

Nanoscale Science and Technology Division Room 304 - Session NS2+AS+EM-WeA

Scanning Probe Metrology of 1D and 2D Materials

Moderators: Maryam Ebrahimi, Iakelhead University, Canada, Aubrey Hanbicki, Laboratory for Physical Sciences

4:20pm **NS2+AS+EM-WeA-7 New on-Surface Synthesis Techniques for Creating Precise 1D Graphene Nanoribbon Heterojunctions and Device-Tunable 2D Molecular Arrays**, *Michael Crommie*, UC Berkeley Department of Physics; *G. Dong*, University of Chicago Department of Chemistry; *J. Lischner*, Imperial College London Department of Materials, UK; *A. Zettl*, *P. Jacobse*, *Z. Wang*, UC Berkeley Department of Physics; *J. Yin*, University of Chicago Department of Chemistry; *H. Tsai*, *F. Liou*, *A. Aikawa*, UC Berkeley Department of Physics

INVITED

Bottom-up fabrication techniques for assembling molecular nanostructures at surfaces typically exploit various surface interactions that (along with random thermal processes) can be biased toward achieving desired structural results via the clever design of molecular precursors. Great progress has been made using this approach, but surface-grown molecular structures remain plagued by random, uncontrolled processes that make complex structural control difficult. Overcoming this problem is one of the grand challenges of this subfield. Here I will discuss two new approaches to molecular surface assembly that have allowed us to improve order in surface-based nanostructures. The first involves 1D materials and utilizes a solution-based polymerization scheme combined with a new surface deposition procedure. The second involves combining molecular surface assembly with 2D field-effect transistors (FETs). The first method is focused on graphene nanoribbons (GNRs), nanometer-wide strips of graphene. Fabricating complex heterostructure sequences in GNRs remains a difficult challenge because we can't sequence GNRs the way we sequence DNA. This makes it hard to fulfill the promise of GNR-based molecular electronics because of the difficulty of fabricating GNRs composed of well-ordered segments that each have controlled properties (e.g., bandgap, doping, magnetism, optical response). We have made progress toward overcoming this challenge by using a new protecting-group-aided-iterative-synthesis strategy. This allows us to create GNR oligomers with perfectly defined monomer sequences in solution that can be deposited onto surfaces for cyclodehydrogenation using a matrix-assisted deposition (MAD) procedure. This has enabled the synthesis of GNR heterojunctions that would not be possible via other techniques. The second technique I will discuss involves the use of an "active substrate" (a graphene FET) to induce reversible 2D molecular assembly through a combination of Coulomb and van der Waals interactions. The trick here is to use a molecule (in our case F_4TCNQ) whose LUMO level (E_L) lies in an energy range accessible to the Fermi level (E_F) of the 2D FET. Manipulating E_F relative to E_L via the device backgate allows charge in the device to reversibly flow between substrate states and the LUMO level of adsorbed molecules. This results in unexpected mechanical responsivity of the molecules, including tunable 2D array formation and a reversible quasi-1D phase transition that we have imaged using scanning tunneling microscopy.

5:00pm **NS2+AS+EM-WeA-9 Temperature-Mediated Adsorption and Assembly of Internally Fluorinated Chevron Graphene Nanoribbon Precursors on Au(111)**, *Jacob Teeter*, Center for Nanophase Materials Sciences, Oak Ridge National Laboratory; *M. Sarker*, University of Nebraska - Lincoln; *C. Tao*, *J. Huang*, Center for Nanophase Materials Sciences, Oak Ridge National Laboratory; *W. Lu*, *J. Bernholc*, North Carolina State University; *A. Sinitskii*, University of Nebraska - Lincoln; *A. Li*, Center for Nanophase Materials Sciences, Oak Ridge National Laboratory

The archetypical chevron-shape graphene nanoribbon (GNR) broke new ground in the on-surface synthesis of carbon-based nanomaterials with its development in 2010 by Cai *et al.*. Subsequent innovation predicated on this discovery introduced a wide variety of GNRs with differing shapes, edge types, heteroatomic substitutions, topological phases, and more. One drawback to studying GNRs arising from surface-assisted synthesis is the intrinsic electronic hybridization between the GNR and the surface upon which it was grown. This convolutes electronic characterization such as scanning tunneling spectroscopy (STS), but can be mitigated somewhat through tip-based manipulation of the GNRs onto an insulating layer on the surface, or by introducing a powder of solution-synthesized GNRs to a semiconducting substrate. Only recently has a method been developed - utilizing rutile $TiO_2(011)$, rationally designed fluorinated precursors, and a

surface-assisted cyclodehydrofluorination reaction - to achieve bottom-up-synthesized atomically precise GNRs on such a surface².

In this work, we have developed more fluorinated precursors to expand the set of atomically precise GNRs grown on semiconducting surfaces and studied their assembly on Au(111) using scanning tunneling microscopy. In particular, we have produced and prototyped on Au(111) a fluorinated chevron precursor intended to yield chevron-type GNRs on $TiO_2(011)$. With all other factors equivalent, the adsorption of the precursor is heavily dependent on the temperature of the surface of the Au(111) crystal on which it is deposited. The lack of adsorption at room temperature is in sharp contrast with the non-fluorinated precursor, which can be deposited at room temperature and post-annealed to produce GNRs in good yield. We attribute this discrepancy to interactions between the internal F atoms and the Au(111) surface, which is supported by theoretical calculations.

