(111). Surface analysis techniques were used to characterize the monolayers before and after electron exposure. LEED was used to determine the structure of the SAM and the rate of disordering and decomposition. It was observed that the diffraction pattern of the lying down phase of the SAM, held near 100 K, almost completely disappears within about three minutes of exposure. However, when the temperature of the irradiated sample was raised to 300 K and then cooled back down to around 100 K, most of the intensity of the diffraction pattern returns, indicating that electron exposure is primarily inducing disorder. TPD was used to evaluate the thermal stability of the SAMs and the resulting desorption products after electron exposure. For the standing up phase SAM, two desorption features for the hydrocarbon fragments of the SAM are observed, one around 130 °C and a second near 220 °C. For the lying down phase, only the higher temperature desorption feature is observed, which indicates that the SAM is converting from the standing up phase to the lying down phase during the heating process. For both phases, desorption peaks for S and H₂S at around 250 °C were observed, suggesting that there is a high probability for the alkane chain of the decanethiol molecule to detach from the sulfur head group. After electron exposure of the standing up phase, a large reduction in the intensity of the two desorption peaks for the masses monitored for the hydrocarbon fragments was observed. However, the intensities of the peaks associated with S and H₂S were similar to those for the samples that were not irradiated with electrons. For the lying down phase, the intensities and positions of all of the desorption peaks were similar to the unexposed SAMs, which indicates that the cross-section for electron beam damage for the lying down phase is much lower than that for the standing up phase. Ex-situ XPS was used to monitor the decomposition of the SAMs. After irradiation with 80 eV electrons, an uptake of oxygen was observed in the XPS measurements for both samples. This oxygen uptake gives evidence that oxygen in the air is reacting with carbon and sulfur atoms whose bonds were broken during electron exposure.

9:40am **2D+AS+MI+NS-TuM-6 Continuous Silicene, Silicene Ribbons and Surface Reconstructions on h-MoSi₂**, *Anna Costine*, *C Volders*, University of Virginia; *M Fu*, Oak Ridge National Laboratory; *P Reinke*, University of Virginia

Silicene has emerged as a 2D material of interest because of its spin-orbit coupling, tunable electronic structure, and Dirac type behavior. Synthesis of silicene with preserved Dirac-type electronic structure has proven

¹ ASSD Student Award Finalist

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challenging, but is critical to realizing theoretically predicted quantum states and devices. To date, Ag(111) remains the most popular substrate for silicene synthesis, but is discussed controversially due to its similarity with surface alloys. Silicene has also been synthesized on other substrates including Ir, IrSi₃, and ZrB₂. Silicene synthesis on a semiconducting substrate with a low buckling conformation to conserve the Dirac-type behavior would be ideal. The synthesis of silicene on new substrates that allow for direct device integration is an important next step.

We developed an alternate approach to silicene synthesis that allows for silicene synthesis on semiconducting silicides. The (0001) surface of h-MoSi₂ has hexagonal symmetry and a lattice constant close to that of silicene. Our recent measurements support the assumption that silicene is electronically decoupled from the substrate. The h-MoSi₂ crystallites, which are terminated by the (0001) plane are grown by depositing Mo onto a Si (001) or Si(111) surface. Upon annealing to ~800°C, the Si atoms decouple from the underlying surface and form a weakly buckled silicene layer with the √3 x√3 surface as seen by STM.

Our recent work expands this study and uses STM/S at 77 K to achieve a comprehensive description of silicene-on-silicide. The amount of Mo deposited (0.3 nm - 18 nm) and annealing temperature (700- 1000°C) were varied. All surface structures discussed here are on h-MoSi₂ crystallites in the (0001) plane. Three distinct surface structures coexist - silicene ribbons, a 4x4 reconstruction, and a complex reconstruction which is very sensitive to variations in the bias voltage. The electronic structure of silicene-ribbons shows a V-shaped density of states close to EF, indicative of Dirac-like behavior, while the other reconstructions are semiconducting. The surface and electronic structures observed on h-MoSi₂ crystallites as a function of the synthesis conditions will be discussed. The preference for silicene-ribbons in the low T STM/STS measurements is currently attributed to a faster post-deposition cooling rate, but the exact mechanism is still open to debate. We will present a detailed discussion of the electronic structure of silicene and silicene ribbons, and suggest mechanisms for the transition from the (0001) surface to silicene. Our goal is to develop synthesis approaches suitable for device integration of both silicene conformations.

