2D Materials

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

2D Materials Characterization by Scanning Probe Microscopy and Spectroscopy

Moderator: Ivan Oleynik, University of South Florida

8:00am 2D+AS+MI+NS-WeM-1 Plasmon Induced Excitation of Doublet Emission at the Single Molecule Level, *Alberto Martin-Jimenez, K Lauwaet,* IMDEA Nanoscience, Spain*; P Merino, J Martinez,* ICMM-CSIC, Spain*; R Miranda, R Otero,* IMDEA Nanoscience, Spain

In this contribution we report a careful investigation of the topographic, electronic, and opto-electronic properties of electronically decoupled C60 nanocrystals by means of Scanning Tunneling Microscopy (STM), Scanning Tunneling Spectroscopy (STS), STM induced Light Emission (STM-LE), and Density Functional Theory (DFT), at the single molecule level. We have observed that depending on the tunneling parameters, we are able to reversibly switch from a broad plasmonic spectrum to a series of very sharp molecular resonances of 10meV width. Based on our STS data and DFT calculations we have reached a model to explain the molecular light emission of the C60 nanocrystals. We demonstrate that the emission arises from the recombination of a doublet exciton of negatively charged molecules (anions). Our results will contribute to the general understanding of the physical mechanisms involved in the light emission of organic molecules. They may also be of importance for applications such as single photon emitters or quantum computing, since future devices may need to be able to switch chromaticity in a controlled fashion.

8:20am 2D+AS+MI+NS-WeM-2 Silicene like Domains on IrSi$_3$ Crystallites, *Nuri Oncel, D Cakir, F Fatima, D Nicholls,* University of North Dakota

Recently, silicene, the graphene equivalent of silicon, has attracted a lot of attention due to its compatibility with Si-based electronics. So far, silicene has been epitaxially grown on various crystalline surfaces such as Ag(110), Ag(111), Ir(111), ZrB$_2$(0001) and Au(110) substrates. Here, we present a new method to grow silicene via high temperature surface reconstruction of hexagonal IrSi$_3$ nanocrystals. The h-IrSi$_3$ nanocrystals are formed by annealing thin Ir layers on Si(111) surface. A detailed analysis of the STM images shows the formation of silicene like domains on the surface of some of the IrSi$_3$ crystallites. We studied both morphology and electronic properties of these domains by using both scanning tunneling microscopy/spectroscopy and first-principles calculation methods.

8:40am 2D+AS+MI+NS-WeM-3 Interfacial and Topological Superconductivity in 2D Layers Studied by Spin-Resolved Scanning Tunneling Spectroscopy, *Roland Wiesendanger,* University of Hamburg, Germany **INVITED**

In this presentation, we will first focus on interfacial superconductivity in novel types of heterostructures. In particular, we will present a low-temperature SP-STS study of ultrathin FeTe1-xSex (x = 0, 0.5) films grown on prototypical Bi-based bulk topological insulators. We observe fully developed U-shaped superconducting gaps in FeTe0.5Se0.5 layers of one unit cell (UC) thickness with a transition temperature (Tc) of ~11 K, close to the one of the corresponding bulk system (Tc ~ 14.5 K) [1]. Surprisingly, we also find clear evidence for superconductivity up to Tc ~ 6 K for one UC thick FeTe layers grown on Bi2Te3 substrates [2], in contrast to the non-superconducting FeTe bulk compound which exhibits bicollinear antiferromagnetic (AFM) order in a wide temperature range up to 70 K. Even more surprisingly, detailed investigations of the atomic-scale spin-resolved local density of states by SP-STS reveal that superconductivity in one UC layers of FeTe grown on Bi2Te3 appears to spatially coexist with bi-collinear AFM order. By using 3D-vector-resolved SP-STM techniques [3] we find an unusual reorientation of the diagonal double-stripe spin structure at Fe1+yTe thin film surfaces [4]. Moreover, variable-temperature SP-STM studies [5] reveal an enhanced Néel temperature for AFM spin ordering of the ultrathin FeTe films grown on topological insulators [6]. These findings open novel perspectives for theoretical studies of competing orders in Fe-based superconductors as well as for experimental investigations of exotic phases in heterostructures of topological insulators and superconducting layers.

