

Monday Afternoon, November 10, 2014

2D Materials Focus Topic

Room: 310 - Session 2D+AS+EM+NS+SS-MoA

Dopants, Defects, and Interfaces in 2D Materials

Moderator: Jun Lou, Rice University

2:00pm **2D+AS+EM+NS+SS-MoA1 Cutting and Assembling 2 Nanometer Voids in Single Layer Hexagonal Boron Nitride**, *Thomas Greber, H.Y. Cun, M. Iannuzzi, A. Hemmi, J. Osterwalder*, University of Zurich, Switzerland

INVITED

Argon implantation beneath hexagonal boron nitride nanomesh on Rh(111) [1] leads to the formation of vacancy and interstitial defects [2]. The nanomesh is a single layer of hexagonal boron nitride on Rh(111), where 13x13 h-BN units accommodate on 12x12 Rh unit cells. The resulting super-honeycomb has a lattice constant of 3.2 nm and consists in regions where the h-BN “wets” the Rh substrate (pores), and regions where h-BN is quasi freestanding (wires) [3].

The interstitial defects are called “nanotents”, where atoms are trapped beneath the ultimately thin “rainfly” made of a single layer of h-BN [2,4]. They are stable at room temperature and survive exposure to air.

The vacancy defects are sites where a boron or a nitrogen atom was kicked out by the Ar ion impact. If the implanted structures are annealed to 900 K the can-opener effect occurs: 2 nm h-BN-flakes or “lids” are cut out of the h-BN nanomesh and 2 nm voids form [2]. At higher temperatures the resulting voids may diffuse and assemble, due to their repulsive interaction, in a super-structure with some order, i.e., a nearest neighbor distance of about 15 nm. Near the disintegration temperature of the h-BN nanomesh we finally observe self-healing of the voids in the nanomesh, which we assign to their annihilation in larger holes in the structure.

The report bases on scanning tunneling microscopy, x-ray photoelectron spectroscopy, molecular dynamics and density functional theory calculations.

Financial support by the Swiss National Science Foundation and support by the EC under the Graphene Flagship (contract no. CNECT-ICT-604391) is gratefully acknowledged. We thank the Swiss National Supercomputer Centre (CSCS) for allocation of computer time.

[1] M. Corso et al. *Science*, 303 (2004) 217.

[2] H. Y. Cun et al. *Nano Letters* 13 (2013) 2098.

[3] S. Berner et al. *Angew. Chem. Int. Ed.* 46 (2007) 5115.

[4] H.Y. Cun et al. *ACS Nano* 8 (2014) 1014.

2:40pm **2D+AS+EM+NS+SS-MoA3 Engineering Structural Defects in Graphene Materials**, *Jeremy Robinson, M. Zhaludinov, J. Culbertson, C. Junkermier, P.E. Sheehan, T. Reinecke, A. Friedman*, Naval Research Laboratory

Graphene's atomic thinness makes it highly sensitive to surface adsorbates or defects within its carbon backbone. Aside from the known effects and impact on electronic properties, here we demonstrate the impact of defects on the mechanical properties and the response of mechanical resonators. In particular, once defects are formed in atomically-thin materials they can be quite mobile and form more complicated defect structures such as bi- or tetra-vacancy clusters. We execute experiments using mechanical drum resonators made from single- to multi- to many-layer graphene systems. We use both CVD grown graphene and reduced graphene oxide (rGO) films to capture a wide range of defect structures. By measuring the fundamental frequency response of the resonators (in the MHz range) we extract properties such as tension, quality factor, and modulus as a function of external manipulation [1]. For highly defective rGO films measuring 10-40nm thick, we can tune the frequency response by 500% and quality factor by 20x through laser annealing, which effectively rearranges defects throughout the film [1]. Alternatively, using graphene 1-4 layers thick, we find the resonator response is significantly more sensitive to the formation and annihilation of meta-stable defects, such as the tetra-vacancy structure. We will show how the defect mobility and resonator response changes with different energy photons and come to understand these differences based on calculated defect migration energies of different defects types in graphene.

[1] *Nano Letters* 12, 4212 (2012)

3:00pm **2D+AS+EM+NS+SS-MoA4 Graphene Cleaning using a Low Energy Ar Ion Beam**, *KiSeok Kim, G. Yeom*, Sungkyunkwan University, Republic of Korea

Recently, graphene has been widely investigated due to the superior electrical, mechanical, thermal, and chemical properties. Especially, CVD graphene which was grown on Cu foil and transferred to various substrates using PMMA has been used most widely due to the possible large area applications such as electronic devices for displays, semiconductors, etc. However, in order to apply the transferred CVD graphene to the various electronic device fabrication, PMMA residue on the graphene surface formed during the transfer process and lithography process needs to be completely removed without damage. Various methods have been investigated to remove the residue on the graphene surface such as current cleaning, heat treatment, chemical cleaning, etc. However, it is reported that these methods are not effective in removing the residue on graphene or not applicable to industry.

