2D Materials Focus Topic
Room 103B - Session 2D+MI-TuM

Novel 2D Materials

Moderators: Daniel Gunlycke, Naval Research Laboratory, Yuanbo Zhang, Fudan University, China

8:00am **2D+MI-TuM1 Computational Design of 2D Materials and Layered Heterostructures for Opto-electronics**, ***Kristian Thygesen,*** Technical University of Denmark **INVITED**

The class of 2D materials is rapidly expanding and now includes semiconductors, insulators, metals, and superconductors. Many of these novel materials exhibit unique properties that are easily tuneable due to their atomically thin nature making them potential candidates for applications in a large range of technological areas. In this talk I will give a general introduction to the electronic structure of 2D materials including the characteristic features of screening and collective excitations. Concrete illustrations will be given from the Computational 2D Materials Repository (1+2) which contains high-accuracy first-principles calculations for a large number of 2D materials. The 2D materials form the basis of a much larger class of materials consisting of vertically stacked 2D layers held together by weak van der Waals forces. I will describe challenges and opportunities for the first-principles modelling of van der Waals heterostructures including our multi-scale Quantum Classical Heterostructure (QEH) model (3) that enables accurate modelling of plasmons, excitons and band structures of general incommensurable heterostructures containing hundreds of layers. Examples of computational designed heterostructures will be given.

(1) Computational Materials Repository, https://cmr.fysik.dtu.dk/

(2) Computational 2D Materials Database: Electronic structure of transition metal dichalcogenides and oxides, F. A. Rasmussen and K. S. Thygesen, J. Phys. Chem. C 119, 13169 (2015)

(3) The Dielectric Genome of van der Waals Heterostructures, K. Andersen, S. Latini, and K. S. Thygesen, Nano Letters 15, 4616 (2015)

8:40am **2D+MI-TuM3 Mo_2Ga_2C: Structural Determination of a New Nanolaminated Carbide and its 2D Modification by Selective Etching**, ***Chung-Chuan Lai****, R. Meshkian, M. Dahlqvist, J. Lu, L.-Å. Näslund,* Linköping University, Sweden*; O. Rivin, E.N. Caspi,* Nuclear Research Center-Negev, Israel*; O. Ozeri,* Nuclear Research Center-Soreq, Israel*; L. Hultman, P. Eklund,* Linköping University, Sweden*; M.W. Barsoum,* Drexel University*; J. Rosen,* Linköping University, Sweden

Studies of molybdenum carbides are motivated by, for example, the electric and the catalysis properties, including the recently predicted high Seebeck coefficient of 2D Mo_2C [1]. It has been reported that 2D transition metal carbides (also known as MXenes) can be made by selective etching of corresponding nanolaminated ternary carbides [2], e.g., $M_{n+1}AC_n$ phases where M is typically from group 4 – 6, A is from group 13 – 14, and n is 1 – 4 [3]. However, no suitable precursor has been available to make 2D Mo_2C until most recently, through the discovery of Mo_2Ga_2C [4]. Here, we determined the structure of Mo_2Ga_2C phase from X-ray and neutron diffraction, scanning transmission electron microscopy and X-ray photoelectron spectroscopy, and further validated the structure by ab initio calculations [5]. The structure of Mo_2Ga_2C can be described as Mo_2C layers interleaved by two Ga layers, standing head-to-head along the *c*-axis of the hexagonal lattice. The Mo_2Ga_2C phase is closely related to another known nanolaminated carbide, Mo_2GaC, in its crystal structures, evident from chemical bonding analysis. However, selective etching of Ga using hydrofluoric acid (HF) is easily attained for the new Mo_2Ga_2C phase, while being more challenging for Mo_2GaC. A reduction in Ga signal with subsequent exfoliation of Mo_2C layers upon etching is here presented for Mo_2Ga_2C, making Mo_2Ga_2C the first precursor for MXene synthesis based on A = Ga, and for MXene synthesis of 2D Mo_2C [6].

References:

[1] M. Khazaei, M. Arai, T. Sasaki, M. Estili, and Y. Sakka, Phys. *Chem. Chem. Phys.* 16 (2014) 7841-7849.

