Surface Science Division
Room 203C - Session SS+EM+NS-ThM

Defects in and Functionalization of 2D Materials

Moderators: Lars Grabow, University of Houston, Greg Kimmel, Pacific Northwest National Laboratory

8:00am **SS+EM+NS-ThM-1 Holes, Pinning Sites and Metallic Wires in Monolayers of 2D Materials***, **Thomas Michely**,* University of Cologne, Germany **INVITED**

The moiré formed by a monolayer of hexagonal boron nitride with Ir(111) provides through a chemisorbed valley region within a physisorbed mesa a unique site for its functionalization. Through gentle ion irradiation and mild annealing a regular array of vacancy clusters is created with the clusters positioned at the valleys where their edges bind to the substrates. Such a nanomesh with a regular array of holes with sizes below 1 nm holds promise for filter applications. Through vapor phase deposition of a variety of materials (e.g. Au or C) arrays of clusters with of tunable size and high thermal stability are formed at valley regions. Compared to the graphene moiré the templating effect of the hexagonal boron nitride moiré is superior due to the uniqueness of the valley pinning site in the unit cell.

Monolayers of hexagonal boron nitride or graphene are also excellent substrates for the on-surface synthesis of new compounds ranging from metal-organic nanowires to transition metal disulfides created by reactive molecular beam epitaxy with elemental sulfur. This synthesis method provides clean, well-decoupled layers with only well-defined defects.

The most exciting defects we observed so far are two types of mirror twin boundaries in MoS_2 islands. In these boundaries we observe for the first time spin-charge separation in real space making use of the unique local spectroscopic capabilities of low temperature STM and STS to identify the position and energy of quantum mechanical states in a one dimensional box. We critically discuss these results in the light of previous related research.

Contributions to this work by Wouter Jolie, Joshua Hall, Clifford Murray, Moritz Will, Phil Valerius, Charlotte Herbig, Carsten Speckmann, Tobias Wekking, Carsten Busse, Fabian Portner, Philipp Weiß, Achim Rosch, Arkady Krasheninnikov, Hannu-Pekka Komsa, Borna Pielić, Marko Kralj, Vasile Caciuc and Nicolae Atodiresei as well as financial support through CRC1238 within projects A01 and B06 of DFG are gratefully acknowledged.

8:40am **SS+EM+NS-ThM-3 CO Chemisorption at Pristine, Doped and Defect Sites on Graphene/Ni(111)***, **Mario Rocca**, G Carraro,* University of Genova, Italy*; M Smerieri, L Savio,* IMEM-CNR, UOS Genova, Italy*; E Celasco, L Vattuone,* University of Genova, Italy

Due to its electrical properties graphene (G) has been successfully used as a sensing element for the detection of different gases reaching ppm sensitivities which are ascribed to the doping induced by adsorption. The sensitivity depends indeed critically on the chemical nature of the gas and is lower for CO than for other poisoning species. The nature of the active sites is, however, still unclear. If it were due to physisorption, the values of the adsorption energy cannot explain the need for high temperature re-generation of the sensing element. Chemisorption must thus be involved, either at defects or by doping, determining the magnitude of the heat of adsorption and consequently the sensitivity and the range of temperatures at which the sensor can operate. In order to clarify these issues we investigated experimentally adsorption of CO on G supported on polycrystalline Cu and Ni(111) by HREELS and XPS.

No adsorbed CO was found at RT while at 100 K chemisorbed CO forms on G supported on Ni(111). G on Cu is on the contrary inert. This result indicates that the nature of the substrate plays an essential role in the adsorption process. The heat of adsorption q is estimated to be about 0.58 eV/molecule at low coverage, so that an equilibrium coverage of 0.1 ML is expected at RT under a CO partial pressure of only 10 mbar. We identify top-bridge graphene as the most reactive configuration.

Doping G/Ni(111) by N_2^+ ion bombardment allows for the formation of a second, more strongly bound moiety, characterized by a CO stretch frequency of 236 meV and by an initial heat of adsorption (0.85 eV/molecule). The presence of N (in pyridinic or substitutional sites) enhances therefore significantly the chemical reactivity of G/Ni(111) towards CO.

