2D Materials Focus Topic
Room 201B - Session 2D+MI+NS-MoA

2D Materials Characterization including Microscopy and Spectroscopy

Moderators: Stephan Hofmann, University of Cambridge, UK, Richard Vanfleet, Brigham Young University

1:20pm 2D+MI+NS-MoA1 Observing the Mechanisms of Graphene Growth during Chemical Vapor Deposition: Routes to Controlling Layer Number and Domain Size*, Robert Weatherup,* University of Manchester, UK **INVITED**
Chemical vapor deposition (CVD) on polycrystalline metal foils has emerged as the most economic and versatile means for producing 2D materials over large areas,[1] and directly integrating them with other device materials to achieve new functionality.[2] To tailor these materials to specific applications, a detailed understanding of the underlying growth mechanisms is required such that parameters such as domain size, defect density, and layer number can be precisely controlled. However, the elevated temperatures and reactive gas environments involved in growth make direct observation challenging, whilst ex situ measurements are often ambiguous.

Here we apply environmental scanning electron microscopy (ESEM) and ambient pressure X-ray photoelectron spectroscopy (APXPS) to directly observe graphene growth under realistic CVD conditions on polycrystalline Pt foils.[3] This reveals a variety of processes involved in graphene formation including isothermal growth by direct hydrocarbon dissociation, isothermal dissolution into the catalyst bulk, and precipitation on cooling. The balance of these processes, and thus growth outcome, is shown to depends critically on the distribution of carbon close to the catalyst surface, which is in turn is intimately linked to the processing profile.We thereby develop a growth model for graphene CVD that considers precursor dissociation, mass-transport, attachment to the edge of growing graphene domains.[4] This is shown to generally applicable to several transition metal catalysts,[5] and serves as a general framework for understanding and optimizing the growth of 2D materials on polycrystalline catalysts.

We thus demonstrate that the CVD process can be rationally designed to yield different desired growth outcomes from the same polycrystalline starting catalyst, including uniform SLG with large domain sizes (>100 µm), large isolated BLG domains (>50 µm), and uniform BLG. Our result show that through targeted operando experiments the influence of key process parameters can be established, enabling precise control over 2D material growth including domain sizes and layer number.

1. S. Hofmann et al. *J. Phys. Chem. Lett.* **6,** 2714–2721 (2015).

2. M. Piquemal-Banciet al. *Appl. Phys. Lett.* **108,** 102404 (2016).

3. R. S. Weatherupet al. *Nano Lett.* **16,** 6196–6206 (2016).

4. R. S. Weatherupet al. *ACS Nano* **6,** 9996–10003 (2012).

5. A. Cabrero-Vilatela et al. *Nanoscale* **8,** 2149–2158 (2016).

2:00pm 2D+MI+NS-MoA3 Band Alignment of 2-D Materials by Internal Photoemission*, Q. Zhang, S. Zhang,* Theiss Research & National Institute of Standards and Technology; *B. Sperling,* **Nhan Nguyen,** National Institute of Standards and Technology
Two-dimensional (2-D) materials have brought new possibilities for the future electronic and optoelectronic applications [1], [2]. Electronic band alignment at the interface is one of the important parameters in many device designs. For instance, staggered band alignment is preferred to separate photon generated electron-hole pairs in optoelectronic and photovoltaic devices [3]. For the 2-D materials in the monolayer (ML) limit, it has been a challenge to accurately measure the electron affinity which determines how the bands align at the interface. In fact, most 2-D heterojunctions are designed using calculated or theoretically predicted band alignments [4]. In this work, we present an experimental measurement using internal photoemission spectroscopy (IPE) to determine the band offset of MX_2 semiconductors (M = Mo, W; X = S, Se) in relative to an oxide barrier and suggest possible combination of the MX_2 materials to be used for optoelectronic and photovoltaic applications. This IPE approach is seen as a unique method that can be applied to characterize other 2-D materials.

The IPE test structure is fabricated by exfoliating MX_2 flakes on to the Al_2O_3/p^+Si substrate and depositing Ti/Pt contacts on the flakes with large open areas for light absorption. By using gold film mediated exfoliation method [5], large area (> 75 x 75 µm²) ML MX_2 flakes are obtained, confirmed by Raman spectrum and photoluminescence mapping.

Photocurrents of the MX_2-Al_2O_3-p^+Si structure are measure with the incident photon energy swept from 2.0 eV to 5.5 eV and gate voltage V_{GS} (applied to the Si back gate) stepped from -1.0 V to 1.6 V. The oxide flat band voltage (V_{FB}) is extracted by the voltage where the photocurrent switches sign near and above photoemission thresholds. The band offsets at the MX_2/Al_2O_3 and Al_2O_3/Si interfaces are extracted as the thresholds of the cube root of photoemission quantum yield (Y) being the ratio of the photocurrent over the incident light flux [6]. At gate bias below V_{FB}, the band offset between Al_2O_3 and Si is measured and found to be 3.4 eV for all the 4 devices, which is also a well-established value. More importantly, the band offset at the MX_2/Al_2O_3 interfaces combined with the known optical band gaps of ML MX_2 suggest that MoS_2/WS_2 and $MoSe_2/WSe_2$ can possibly form the staggered heterojunction.