This research was performed at the Center for Nanophase Materials Sciences which is a DOE Office of Science User Facility.

1. Cai, J.; Ruffieux, P.; Jaafar, R.; Bieri, M.; Braun, T.; Blankenburg, S.; Muoth, M.; Seitsonen, A. P.; Saleh, M.; Feng, X.; Müllen, K.; Fasel, R., Atomically precise bottom-up fabrication of graphene nanoribbons. *Nature* 2010, 466.

2. Kolmer, M.; Steiner, A.-K.; Izydorczyk, I.; Ko, W.; Engelund, M.; Szymonski, M.; Li, A.-P.; Amsharov, K., Rational synthesis of atomically precise graphene nanoribbons directly on metal oxide surfaces. *Science* 2020, 369 (6503), 571-575

5:20pm **NS2+AS+EM-WeA-10 STM Study of Superconducting Film $FeTe(1-x)Se(x)$ on Topological Insulator Bi_2Te_3** , *Hoyeon Jeon*, *W. Ko*, *M. Brahlek*, *R. G. Moore II*, *A. Li*, Oak Ridge National Laboratory, USA

Topological superconductors (TSCs) have attracted great attention because they can host Majorana fermions for quantum computation. Because natural TSCs are rarely found, alternative ways to make TSCs are badly needed. One of them is using proximity effect by combining two-dimensional Dirac surface states of topological insulator (TI) with *s*-wave superconductivity (SC) to generate localized topological Majorana zero modes in vortex cores. Here we report the epitaxial growth of SC films of $FeTe(1-x)Se(x)$ on TI of Bi_2Te_3 , their electronic structures and surface inhomogeneities of superconductivity using scanning tunneling microscope/spectroscopy (STM/STS). A variety of samples are examined with different thicknesses of superconducting layer and selenium concentrations. We expect our results to be relevant for searching for materials platforms to host topological superconductivity.

The research is supported by the U.S. Department of Energy (DOE), Office of Science, National Quantum Information Science Research Centers., the Quantum Science Center (QSC), a National Quantum Information Science Research Center of the U.S. Department of Energy (DOE).

5:40pm **NS2+AS+EM-WeA-11 Atomic-Scale Mapping of Thermoelectric Properties of Noble Transition Metal Dichalcogenides**, *Saban Hus*, *A. Li*, Oak Ridge National Laboratory; *L. Liu*, *Y. Chen*, Purdue University

Monolayer noble transition metal dichalcogenides with hexagonal lattice structure are predicted to be high performance thermoelectric materials at room temperature [1]. Their pentagonal counterparts promise even better performance due to the in-plane anisotropy of the lattice [2]. However, like many other features of 2D materials, their thermoelectric properties can significantly be altered by the heterogeneities in the atomically thin layers [3]. Using a scanning tunneling microscope (STM), we investigate the thermoelectric properties of both pentagonal and hexagonal noble transition metal dichalcogenide monolayers in atomic resolution. We observe that atomic-scale defects and variations in 2D layer-substrate interface create a rich thermoelectric landscape invisible to mesoscopic scale measurements. Precise control and utilization of these heterogeneities can lead to next-generation thermoelectric devices and materials for energy applications.

[1] B. Marfoua and J. Hong, *ACS Appl. Mater. Interfaces* 11, 38819 (2019)

[2] D. Qin, et al., *Sci. Reports.* 8, 2764 (2018).

[3] S.M. Hus, A-P. Li, *Progress in Surface Science* 92, 176 (2017)

Wednesday Afternoon, November 9, 2022

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Author Index

Bold page numbers indicate presenter

— A —

Aikawa, A.: NS2+AS+EM-WeA-7, 1

— B —

Bernholc, J.: NS2+AS+EM-WeA-9, 1

Brahlek, M.: NS2+AS+EM-WeA-10, 1

— C —

Chen, Y.: NS2+AS+EM-WeA-11, 1

Crommie, M.: NS2+AS+EM-WeA-7, 1

— D —

Dong, G.: NS2+AS+EM-WeA-7, 1

— G —

G. Moore II, R.: NS2+AS+EM-WeA-10, 1

— H —

Huang, J.: NS2+AS+EM-WeA-9, 1

Hus, S.: NS2+AS+EM-WeA-11, 1

— J —

Jacobse, P.: NS2+AS+EM-WeA-7, 1

Jeon, H.: NS2+AS+EM-WeA-10, 1

— K —

Ko, W.: NS2+AS+EM-WeA-10, 1

— L —

Li, A.: NS2+AS+EM-WeA-10, 1; NS2+AS+EM-WeA-11, 1; NS2+AS+EM-WeA-9, 1

Liou, F.: NS2+AS+EM-WeA-7, 1

Lischner, J.: NS2+AS+EM-WeA-7, 1

Liu, L.: NS2+AS+EM-WeA-11, 1

Lu, W.: NS2+AS+EM-WeA-9, 1

— S —

Sarker, M.: NS2+AS+EM-WeA-9, 1

Sinitskii, A.: NS2+AS+EM-WeA-9, 1

— T —

Tao, C.: NS2+AS+EM-WeA-9, 1

Teeter, J.: NS2+AS+EM-WeA-9, 1

Tsai, H.: NS2+AS+EM-WeA-7, 1

— W —

Wang, Z.: NS2+AS+EM-WeA-7, 1

— Y —

Yin, J.: NS2+AS+EM-WeA-7, 1

— Z —

Zettl, A.: NS2+AS+EM-WeA-7, 1