[2] M. Naguib, G. W. Bentzel, J. Shah, J. Halim, E. N. Caspi, J. Lu, L. Hultman, and M. W. Barsoum, *Mater. Res. Lett.* 2 (2014) 233-240.

[3] P. Eklund, M. Beckers, U. Jansson, H. Högberg, and L. Hultman, *Thin Solid Films* 518 (2010) 1851-1878.

[4] C. Hu, C.-C. Lai, Q. Tao, J. Lu, J. Halim, L. Sun, J. Zhang, J. Yang, B. Anasori, J. Wang, Y. Sakka, L. Hultman, P. Eklund, J. Rosen, and M. W. Barsoum, *Chem. Commun.* 51 (2015) 6560.

[5] C.-C. Lai, R. Meshkian, M. Dahlqvist, J. Lu, L.-Å. Näslund, O. Rivin, E. N. Caspi, O. Ozeri, L. Hultman, P. Eklund, M. W. Barsoum, and J. Rosen, *Acta Mater.* 99 (2015) 157-164.

[6] R. Meshkian, L.-Å. Näslund, J. Halim, J. Lu, M. W. Barsoum, and J. Rosen, *Scripta Mater.* 108 (2015) 147-150.

9:00am **2D+MI-TuM4 Synthesis of Borophenes: Anisotropic, Two-Dimensional Boron Polymorphs**, ***Andrew Mannix***[*][†]*, B. Kiraly,* Northwestern University/Argonne National Lab.*; J.D. Wood, M.C. Hersam,* Northwestern University*; N.P. Guisinger,* Argonne National Laboratory

As the lightest metalloid element, bulk boron exhibits great physical and chemical complexity. In contrast, atomic clusters of boron form simple planar and cage-like structures that resemble those of carbon. Theoretical studies suggest that nanostructured boron allotropes (e.g., nanotubes and sheets) should exhibit structures similar to atomic boron clusters. To date, however, boron nanostructures have been scarcely explored experimentally, partly due to difficulties in synthesis and the need for atomically pristine experimental conditions. Recently, we have reported the synthesis of two-dimensional boron sheets (i.e., borophenes) on a silver surface under ultra-high vacuum conditions [*Science* **350,** 1513–1516 (2015)]. Atomic-scale scanning tunneling microscopy shows the growth of two distinct phases, both of which exhibit anisotropic, chain-like structures. We confirm that these sheets are planar, chemically distinct, and atomically thin through extensive ex situ characterization supported by first principles calculations. Furthermore, in situ scanning tunneling spectroscopy of the borophene sheets shows metallic characteristics consistent with theoretical predictions, in contrast to semiconducting bulk boron.

9:20am **2D+MI-TuM5 Atomic and Electronic Structures of Graphitic Carbon Nitride (g-C3N4) Monolayers on HOPG**, ***Sangwoo Park****, HM. Kang,* Sungkyunkwan University, Republic of Korea*; J.H. Yang, J.H. Choy,* Ewha Womans University, Republic of Korea*; YJ. Song,* Sungkyunkwan University, Republic of Korea

In this work, we report atomic and electronic studies of graphitic carbon nitride (g-C3N4) monolayers on a highly-ordered pyrolytic graphite (HOPG) by using atomic force microscope (AFM), kelvin probe force microscope (KPFM) and low temperature scanning tunneling microscope (LT-STM). The g-C3N4 is the most stable allotrope of carbon-nitrides and a very promising candidate for metal-free coordination chemistry and heterogeneous catalyst. Also it is applicable photocatalytic hydrogen production and fuel cell. After successful spin-coating of the g-C3N4 monolayers on HOPG, we found the inter-molecular interactions between the flakes or the atomic registries of adsorption on the substrate. This coating mechanism and atomic/electronic properties of g-C3N4 on HOPG will be discussed in detail.