[1] G. Fiori, et al, Nat. Nanotech. **9**, 768 (2014).

[2] F. Xia, et al, Nat. Photonics **8**, 899 (2014).

[3] X. Hong, et al, Nature Nanotech. **9**, 682 (2014)

[4] J. Kang, et al, Appl. Phys. Lett. **102**, 012111 (2013)

[5] S. B. Desai, et al, Adv. Mater. **28**, 4053 (2016).

[6] V. V. Afanasev and A. Stesmans, J. Appl. Phys. **102**, 081301 (2007).

2:20pm 2D+MI+NS-MoA4 Visible to mid-IR Nanoscale Characterization of 2D Materials via Photo-induced Force Microscopy*, Padraic O'Reilly, D. Nowak, S. Park,* Molecular Vista
While several 2D materials have been studied with scattering scanning near-field optical microscopes (s-SNOM) with nanoscale spatial resolution, most have focused on the study of surface phonon polariton (SPP) [1]. In this paper, we introduce a relatively new technique called photo-induced force microscopy (PiFM), which combines atomic force microscope (AFM) and broadband optical spectroscopy to analyze both topography and polarizability of samples with sub-10 nm spatial resolution [2]. With PiFM, the near-field optical information is acquired by measuring the photo-induced force between the AFM tip and the sample rather than by collecting photons with a far-field photo-detector; this near-field excitation and near-field detection configuration provides excellent signal-to-noise without the far-field background signal from the much larger focal spot, making the technique robust and easy-to-use. With mid-IR sources, PiFM can image nanoscale SPP as with s-SNOM. With supercontinuum visible-infrared light source, it can directly probe the exciton resonances with equally impressive spatial resolution. With its capability to image number of layers, quality of samples, and plasmonic fields, PiFM is an ideal nanoscale characterization tool for wide range of 2D materials. Results from graphene, MoS_2, WS_2, and hBN will be presented.

[1] T. Low et al., Nature Materials 16, 182–194 (2017).

[2] R. A. Murdick et al., Jap. J. of Appl. Phy., 56, 08LA04 (2017).

2:40pm 2D+MI+NS-MoA5 Polymorphic Structures and Diversified Properties of Low-dimensional Materials Investigated by In situ Electron Microscopy*, Kazu Suenaga,* National Institute of Advanced Industrial Science and Technology (AIST), Japan **INVITED**
Two-dimensional transition metal dichalcogenides (TMDs), consisting of an atomic plane of a transition metal (M: Ti, Nb, Mo, Re, etc.) sandwiched between two chalcogen atomic planes (X: S, Se, Te). This crystalline structure combined with a wide variety of constituent elements give rise to diverse electronic properties, strongly governed by the number of its *d*-orbital electrons. MoS_2 and WS_2 are the most representative "group 6" TMDs featuring trigonal prismatic (H) phase semiconductor with a direct band gap. The TMDs can exhibit various polymorphs and present different electronic properties as the atomic arrangement changes originating from charge transfer. A metallic octahedral (T) phase has been reportedly stabilized by alkali metal intercalation [1], and another distorted octahedral phase zigzag-shape phase (Z) with clusterization of metal atoms into zigzag chains by using solvent-based exfoliation. Some simulations indicate that the Z phase may undergo the Peierls distortion and be transformed into a diamond-shape (DS) phase where atoms reconstruct in a way that four metal atom appear as a diamond (rhombus) in the plane [2]. We show in this talk the experimental evidences for these polymorphic structures and diversified properties found in a family of 2D TMDs.

These monolayer forms in TMDs are typically the same as a single layer of the bulk material. However, $PdSe_2$ presents a puzzle. Its monolayer form has been theoretically shown to be stable, but there have been no reports that monolayer $PdSe_2$ was fabricated. Here, we demonstrate that the preferred monolayer form of this material amounts to a melding of two

bulk monolayers accompanied by the emission of Se atoms so that the resulting stoichiometry is Pd_2Se_3[3].

[1] Y.-C. Lin, D. O. Dumcenco, Y.-S. Huang and K. Suenaga, *Nature Nanotechnology*, 9 (2014) pp.391-396

[2] Y.-C. Lin, H.-P. Komsa, C.-H. Yeh, T. Bjorkman, Z.-Y. Liang, C.-H. Ho, Y.-S. Huang, P.-W. Chiu, A. V. Krasheninnikov, and K. Suenaga, *ACS Nano* 9 (2015) pp.11249-11257

[3] J. Lin, S. Zuluaga, P. Yu, Z. Liu, S. T. Pantelides, and K. Suenaga *Phys. Rev. Lett.*, 119 (2017) 016101

[4] This research was supported by JSPS KAKENHI (JP16H06333 and JP25107003).