Finally in presence of isolated defects, created by low energy Ne^+ ions bombardment on single layer graphene supported on different substrates (polycrystalline Cu and Ni(111)), no CO adsorption occurs for defected G/Cu, while HREELS peaks form promptly for G/Ni(111). Two moieties, desorbing just above 350 K, are present under vacuum conditions after exposure at RT. The CO stretch frequencies and the ratio of their intensities indicate that they are due to chemisorbed CO at the G/Ni(111) interface close to the vacancies rather than at the defected G layer. The red-shift of the C1s binding energy indicates that in such regions detachment of the G layer from the substrate occurs.

Amending of vacancies occurs for subsequent exposures, as demonstrated by the reduction of the adsorbed coverage in subsequent CO doses followed by annealing at 380 K, indicating that a Bouduard-like reaction takes place under the graphene cover.

9:00am **SS+EM+NS-ThM-4 Geometry of Cu Islands Buried Beneath the Surface of Graphite***, A Lii-Rosales,* Ames Laboratory and Iowa State University*; S Julien,* Northeastern University*; Y Han, J Evans,* Ames Laboratory and Iowa State University*; K Wan,* Northeastern University*; **Patricia A. Thiel**,* Ames Laboratory and Iowa State University

Deposition of Cu on a sputtered graphite surface, in ultrahigh vacuum, can be manipulated to produce buried islands of metallic, multilayer Cu. The Cu islands are covered by a graphitic layer consisting of several graphene sheets. This layer drapes like a tarpaulin over the Cu islands. We have observed flat-topped islands as tall as 40 nm and as wide as 600 nm. One of the most striking features of island geometry is the fact that the slope of the tarpaulin at the sides of the islands is invariant over a wide range of island volumes. The variation of the ratio of island diameter to height as a function of island volume is far less regular in the experimental data, suggesting that kinetic limitations may play a role in determining this parameter. To investigate the physical forces responsible for the island geometries, we develop a model for island shape that incorporates the distortion energy of graphene, adhesion of Cu with graphitic surfaces, adhesion of graphene with graphite, and other parameters. The energy parameters involving Cu surfaces and Cu-carbon interfaces are derived from DFT calculations. The values and trends predicted by the model are discussed and compared with experiment. In particular, the model indicates that the slope of the island sides should be invariant, consistent with experiment.

9:20am **SS+EM+NS-ThM-5 Intercalation of O_2 and CO between Graphene and Ru(0001) and the Role of Defects***, **Jory Yarmoff**, T Li,* University of California, Riverside

Graphene (Gr) is a fascinating 2D material that is being widely being considered for applications in electronic devices due to its unique electronic and materials properties. Also, because of its high thermal stability and inertness, it is a promising candidate for use as a protection layer for metal substrates. Here, graphene films grown on Ru(0001) are exposed to O_2 and ^{13}CO and investigated with helium low energy ion scattering (LEIS). LEIS spectra collected at different scattering angles can distinguish between adsorbed and intercalated molecules. It is found that O_2 and CO do not adsorb to the graphene surface but instead intercalate between Gr and the substrate. It is shown that a much lower annealing temperature is needed to remove intercalated oxygen than chemisorbed oxygen on bare Ru. During the thermal desorption, some of the graphene is etched away via chemical reaction forming gaseous CO or CO_2. In addition, carbon vacancy defects are produced in the Gr films via 50 eV Ar^+ bombardment. Isolated single carbon vacancy defects enable molecular adsorption at the defect sites and ease the overall intercalation of oxygen. The defects also improve the thermal etching efficiency of Gr by intercalated oxygen. When the defects are large enough to consist of open areas of bare substrate, oxygen dissociatively chemisorbs to Ru. Intercalated ^{13}CO molecules sit upright with the O end on top, as on clean Ru. The CO molecules tilt, however, when the temperature is raised. This is likely due to increased vibrational amplitudes combined with the confining effect of the Gr film.