In a second part, we will address experimental and theoretical studies of monolayer topological superconductivity and chiral Majorana edge modes in model-type 2D magnetic Fe islands on elemental superconducting Re [7]. In particular, we demonstrate that interface engineering by an atomically thin oxide layer is crucial for driving the studied hybrid system into a topologically non-trivial state as confirmed by theoretical calculations of the topological invariant, the Chern number.

This work is supported by the EU via the ERC Advanced Grant No. 786020 "ADMIRE".

[1] A. Kamlapure et al., Phys. Rev. B 95, 104509 (2017).

[2] S. Manna et al., Nature Commun. 8, 14074 (2017).

[3] S. Meckler et al., Rev. Sci. Instrum. 80, 023708 (2009).

[4] T. Hänke et al., Nature Commun. 8, 13939 (2017).

[5] J. Warmuth et al., NPG Quantum Materials 3, 21 (2018).

[6] U. R. Singh et al., Phys. Rev. B 97, 144513 (2018).

[7] A. Palacio-Morales, E. Mascot, S. Cocklin, H. Kim, S. Rachel, D. K. Morr, and R. Wiesendanger, arXiv:1809.04503 (2018).

9:20am 2D+AS+MI+NS-WeM-5 Geometric Imaging of Borophene Polymorphs, *Xiaolong Liu,* Northwestern University*; L Wang,* Rice University*; S Li, M Rahn,* Northwestern University*; B Yakobson,* Rice University*; M Hersam,* Northwestern University

Two-dimensional (2D) boron, known as borophene, has recently been experimentally realized[1,2] revealing a number of polymorphic structures. A common characteristic of those borophene polymorphs is the presence of hollow-hexagons (HH) in an otherwise triangular lattice. The vast number of possible HH lattices underlies the polymorphic nature of borophene. Superlattices of HHs could be further realized when borophene phases periodically intermix in the form of line defects[3]. While scanning tunneling microscopy (STM) of borophene with conventional metal probes has revealed key features of borophene, significant ambiguity of the exact atomic lattice structure exists due to the convolution of electronic and structural details. With CO-functionalized atomic force microscopy, we unambiguously resolve the HH lattice and reveal features corresponding to B-B covalent bonds[4] that are supported by numerical simulations. We further show that CO-functionalized STM is an equivalent but more accessible technique for HH imaging, allowing us to assemble a growth phase diagram of borophene involving non-rotated, 30°-rotated and randomly rotated borophene phases on Ag(111), confirming the $v_{1/5}$ and $v_{1/6}$ models as the unifying structures for all observed phases. In particular, a transition from rotationally commensurate to incommensurate phases is observed at high growth temperatures, corroborating the chemically discrete nature of borophene.

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1. A. J. Mannix, X.-F. Zhou, B. Kiraly, J. D. Wood, D. Alducin, B. D. Myers, X. Liu, B. L. Fisher, U. Santiago, J. R. Guest, M. J. Yacaman, A. Ponce, A. R. Oganov, M. C. Hersam, N. P. Guisinger, *Science* **350**, 1513–1516 (2015).

2. B. Feng, J. Zhang, Q. Zhong, W. Li, S. Li, H. Li, P. Cheng, S. Meng, L. Chen, K. Wu, *Nat. Chem.* **8**, 563–568 (2016).

3. X. Liu, Z. Zhang, L. Wang, B. I. Yakobson, and M. C. Hersam, *Nat. Mater.* **17**, 783–788 (2018).

4. X. Liu, L. Wang, S. Li, M. S. Rahn, B. I. Yakobson, and M. C. Hersam, *Nat. Commun.* **10**, 1642 (2019).

9:40am 2D+AS+MI+NS-WeM-6 Atomic Manipulation of Defects in the Layered Semiconductor 2H-MoTe$_2$, *Sara Mueller, S Deng,* The Ohio State University*; B St. Laurent,* University of New Hampshire*; Y Wang, W Windl,* The Ohio State University*; S Hollen,* University of New Hampshire*; J Gupta,* The Ohio State University