11:00am 2D+AS+MI+NS-TuM-10 Epitaxial Growth and Characterization of Single-Orientation Single-Layer Transition Metal Dichalcogenides on Au(111), *L Bignardi*, University of Trieste, Italy; *Daniel Lizzit*, Elettra - Sincrotrone Trieste, Trieste, Italy; *B Harsh*, *E Travaglia*, Department of Physics, University of Trieste, Italy; *C Sanders*, iNANO, Aarhus University, Denmark, UK; *M Dendzik*, Aarhus University, Denmark, Germany; *P Lacovig*, Elettra-Sincrotrone Trieste, Italy; *M Michiardi*, iNANO, Aarhus University, Denmark, Canada; *M Bianchi*, Aarhus University, Denmark; *R Larciprete*, CNR-Institute for Complex Systems, Roma, Italy; *J Flege*, *J Falta*, University of Bremen, Germany; *P Das*, Abdus Salam International Centre for Theoretical Physics, Trieste, Italy; *J Fujii*, *I Vobornik*, IOM-CNR, Laboratorio TASC, Trieste, Italy; *M Ewert*, *L Buß*, University of Bremen, Germany; *A Baraldi*, University of Trieste, Italy; *P Hofmann*, Aarhus University, Denmark; *S Lizzit*, Elettra - Sincrotrone Trieste, Trieste, Italy

It has been widely demonstrated that Transition Metal Dichalcogenides (TMDs), and in particular MoS₂ and WS₂ could be good candidates for future electronic devices because of their intrinsic electronic properties and their potential for ultimate device scaling. In the single layer (SL) form, the inversion symmetry breaking and the strong spin-orbit coupling of the heavy transition metals (Mo or W) open new possibilities for data storage and computing thanks to the spin and valley degrees of freedom. However, in order to investigate the fundamental physics behind these materials and to produce high quality electronic devices, SL TMDs with enough large area and high quality are demanded. In particular, single domain oriented layers, that are SLs without mirror domains, allow to strongly suppress defects due to the absence of grain boundaries which are known to degrade the overall performances.

We here present a successful synthesis method based on physical vapor deposition that consists in dosing W or Mo in H₂S atmosphere onto Au(111), and provide an in-depth characterization of the synthesized SL TMDs through different surface science techniques. Synchrotron radiation based photoelectron spectroscopy in the fast modality (fast-XPS) was used to carefully tune the growth parameters whereas high resolution (HR-XPS) was used for the characterization. In particular fast-XPS allowed to optimize the growth parameters which turned out to be different for MoS₂ [1] with respect to WS₂[2]. Then, photoelectron diffraction (XPD) was employed to find the structural parameters of the SLs and to unambiguously determine their single orientation character and the relative alignment with respect to the underlying substrate. Scanning Tunneling Microscopy (STM), Low Energy Electron Diffraction (LEED) and

Microscopy (LEEM) added further insight into the lateral extension of the SLs and the structural order at the atomic level.

[1] H. Bana, E. Travaglia, L. Bignardi, P. Lacovig, C. E. Sanders, M. Dendzik, M. Michiardi, M. Bianchi, D. Lizzit, F. Presel, D. D. Angelis, N. Apostol, P. K. Das, J. Fujii, I. Vobornik, R. Larciprete, A. Baraldi, P. Hofmann and S. Lizzit, 2D Materials, 2018, 5, 035012.

[2] L. Bignardi, D. Lizzit, H. Bana, E. Travaglia, P. Lacovig, C. E. Sanders, M. Dendzik, M. Michiardi, M. Bianchi, M. Ewert, L. Buss, J. Falta, J. I. Flege, A. Baraldi, R. Larciprete, P. Hofmann, and S. Lizzit, Physical Review Materials 3, 014003 (2019).