9:40am **2D+MI-TuM6 Periodic Array of Graphene Quantum Dots Embedded in a Carbon-Boron-Nitrogen Alloy**, ***Jakob Jørgensen,*** Aarhus University, Denmark*; L. Camilli, A. Stoot,* Technical University of Denmark*; A. Cassidy, R. Balog,* Aarhus University, Denmark*; J. Sadowski,* Brookhaven National Laboratory*; P. Bøggild,* Technical University of Denmark*; L. Hornekær,* Aarhus University, Denmark

Two-dimensional (2D) materials have received enormous attention in the field of materials science and condensed matter physics in the last decade, with the ultimate goal being developing a new technology based on these materials [1]. A huge variety of promising 2D materials have been identified and the ability to combine these into complex structures is essential. For this reason the synthesis of 2D hetero-structures – i.e., structures resulting from the combination of two or more 2D materials – have been subject to an intense research effort over the last few years [2]. Here we report the first observation of spontaneous formation and self-assembly of graphene quantum dot superlattices embedded in a two-dimensional boron-carbon-nitrogen alloy.

By exposing a hot Ir(111) surface to carbon and boron-nitrogen precursor molecules it is found, using scanning tunnelling microscopy (STM), that the otherwise bulk-immiscible graphene and hexagonal boron nitride (hBN) materials can form a stress induced BCN alloy. Furthermore, pure-phase dislocations are found to co-exist with the alloy resulting in the bright triangular pattern of carbon enriched nanoribbons with a width of approximately 1 nm. Above a critical carbon concentration, an array of quantum dots (QD) of highly regular size and periodicity appears. Based on

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[*] **Morton S. Traum Award Finalist**

[†] **National Student Award Finalist**

STM in combination with synchrotron x-ray photoemission spectroscopy (XPS) these QDs are determined consist of pure phase carbon, i.e. they are graphene QDs. These findings are consistent with well-established theories on elastic relaxations in ultrathin strained systems [3]. Thus our findings show a pathway to grow a highly periodic array of graphene quantum dots imbedded in a semiconducting BCN alloy.

In addition, using low energy electron microscopy (LEEM), the growth of the alloy structure is followed *in-situ* and diffraction experiments confirm the presence of the ordered quantum dot pattern even on a macroscopic level.

[1] A.C. Ferrari et al. Nanoscale 7, (2015) 4598

[2] H. Lim et al., Chemistry of Materials 26 (2014) 4891

[3] V. Ozolins et al. Phys. Rev. Lett. 88 (2002) 096101

11:00am **2D+MI-TuM10 Electric Field Control of 2D Materials with Electron Correlation*, Yoshi Iwasa,*** University of Tokyo, Japan **INVITED**

Scaling down materials to an atomic-layer level produces rich physical and chemical properties as exemplified in various two-dimensional (2D) crystals extending from graphene, transition metal dichalcogenidesto black phosphorous. These include Dirac physics, quantum Hall physics, and valleytronic functions, which are caused by the dramatic modification of electronic band structures, simply by thinning. In the case of transition metal dichalcogenides (TMDs), the band gap becomes direct in monolayers, and the broken inversion symmetry and the strong spin-orbit interaction causes peculiar valley-dependent spin polarization in zero-magnetic field [1], as well as peculiar opto-valleytronics [2, 3].

In reduced dimensions, on the other hand, the electron correlation effects and their consequence, electronic phase transitions, are also significantly changed from bulk systems, and thus result in new properties and functions. Here we address unique physical properties of correlated 2D electron system 1T-TaS_2, which was achieved simply by thinning. The ordering kinetics of the charge density wave transition was revealed to become extremely slow with reduction of thickness [4], resulting in an emergence of metastable states [5]. Furthermore, we realized the unprecedented memristive switching to multi-step non-volatile states by applying in-plane electric field.

[1] R. Suzuki et al, *Nat. Nano.* 9, 611 (2014).

[2] Y. J. Zhang et al., *Nano Lett.* 12, 1136 (2012), *ibid.* 13, 3023 (2013).

[3] Y. J. Zhang et al., *Science* 344, 725 (2014).

[4] M. Yoshida et al., *Sci. Rep*. 4, 7302 (2014).

[5] M. Yoshida et al., *Sci. Adv.* 1, e1500606 (2015).