Here we present a charge control of native defects in the bulk transition metal dichalcogenide, MoTe$_2$ by scanning tunneling microscopy (STM). Bulk MoTe$_2$ was cleaved at room temperature in ultrahigh vacuum and imaged with a cut PtIr tip at 9K. Native defects in the MoTe$_2$ are present throughout the sample and image with complex structure. In topographic imaging, the long-range protrusion of a bright defect indicates the species is charged and we image the defects at different depths below the surface. They present with an ionization feature in tunneling spectroscopic mapping which indicates that the charge state of this defect can be manipulated by the band bending caused by the tip. Voltage pulses from the tip migrate the subsurface defects to the surface layer. The migrated defects present with the same spectroscopic signature as native surface defects. We also present DFT results that we use to clarify the identification of these native defects and energy barriers for migration between layers of 2H-MoTe$_2$.

11:00am 2D+AS+MI+NS-WeM-10 Scanning Tunneling Microscopy and Spectroscopy of a Heterotriangulene-based 2D Polymer, *Zachery Enderson, H Murali, R Dasari, T Parker, S Marder, H Li, Q Dai, S Thomas, J Brédas, P First,* Georgia Institute of Technology

Covalent Organic Frameworks (COFs) and similar materials synthesized from bottom-up procedures grant scientists a means to customize a 2D material's final properties from its initial precursors. The dimethylmethylene-bridged triphenylamine (DTPA) COF is an excellent example of the unique systems one can fabricate with these techniques[1]. The DTPA COF is initially synthesized on Au(111) or Ag(111) which facilitates crystalline growth through Ullman-type coupling. With an even number of electrons per unit cell, theory predicts a semiconducting electronic structure for the COF. Further heating in vacuum selectively cleaves the dimethyl groups but leaves the framework intact. This final COF resembles an ultra-flat covalent network of triangulene molecules with enticing proposed electronic properties, which depend on how the demethylated sites are terminated. In the case of hydrogen termination at these sites, calculations indicate that the "radical" COF on a metallic substrate will be a half-metal (fully spin-polarized density of states at the fermi energy)[2]. Using a low-temperature scanning tunneling microscope, the work outlined in this talk presents new information on the electronic structure of the DTPA COF in both its intact (methylated) and radical (demethylated) forms.

[1] Bieri, Marco, Stephan Blankenburg, Milan Kivala, Carlo A. Pignedoli, Pascal Ruffieux, Klaus Müllen, and Roman Fasel. "Surface-Supported 2D Heterotriangulene Polymers." *Chem. Commun.* 47, no. 37 (2011): 10239–41. https://doi.org/10.1039/C1CC12490K .

[2] Kan, Erjun, Wei Hu, Chuanyun Xiao, Ruifeng Lu, Kaiming Deng, Jinlong Yang, and Haibin Su. "Half-Metallicity in Organic Single Porous Sheets." *Journal of the American Chemical Society* 134, no. 13 (April 4, 2012): 5718–21. https://doi.org/10.1021/ja210822c .

11:20am 2D+AS+MI+NS-WeM-11 Scanning Tunneling Microscopy Investigations of Molecules Adsrobed on Semiconducting Graphene Nanoribbons, *Sineth Premarathna, K Latt, S Hla,* Ohio University

Unlike graphene, semiconducting graphene nanoribbons poccess a band gap and they have the capability to electronic decouple the molecules from the supporting substrate. Here, we study the structural, electronic and vibrational properties of individual para-sexiphenyl molecules adsorbed on semiconducting graphene nanoribbons. The graphene nanoribbons here are grown on the surface of Au(111) using DBBA molecules as the initial building blocks. Para-sexiphenyl molecules adsorb on the graphene naribbons with their long molecular axis positioning parallel to the long axis of the graphene nanoribbons. As expected, the tunneling spectroscopy data reveal the HOMO-LUMO gap of the molecule on graphene nanoribbons much closer to their gas phase values. Moreover, teh vibration spectroscopy measurements of the molecules further provide a strong vibration mode associate with the C=C ring stretching of the molecules. This work provide single molecule level information on the electronic, vibronic and structural properties of the molecules adsorbed on vertically stacked heterostructures formed by graphene nanoribbons on Au(111) surface.