9:40am **SS+EM+NS-ThM-6 Organic-2D Transition Metal Dichalcogenide van der Waals Heterostructures***, **Yu Li Huang**,* Institute of Materials Research & Engineering (IMRE), A*STAR, Singapore*; Z Song,* National University of Singapore, Singapore*; D Chi,* Institute of Materials Research & Engineering (IMRE), A*STAR, Singapore*; A Wee,* National University of Singapore, Singapore

The recent emergence of two-dimensional transition metal dichalcogenides (2D TMDs) has led to a rapid burgeoning of the field due to their novel electronic and optical properties with potential electronics/photonics applications. Organic materials, on the other hand, have exhibited great success in the field of flexible electronics, with an extensive number of available molecules with tunable properties. Marrying the fields of organics and 2D TMDs will bring benefits that are not present in either material alone, enabling even better, multifunctional flexible devices. In parallel, the integration of 2D TMDs with selected organics is also a promising and controllable approach to modulate the properties of the TMDs without structural damage, thereby optimizing or even enhancing their desired properties for specific device applications. Central to the realization of all those applications is a fundamental understanding of the organic-2D TMD interface.[1]

Here, we will present our recent studies on hybrid organic/2D TMD heterostructures.[2-4] With combined experiments and theoretical modeling, the interfacial interactions between the organic layers and the TMDs as well as the energy level alignment at the interface are explored. The comprehensive understanding of the underlying physical mechanisms that govern the properties of organic-2D TMD interfaces at the atomic scale is of fundamental importance for developing this technique further for device applications.

References:

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4. Y. J. Zheng, Y. L. Huang, Y. Chenp, W. Zhao, G. Eda, C. D. Spataru, W. Zhang, Y.-H. Chang, L.-J. Li, D. Chi, S. Y. Quek and A. T. S. Wee, *ACS Nano*, 2016, **10**, 2476-2484.

11:00am **SS+EM+NS-ThM-10 Influence of Surface Functionalization on Surface Topography and Growth of Metal Oxide Structures on HOPG***, **Kathryn Perrine**, M Trought, I Wentworth, C de Alwis, T Leftwich,* Michigan Technological University

Growth of heterogeneous catalysts, plasmonic and other nanostructured materials requires atomic level control and molecular level understanding of the growth of metals and metal oxides on surfaces. Surface functionalization of 2D materials can be used to promote selective nucleation of metal oxides with control over the deposition and growth. However, this requires an understanding of surface functionalization. This surface chemical functionalization can be combined with the atomic-level control of atomic layer deposition (ALD). ALD is a vapor deposition technique that utilizes self-limiting surface reactions to grow metal oxides, where the surface functional group initiates the first step in the deposition process.

2D materials are ideal for selective functionalization that may not require lithography steps due to the fact that their sheets are in a stable configuration making them chemically unreactive. Highly oriented pyrolytic graphite (HOPG) is an ideal model of the graphene surface, a well-known 2D material, which is comprised of sp^2 hybridized aromatic hydrocarbon sheets. HOPG consists of stacked graphene sheets where the terraces of the carbon sheets are chemically unreactive in ambient conditions and their defects are highly reactive. Oxidation methods are used to produce an assortment of different functional groups on HOPG and can lead to different types of functionalities on the surface and its defects.

We investigate how surface oxidative etching and functionalization influences the growth of metal oxide structures at tailored defects and functional sites on HOPG. Two different acids were used to etch the HOPG surface to produce functional groups resulting in different surface topographies. The functionalized HOPG was then exposed to trimethylaluminum and water, a well-known ALD reaction, to produce Al_2O_3 as a proof-of-concept to observe the growth of Al_2O_3 on both functional and defect sites. Vibrational spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS) were used to measure surface functionalization and Al_2O_3 growth on HOPG. Field emission scanning electron microscopy (FESEM), atomic force microscopy (AFM) and Raman spectral imaging were used to image the changes in surface topography after etching and ALD deposition. Results indicate that the Al_2O_3 deposition and growth is dictated by the surface functionalization and topography. This suggests that understanding the effects of surface functionalization of 2D materials is necessary for controlling the growth of metal oxide structures.