In this study, a controlled Ar ion beam has been used to effectively remove the PMMA residue on graphene surface. By controlling the Ar ion beam condition, the residue on graphene surface could be removed while minimizing the damage on the graphene surface. Especially, by lowering the Ar beam energy less than 10 eV, it was possible to effectively remove the PMMA residue without damaging the graphene. The removal of PMMA residue on the graphene surface could be identified using Raman Spectroscopy showing the red shift of 2D peak (2670 cm^{-1}) and blue shift of G peak (1580 cm^{-1}) in addition to the decrease of RMS roughness from 1.3nm to 0.3 nm using an AFM (Atomic Force Microscopy). The effectiveness of graphene cleaning was also confirmed by XPS (X-ray Photoelectron Spectroscopy), by the uniform deposition of ALD HfO_2 layer on the cleaned graphene surface, by measuring the electrical properties of deposited ALD HfO_2 , etc.

3:40pm **2D+AS+EM+NS+SS-MoA6 Electronic Structure Modification in van der Waals Heterostructures: Interlayer Hybridization in the Case of Graphene/MoS₂**, *Matthias Batzill, H. Coy-Diaz*, University of South Florida, *M.C. Asensio*, Synchrotron Soleil, France, *J. Avila*, Synchrotron Soleil

Artificial van der Waals heterostructures promise to combine materials with diverse properties. Simple mechanical stacking or conventional growth of molecular hetero-layers would enable fabrication of novel materials or device-structures with atomically precise interfaces. Because covalent bonding in these layered materials is limited to molecular-planes, interface interactions between dissimilar materials are expected to modify the properties of the individual layers only weakly. Here we prepare graphene/MoS₂ heterostructures by transferring CVD-grown graphene onto a MoS₂ substrate. It is shown that high quality interfaces between graphene and MoS₂ can be obtained by UHV annealing. The quality of the graphene is demonstrated by atomic resolution scanning tunneling microscopy of ultraflat graphene. The electronic structure of the interface between the polycrystalline graphene and a MoS₂ substrate is measured by angle resolved photoemission spectroscopy (ARPES) and nano-ARPES utilizing a focused photon beam at the SOLEIL synchrotron. We show that at the Fermi-level graphene exhibits a perfect, gapless and undoped Dirac-cone. However, in regions where the π -band of graphene overlaps with states of the MoS₂ substrate, opening of several band-gaps are observed. This demonstrates that the electronic properties in van der Waals heterostructures can be significantly modified by interlayer interaction and thus exemplifying opportunities for tuning materials properties of graphene and other 2D-materials by interfacing them with dissimilar van-der Waals materials.

4:00pm **2D+AS+EM+NS+SS-MoA7 Edge States and Exposure to Hydrogen of Silicon at the 2D Limit on Ag(111)**, *A.J. Mannix, B.T. Kiraly*, Argonne National Laboratory, *M.C. Hersam*, Northwestern University, *Nathan Guisinger*, Argonne National Laboratory

Chemical functionalization of atomically thin materials results in significant modifications to their electronic properties, which can be exploited in device applications. Compared to the chemical inertness of graphene, 2D silicon is expected to exhibit greater reactivity, and thus a greater amenability to chemical functionalization. Among potential functionalization chemistries, hydrogen termination is favored for its relative simplicity and proven efficacy with graphene and bulk Si surfaces. Using ultra-high vacuum (UHV) scanning tunneling microscopy (STM), we have studied the temperature-dependent effects of exposing 2D silicon platelets grown on Ag(111) to molecular and atomic hydrogen. At low doses, atomic hydrogen results in limited adsorption and temperature dependent etching. In the bulk, the formation of vacancies and extended

etch pits is observed. In addition, edge states can play a critical role in the electronic properties of 2D materials. We have also examined at the atomic-scale the edges of 2D silicon platelets.

4:20pm **2D+AS+EM+NS+SS-MoA8 Chlorine Trap-Doping for Transparent, Conductive, Thermally Stable and Damage-Free Graphene.** *Pham Viet Phuong, K.N. Kim, M.H. Jeon, K.S. Kim, G. Yeom*, Sungkyunkwan University, Republic of Korea

We propose a novel doping method of graphene by cyclic trap-doping with low energy chlorine adsorption. Low energy chlorine adsorption for graphene chlorination avoided defect (D-band) formation during doping by maintaining the π -bonding of the graphene, which affects conductivity. In addition, by trapping chlorine dopants between the graphene layers, the proposed doping method dramatically decreased the sheet resistance by ~88% at an optimized condition. Among the reported doping methods including chemical, plasma, photochemical methods etc., the proposed doping method is believed to be the most promising for producing graphene of extremely high transmittance, low sheet resistance, high thermal stability, and high flexibility for use in various flexible electronic devices. Results of angle resolved X-ray photoelectron spectroscopy (XPS), high-resolution transmission electron spectroscopy (HR-TEM), Raman spectroscopy, ultraviolet-Visible spectroscopy (UV-Vis) and sheet resistance, showed that this method is also non-destructive and controllable. The sheet resistance of the doped tri-layer graphene was 70 Ω /sq at 94% transmittance, which was maintained for more than 6.5 h at 230°C. Moreover, the defect intensity of graphene was not increased during the cyclic trap-doping.