11:40am 2D+AS+MI+NS-WeM-12 Molecular Flexure and Atom Trapping with Sexiphenyl Molecules by Scanning Tunneling Microscope Manipulation, *Y Zhang, Shaoze Wang, K Braun, S Hla,* Ohio University

Molecular flexure, and molecule-metal contact of para-sexiphenyl molecules on a Ag(111) surface are investigated by using low temperature scanning tunneling microscopy, and molecular manipulations. Atom trapping with sexiphenyl molecules is realized by laterally manipulating the molecules onto individual silver atoms and up to three silver atoms have been trapped. We also demonstrate breaking of a silver dimer into individual silver atoms by atom trapping. STM manipulation experiments show that the molecule-metal complexes formed by the atom trapping are mechanically stable. Moreover, lateral manipulation of a single seziphenyl across a Ag(111) atomic step highlights how the molecule moves across step-edges; the molecule can easily conform across the step and it recovers original configuration after the manipulation.

12:00pm 2D+AS+MI+NS-WeM-13 Localized Strain Effects in Spin-Polarized Density of States for 2D-MnGaN – a Room Temperature Ferromagnetic Monolayer, *Y Ma,* Ohio University; *K Meng,* The Ohio State University; *D Hunt, M Barral, V Ferrari,* CAC-CNEA, Argentina; *F Yang,* The Ohio State University; *Arthur Smith,* Ohio University

We recently demonstrated the first observation of a 2D *room-temperature-ferromagnetic monolayer* of MnGaN (2D-MnGaN) using spin-polarized scanning tunneling microscopy and spectroscopy. The sample is grown by molecular beam epitaxy on gallium nitride substrates. We resolved ferromagnetic domains using SP-STM, demonstrated magnetic hysteresis using small *out-of-plane* magnetic fields, observed magnetic rim states, and measured magnetic DOS profiles using tunneling spectroscopy which are in excellent agreement with the predicted spin-polarized & spin-split DOS peaks obtained from first-principles theory. This work was published online in December 2017 in *Nano Letters*.[1]

More recently, we are investigating the dependence of magnetization anisotropy on *in-plane* lattice strain. First of all, we have observed from the spectroscopy measurements that the position of the spin-polarized Mn DOS peak varies from spectrum to spectrum, ranging from -1.69 eV up to -1.22 eV (relative to E_Fermi). In order to investigate if these variations could be related to structural variations, we have also carried out theoretical calculations based on first principles for both isotropic and local anisotropic lattice strains. The isotropic strain case shows that the occupied-states Mn peak can indeed shift by many tenths of an eV if the 2D-MnGaN is strained *in-plane*; for example, E = -1.58 eV for the no-strain case, whereas E = -1.33 eV for tensile strain (+9.1%) and E = -2.22 eV for compressive strain *(-6.0%)*. On the other hand, we find an opposite behavior in the local anisotropic calculation.

Using atomic resolution STM, we have also found that significant strain variations exist within the 2D-MnGaN. As compared to an ideally periodic hexagonal lattice, the 2D-MnGaN lattice displays local spacing variations, and the spacing distribution is highly non-Gaussian and may instead be characterized as *tri-modal* with the central peak matching closely the expected average for 2D-MnGaN of 5.52 Å, but with left and right peaks centered around 5.00 Å and 5.92 Å. Therefore, the Mn atoms, centered between Ga adatoms, are under highly varying strains, ranging from tensile to compressive.

By mapping the observed Mn peak energies onto theoretical energy-strain curves, we can then estimate the expected lattice parameters corresponding to particular energies and compare with the lattice spacing distribution. These results will be discussed as well as the additional discovery of a dependence of the spin anisotropy on the lattice strain.

[1] *Yingqiao Ma, Abhijit V. Chinchore, Arthur R. Smith, María Andrea Barral, and Valeria Ferrari, Nano Letters* **18**, *158 (2018).*

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