11:40am **2D+MI-TuM12 Graphene-based Hybrid Materials by Designer Interfaces for High-Performance Hybrid Supercapacitors*, Sanju Gupta,*** Western Kentucky University

Intense research in renewable energy is stimulated by global demand of electric energy. E lectrochemical energy storage and conversion systems namely, supercapacitors and batteries,represent the most efficient and environmentally benign technologies. Moreover, controlled nanoscaled architectures and surface chemistry of electrochemical electrode materials is enabling emergent next-generation devices approaching theoretical limit of energy and power densities and deliver electrical energy rapidly and efficiently. This talk will present our recent activities to advance design, development and deployment of composition, morphology and microstructure controlled graphene-base hybrid multilayer architectures with carbon nanotubes, conducting polymers, transition metal oxides and mesoproprous silicon wrapped with grapheme sheets as engineered electrochemical electrodes for supercapacitor cathodes and battery anodes. Experimental studies showed significant enhancement towards integrating graphene with other nanomaterials in terms of gravimetric specific capacitance, interfacial capacitance, charging-discharging rate and cyclability. We also present fundamental physical-chemical interfacial processes that govern the underlying mechanisms (surface ion adsorption versus redox reactions) in these electrodes revealed using scanning electrochemical microscopy. The findings are discussed from viewpoint of reinforcing the role played by heterogeneous 'hybrid' electrode surfaces composed of nanoscale graphene sheets (conducting) and other nanomaterials (semiconducting) via higher/lower probe current distribution maps. It allows us to determine ion transfer kinetics and diffusion constant, imaging electrochemical reactions and topography in a microscale at electrode/electrolyte interface.

12:00pm **2D+MI-TuM13 Realization of TaS_2 in the Single-Layer Limit*, Charlotte Sanders,*** *M. Dendzik,* Aarhus University, Denmark*; A.S. Ngankeu,* Aarhus University*; A. Eich,* Radboud University, Netherlands*; A. Bruix, J.A. Miwa, B. Hammer,* Aarhus University, Denmark*; A.A. Khajetoorians,* Radboud University, Netherlands*; P. Hofmann,* Aarhus University, Denmark

The electronic properties of bulk TaS_2 have long been a topic of significant interest, due to the fact that the material exhibits unusual charge density wave phases alongside Mott physics and superconductivity. However, little has been known about single-layer (SL) TaS_2. How the electronic properties of this material may change in the SL limit is of great interest, raising questions about the effects of quantum confinement and substrate interactions on exotic electronic states already seen in the bulk. Work on related materials that have been successfully fabricated as SLs points to complex consequences for the CDW and superconducting states. [1] In order to address this topic, one needs to be able to controllably fabricate high-quality, uniform samples with low defect densities for probing *in situ*. We have now succeeded in epitaxially growing high-quality SL TaS_2. We have characterized the SL with angle-resolved photoemission spectroscopy (ARPES), low-temperature scanning tunneling microscopy and spectroscopy (LT-STM/S), and low-energy electron diffraction (LEED). Using the Au(111) substrate as a starting point, we find that the TaS_2 SL on Au(111) assumes a well-defined orientation with respect to the substrate, and a moiré superstructure; simultaneously, and counterintuitively, it adopts a "carpet flow" growth mode over substrate steps, suggesting weak interaction with the substrate. Comparing our measurements to calculations from density functional theory (DFT), we have determined that the SL assumes the trigonal prismatic ("1H") phase. While the bulk parent material is characterized by a CDW transition temperature T_{CDW} = 75K [2], we do not observe either CDWs or superconductivity at temperatures down to 4.7K on Au(111) using STM/STS. We do, however, observe slight doping of the TaS_2 epilayer. While the absence of superconductivity at this temperature is not surprising, considering that the superconducting transition temperature T_C in the bulk is only 600mK [3], the absence of CDWs is of interest. This is particularly so in light of recent research on the closely related system SL-$NbSe_2$ on bilayer graphene: despite having a lower bulk CDW onset at T_{CDW} = 33K, $NbSe_2$ in the SL exhibits complete transition to the CDW state by T_{CDW} = 5K. [1]

[1] M. M. Ugeda *et al.*, *Nat. Phys.***12**, 92 (2016). http://dx.doi.org/10.1038/nphys3527

[2] J. A. Wilson and A. Yoffe, *Adv. Phys.***18**, 193 (1969). http://dx.doi.org/10.1080/00018736900101307

[3] P. Garoche *et al.*, *J. Low Temp. Phys.***30**, 323 (1978). http://dx.doi.org/10.1007/BF00114956

Author Index

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