4:40pm **2D+AS+EM+NS+SS-MoA9 Modification of Graphene by Neutral Beam Irradiation and Edge Structure Analysis.** *Takeru Okada, S. Samukawa*, Tohoku University, Japan

Since the discovery of single layer of Graphite, Graphene, a single layer of hexagonal carbon atoms, has attracted much attention and shown exciting specific properties. Graphene is a zero band gap semiconductor. Therefore band gap control is one of most important issue to apply for electronic device applications. In order to construct electronic devices with logic operation, both p- and n-type conduction and the control of the carrier density in an active channel are required. Doping with foreign atoms, such as N and B, has proven to be an effective way to modify the electronic properties of carbon related materials and extend their applications. In particular, nitrogen doping brings a carrier which could turn carbon nanotube into n-type semiconductors. It is also feasible to modify the electronic properties of Graphene. Although several doping methods have reported so far, process damages (defect generation) cause degradation of electronic properties.

In this paper, we introduce ultra-low damage neutral beam system which consists of a plasma and process chambers that are separated by a carbon aperture. Charged species and ultra-violet photon from the plasma can be effectively eliminated by the aperture. As a result, only the neutral beam arrives the surface of the sample at the substrate in the process chamber.

We used nitrogen gas for plasma generation and adopted multi-layer Graphene to investigate nitridation mechanism. Graphene multi-layer was irradiated by nitrogen neutral beam with controlled energy of 10 eV at room temperature. The surface modification was analyzed by x-ray photoelectron spectroscopy (XPS). XPS analysis indicated that the carbon atoms were substituted to nitrogen atom and atomic concentration of nitrogen reaches 15 %. Additionally, bonding state of C and N was found to depend on neutral beam irradiation time. Thus beam energy controlled neutral beam can selective nitridation of Graphene. Furthermore the doping density is estimated by Raman spectroscopy and result in 10^{12} [cm⁻²], which is enough to n-type doping of Graphene.

5:00pm **2D+AS+EM+NS+SS-MoA10 Growth Mechanism of Metal Clusters on a Graphene/Ru(0001) Template.** *Shixuan Du, L.Z. Zhang*, Chinese Academy of Sciences, *W. Hofer*, University of Liverpool, UK, *H.-J. Gao*, Chinese Academy of Sciences

Metal nano-clusters have attracted considerable interest because of the potential applications in catalysis and information storage. Due to the soft nature of epitaxial graphene and the lattice mismatch between graphene and metal substrates periodic moiré patterns can be formed. A graphene/metal template, moiré template, can be used to grow dispersed metal nano-clusters with controllable size and shape, or metal clusters with large size and metal layers. However, how intrinsic properties of metal atoms and the moiré template influence the selective adsorption and the growth mode of metal clusters is still open to debate. A general rule, predicting the morphology of metal nano-clusters on a G/metal surface, important to guide experimenters, is still missing. Using first-principles calculations combined with scanning tunneling microscopy experiments, we investigated the adsorption configurations, electronic structures and the corresponding growth mechanism of several transition metal (TM) atoms (Pt, Ru, Ir, Ti, Pd, Au,

Ag, and Cu) on a graphene/Ru(0001) moiré template (G/Ru(0001)) at low coverage. We find that Pt, Ru, Ir, and Ti selectively adsorb on the fcc region of G/Ru(0001) and form ordered dispersed metal nano-clusters. This behavior is due to the unoccupied *d* orbital of the TM atoms and the strong *sp*³ hybridization of carbon atoms in the fcc region of G/Ru(0001). Pd, Au, Ag, and Cu form nonselective structures because of the fully occupied *d* orbital. This mechanism can be extended to metals on a graphene/Rh(111) template. By using Pt as an example, we provide a layer by layer growth path for Pt nano-clusters in the fcc region of the G/Ru(0001). The simulations agree well with the experimental observations. Moreover, they also provide guidance for the selection of suitable metal atoms to form ordered dispersed metal nano-clusters on similar templates.

References:

1. L.Z. Zhang *et al.* Advanced Materials Interfaces, accepted.
2. Y. Pan *et al.* Applied Physics Letter, 95, 093106 (2009)

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