11:20am **SS+EM+NS-ThM-11 Impurity Induced Chemical Properties of BN on Rh(111) Studied by First Principle Calculations: A New Phase***, **Zahra Hooshmand**[1], D Le, T Rahman,* University of Central Florida

Hexagonal boron nitride (h-BN), an insulating layer of sp^2 hybridized structure between B and N, grown on Rh(111) forms a Moiré pattern with elevated (rim) and depression (valley) areas. The valleys are circular dipole rings which act as trapping centers for the adsorption of nanoparticles and molecules [1]. The presence of the native carbon impurities in Rh potentially gives rise to the formation of hexagonal carbon rings under every other rim area as suggested by recent experiments [2] and could lead to new structures and novel chemistry. Here, on the basis of Density Functional Theory (DFT) simulations with dispersion corrections, we show that these rings tend to grow in a manner in which the center of each ring is placed on top of the Rh atom. These rings grow next to each other and form islands which are separated from each other by an equal distance while the BN monolayer remains untouched, i.e. there is no C-B or C-N bond formed. Our calculations show that while no broken bonds between B and N were observed, the increase in the concentration of carbon impurities will enhance the height modulations among different regions of BN Moiré pattern leaving the former valleys unchanged while decreasing their area. The new higher elevated regions show strong accumulation of charge and the lower elevated regions display depletion of charge. This gives rise to modification of dipole rings and results in altered adsorption of pentacene on BN. Our simulations of Scanning Tunneling Microscope (STM) images from this structure, are in good agreement with experimental data for number of rings from 3 to 5. However spatial density of states analysis shows that in the presence of 5 rings islands the gap in BN on the higher elevated regions vanishes and the band gap on these areas for 3 and 4 rings islands reduces. The calculations of local variations in work function also show that these variations become more pronounced by growth of islands and reduces the work function of lower elevated regions in new phase. This results show that by control of the concentration of local impurities underneath the rim areas in BN, the chemical properties are modified and the monolayer could be engineered for interesting chemical reactions. [1] H. Dil et al., *Science*, 2008, 319, 1824-1826. [2] Koslowski et al. Private communication.

This work was supported by National Science Foundation, Grant #NSF CHE-1465105"

11:40am **SS+EM+NS-ThM-12 Texture of Atomic-layer Deposited MoS: A polarized Raman Study***, **Vincent Vandalon**, A Sharma, E Kessels,* Eindhoven University of Technology, The Netherlands, Netherlands*; A Bol,* Eindhoven University of Technology, Netherlands

Advances in optical characterization techniques for 2D transition metal dichalcogenides (2D-TMDs) such as MoS2 are essential in the context of tailoring the texture and surface functionalization of these materials. Tailoring of the texture of *synthesized* MoS2 results in uniquely different material characteristics: out-of-plane fins of MoS2 have been demonstrated to possess excellent catalytic performance, most likely due to exposed catalytically active edge sites, whereas basal plane oriented MoS2 shows excellent electronic properties. The large impact of texture on the exhibited properties underlines the need for rapid and facile characterization of the texture and especially the angular grain orientation. So far, cross section high-resolution transmission electron microscopy (HR-TEM) is widely employed to obtain insight into texture but it suffers from a limited throughput. On the other hand, Raman spectroscopy has been established as the *go-to* technique for the determination of e.g. film thickness of these TMDs. Here we will show that the angular grain distribution can also be determined using *polarized* Raman spectroscopy

We have found that plasma-enhanced atomic-layer deposition (PE-ALD) of MoS2 allows control over the texture and results in out-of-plane fins or basal plane oriented material depending on the processing conditions using HR-TEM. To study the texture of the PE-ALD synthesized films with Raman spectroscopy, we have investigated the so far unknown impact of the angular grain distribution on the Raman response. The Raman response of nanocrystalline MoS2 was modeled for a range of different textures. This allowed us to determine the angular grain distribution from the peak ratio of the two dominant Raman peaks (i.e. the A1g and E2g modes). Furthermore, the modeling also showed that performing *polarized* variant of Raman spectroscopy is essential for the accurate determination of the angular grain distribution because of the additional information it provides. A systematic polarized Raman study into the evolution of the fraction of out-of-plane material with film thickness allowed us to gain insight into the

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[1] **National Student Award Finalist**

growth process. Moreover, the influence of a post-deposition high-temperature anneal in a H2S atmosphere on the texture, known to yield improved material properties, was also investigated. To conclude, polarized Raman spectroscopy offers a rapid method to gain insight into the angular grain distribution of synthesized MoS2 and this approach can be readily extended to other MX2 materials.

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