11:20am 2D+AS+MI+NS-TuM-11 Surface Reactivity of MoS₂ by ambient pressure X-ray Photoelectron Spectroscopy, *Rafik Addou*, *D Dardzinsky*, *G Herman*, Oregon State University

Molybdenum disulfide (MoS₂) has potential applications as a low-cost catalyst for the hydrogen evolution reaction (HER). Defect sites in MoS₂ have been demonstrated to have high catalytic activities, where edge sites and sulfur vacancies are the major active sites for HER. Intentionally inducing defects offers a simple way to enhance the reactivity of MoS₂ and other 2D materials. In this study, we have characterized the surface reactivity and the catalytic activities of bulk MoS₂ samples using ambient pressure X-ray photoelectron spectroscopy (APXPS). The pristine surface was exposed to 1 mbar of H₂O vapor for temperatures ranging from 300 to 573 K. APXPS Mo 3d, S 2p, and O 1s core levels do not show any significant changes under these reaction conditions due to the inert nature of the MoS₂ surface. To activate the MoS₂ basal plane to improve surface reactivity, we have formed well-controlled densities of defects using Ar⁺ sputtering. The defective surfaces were exposed to 1 mbar of H₂O vapor for temperatures ranging from 300 to 600 K. Changes in the APXPS Mo 3d, S 2p, and O 1s core levels indicate that the surface is much more reactive to H₂O, with the formation of Mo-O bonds. These results are consistent with the reduction in the H₂O gas phase which was measured by operando mass spectrometry. We have found that the reactivity strongly depends on the temperature and the size and density of defects. Following this first report of APXPS on MoS₂ acquired at more realistic pressure, we will also report the HER activity and X-ray absorption spectroscopy (XAS) on the pristine surface and compare it with defective surfaces. Our findings demonstrate that the reactivity and the catalytic activity of MoS₂ are significantly improved through the formation of defects.

11:40am 2D+AS+MI+NS-TuM-12 Surface Characterization of 2D Materials and their 3D Analogues using XPS, *Jonathan Counsell*, *S Coultas*, *C Blomfield*, *N Gerrard*, Kratos Analytical Limited, UK; *C Maffitt*, Kratos Analytical Limited; *A Roberts*, Kratos Analytical Limited, UK

Since the synthesis of Graphene in 2004 there has been significant interest in novel 2D materials. Indeed this area has produced an abundance of high impact publications and so far >\$10bn has been committed globally to both fundamental research and commercialisation. This interest has been due to the unique properties exhibited such as mechanical strength and charge/heat transfer. The potential commercial possibilities are diverse with applications as varied as heat management and dissipation to increasing computer processing power. To fully understand the nature and potential of these materials a comprehensive surface characterisation is necessary.

Herein we illustrate how by applying conventional surface analysis techniques with novel methodologies it is possible to create a more complete picture of the chemical and physical nature of deposited 2D materials. Both organic and inorganic 2D materials will be explored to demonstrate the methods and capabilities. Dichalcogenide materials (sulphides and selenides) containing different metal centres were analysed with XPS, and angular resolved methods, to calculate layer thicknesses, stoichiometry and chemical states. The lateral distribution of CVD ultra-thin films was studied using both macro and micro area XPS imaging modes to distinguish uniformity and evenness. The application of UPS will explore the bonding structure, sensitivity of the materials and as a potential tool for identifying damage/defects in the surface lattice. The merits and pitfalls of ion etching will be discussed and a complete method and protocol will be proposed for limiting spectral artefacts and therefore misleading results. The effects of deposition and analysis on the 2D materials' structure and composition will be highlighted as will the characterisation of unwanted reduction/oxidation, contamination and structural defects. Utilising the complete surface analysis tool box allows the analyst to gain further insight and to fully understand the complex nature of these novel materials.

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12:00pm **2D+AS+MI+NS-TuM-13 Characterization of Catalytic Active Sites on the Surface of MoS₂ 2-D Materials**, *Miguel Jose Yacaman*, University of Texas at San Antonio; *T Zepeda, S Fuentes Moyado*, CNYN UNAM Ensenada, Mexico

Materials such as the MoS₂ have been used in catalysis at industrial level for many decades mostly on the hydrodesulfurization of naftas.

However more stringent regulations about the sulfur amount in diesel has printed the need to improve the catalysts .In order to achieve that it is important to understand the nature of the active sites and ways to improve the activity.In this presentation we discuss the use of in-situ techniques to study the surfaces of MoS₂ materials made of few layers and discuss the role of the sites on the crystal edges.We also demonstrate that during the reaction the MoS₂ material becomes crumpled and changes from semiconductor to metallic.

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