3:40pm **2D+MI+NS-MoA8 Probing Interlayer Interaction in van der Waals Materials by Low-energy Electron Microscopy (LEEM)**, *Johannes Jobst, D. Geelen,* Leiden University, Netherlands*; R.M. Tromp,* IBM, T.J. Watson Research Center*; S.J. van der Molen,* Huygens-Kamerlingh Onnes Laboratory, Netherlands **INVITED**

Knowledge on the interaction between layers is crucial to tailor the properties of van der Waals (vdW) materials. We investigate these using newly developed techniques based on low-energy electron microscopy (LEEM). With LEEM, we probe the reflection of electrons as a function of incoming energy (0-100 eV). We have recently extended our UHV instrument to also measure low-energy electron transmission (eV-TEM).

We apply LEEM and eV-TEM to few-layer graphene. With each layer, an unoccupied interlayer state is added, which hybridizes with the other states. In LEEM, the resulting eigenstates appear as minima in the reflection spectrum. In transmission, they show up as maxima. From both functions, we determine the hybridization energies of the interlayer states, which extend in 2D.

Next, we study the 2D-dispersion relations of these states. For that, we have developed *angle-resolved reflected-electron spectroscopy* (ARRES) [1]. With ARRES, we investigate few-layer graphene, hBN, as well as their combination. For the latter case we find negligible interaction. [2]

[1] Jobst *et al.*, Nat. Comm. **6**, 8926 (2015)

[2] Jobst *et al.,* Nat. Comm. **7**, 13621 (2016)

4:20pm **2D+MI+NS-MoA10 Fast Full Wafer Analysis for Graphene and 2D-materials by Imaging Ellipsometry**, *Sebastian Funke,* Accurion GmbH, Germany*; P. Braueniger-Weimer, S. Hofmann,* University of Cambridge, UK*; P.H. Thiesen,* Accurion GmbH, Germany

By combining the resolution of optical microscopy and the sensitivity of thin films, imaging ellipsometry (IE) is a powerful tool to characterize thin materials. It allows to measure monolayers of 2D-materials but also to visualize these monolayers on arbitrary substrates. It overcomes the need of specially tuned SiO_2 thicknesses to visualize e.g. Graphene in an optical microscope.

In the talk we present [1], the characterization of Graphene throughout all stages of the manufacturing process from the growth on Cu-foil up to the transferred sample on Si wafers. Unlike other methods IE directly visualizes graphene on the rough Cu. We apply IE to resolve a large area map of Graphene on Cu. The Graphene is directly characterized on the Cu-foil, no oxidation of the Cu is needed. To overcome the waviness of the foil, an autofocus algorithm is developed and applied.

IE is also able to distinguish a Graphene monolayer and hBN monolayer after the transfer process to a Si/SiO_2 substrate. We show large area map of the transfered sample. The contrast mode of IE is able to distinguish the different regions: (a) substrate only, (b) hBN only, (c) Graphene only and (d) an overlapping region of hBN and Graphene. The complete sample approx. 1cm x 0.8 cm is recorded in less than 6 minutes and shows defects and wrapping of hBN of a size as small as 4 µm.

Lastly, we apply IE to characterise full 4'' wafers of graphene on Si.

[1] Braueniger, Funke et al. submitted

Author Index

Bold page numbers indicate presenter

— B —
Braueniger-Weimer, P.: 2D+MI+NS-MoA10, 2

— F —
Funke, S.: 2D+MI+NS-MoA10, **2**

— G —
Geelen, D.: 2D+MI+NS-MoA8, 2

— H —
Hofmann, S.: 2D+MI+NS-MoA10, 2

— J —
Jobst, J.: 2D+MI+NS-MoA8, **2**

— N —
Nguyen, N.: 2D+MI+NS-MoA3, **1**
Nowak, D.: 2D+MI+NS-MoA4, 1

— O —
O'Reilly, P.: 2D+MI+NS-MoA4, **1**

— P —
Park, S.: 2D+MI+NS-MoA4, 1

— S —
Sperling, B.: 2D+MI+NS-MoA3, 1
Suenaga, K.: 2D+MI+NS-MoA5, **1**

— T —
Thiesen, P.H.: 2D+MI+NS-MoA10, 2
Tromp, R.M.: 2D+MI+NS-MoA8, 2

— V —
van der Molen, S.J.: 2D+MI+NS-MoA8, 2

— W —
Weatherup, R.S.: 2D+MI+NS-MoA1, **1**

— Z —
Zhang, Q.: 2D+MI+NS-MoA3, 1
Zhang, S.: 2D+MI+NS-MoA3, 1