

# Wednesday Morning, November 12, 2014

## 2D Materials Focus Topic

Room: 310 - Session 2D+EM+NS+SS+TF-WeM

### Novel 2D Materials

Moderator: Evan Reed, Stanford University

8:00am **2D+EM+NS+SS+TF-WeM1 Silicene and Germanene: Novel Graphene-like Artificial Silicon and Germanium Allotropes, Guy Le Lay, Aix-Marseille University, France** **INVITED**

Silicene, graphene's cousin, and germanene, a new born in Terra Plana, are predicted to combine the unique electronic properties of graphene associated to quasiparticles behaving as massless Dirac fermions to a character of two-dimensional topological insulators, and, even, possibly, high temperature superconductors. In this talk, I will present fundamental results on these novel synthetic 2D materials, which do not exist in nature, but which might open the way to practical applications, because of their expected direct compatibility with the current nano/micro electronic technologies.

8:40am **2D+EM+NS+SS+TF-WeM3 Silicon Growth at the Two-Dimensional Limit on Ag(111), Andrew Mannix, B.T. Kiraly, Northwestern University, B.L. Fisher, Argonne National Laboratory, M.C. Hersam, Northwestern University, N.P. Guisinger, Argonne National Laboratory**

Bulk silicon has played a dominant role in the growth of microelectronics over the past 50 years. Considering the immense interest in two-dimensional (2D) materials (e.g., graphene, MoS<sub>2</sub>, phosphorene, etc.), the growth of Si in the 2D limit is of high relevance to the evolution of electronic materials. Utilizing atomic-scale, ultra-high vacuum (UHV) scanning tunneling microscopy (STM), we have investigated the 2D limits of Si growth on Ag(111). In agreement with previous reports of *sp*<sup>2</sup>-bonded silicene,<sup>1,2</sup> we observe the evolution of ordered 2D phases, which we attribute to apparent Ag-Si surface alloys. At sufficiently high Si coverage, we observe the precipitation of crystalline, *sp*<sup>3</sup>-bonded Si(111) domains. These domains are capped with a  $\sqrt{3}$  honeycomb phase that is indistinguishable from the  $\sqrt{3}$  honeycomb-chained-trimer (HCT) reconstruction of Ag on Si(111).<sup>3,4,5</sup> Additional evidence suggests that silicon intermixing with the Ag(111) substrate is followed by the precipitation of crystalline, *sp*<sup>3</sup>-bonded silicon nanosheets. These conclusions are supported by *ex-situ* atomic force microscopy (AFM), Raman spectroscopy, and X-ray photoelectron spectroscopy (XPS). Even at the 2D limit, scanning tunneling spectroscopy shows that the *sp*<sup>3</sup>-bonded silicon nanosheets exhibit semiconducting electronic characteristics.

[1] Vogt, P., *et al.* Silicene: Compelling Experimental Evidence for Graphene-like Two-Dimensional Silicon. *Phys. Rev. Lett.*, 108(15), 155501 (2012).

[2] Feng, B., *et al.* Evidence of silicene in honeycomb structures of silicon on Ag(111). *Nano Lett.*, 12(7), 3507–11 (2012)

[3] Le Lay, G. Physics and electronics of the noble-metal/elemental-semiconductor interface formation: A status report. *Surf. Sci.*, 132(1-3), 169–204 (1983).

[4] Aizawa, H., Tsukada, M., Sato, N., & Hasegawa, S. Asymmetric structure of the Si(111)- $\sqrt{3}\times\sqrt{3}$ -Ag surface. *Surf. Sci.*, 429 (0–5) (1999).

[5] Ding, Y., Chan, C., & Ho, K. Structure of the ( $\sqrt{3}\times\sqrt{3}$ ) R30° Ag/Si(111) surface from first-principles calculations. *Phys. Rev. Lett.*, 67(11), 1454–1458 (1991).

9:00am **2D+EM+NS+SS+TF-WeM4 Growth, Structure, and Properties of 2D SiO<sub>2</sub> Polymorphs, Eric Altman, J. Götzén, X. Zhu, A. Sonnenfeld, U.D. Schwarz, Yale University**

Recently it has been shown that SiO<sub>2</sub> can form closed 2D bilayers; because the layers have no dangling bonds they are expected to interact solely through van der Waals interactions. Despite the expected weak interactions, hexagonal crystalline bilayers on Pd(100) are stretched 4% to match the lattice constant of the substrate. Both electron diffraction and STM reveal that the size of the crystalline domains is limited along Pd[011] and one of the other bilayer close-packed directions but was long along the third one. The formation of regular domain boundaries on the square Pd substrate is attributed to stress relief in the crystalline layer. *Ab initio* calculations indicate that much of the remaining strain energy can be relieved by allowing the film to relax along the incommensurate direction. In this way the square substrate actually aids the templating of the overlayer despite the severe geometric mismatch. The calculations also indicate that the bilayer is surprisingly compliant, explaining the lattice matching despite the weak

interaction and poor match. Amorphous bilayers could also be prepared on Pd(100). Atomic-scale features in STM images of the amorphous film could be associated with 4-9 membered rings of corner-sharing SiO<sub>4</sub> tetrahedra. In addition to the structural heterogeneity, spectroscopic STM imaging revealed electronic heterogeneity with oxygen sites joining larger rings of corner-sharing SiO<sub>4</sub> tetrahedra fading at low bias; spectra revealed two distinct electronic states responsible for this phenomenon. MBE growth of silica bilayers on graphene layers grown on epitaxial Ru on sapphire will also be discussed.

9:20am **2D+EM+NS+SS+TF-WeM5 Layer-dependent Electronic and Vibrational Properties of SnSe<sub>2</sub> and SnS<sub>2</sub> 2D Materials, Joseph Gonzales, R. Schlaf, I.I. Oleynik, University of South Florida**

Layered metal chalcogenides possess a wide range of unique electronic properties, which are currently explored for applications as novel two-dimensional electronic materials. SnS<sub>2</sub> and SnSe<sub>2</sub> layered materials consist of covalently bonded S-Sn-S (Se-Sn-Se) sheets bonded together by weak van der Waals interactions. The atomic, electronic and vibrational properties of SnS<sub>2</sub> and SnSe<sub>2</sub> thin films are investigated using first-principles density functional theory (DFT). The accurate prediction of electronic and optical properties of SnS<sub>2</sub> and SnSe<sub>2</sub> layered 2D materials is achieved by applying state of the art many-body perturbation theory in GW approximation followed by solving the Bethe-Salpeter equation (BSE) to take into account excitonic effects. The evolution of the thickness-dependent band structure, optical and Raman spectra are discussed. The strain effects due to interactions with the substrate are also considered. The first-principles results are compared with available experimental data.

9:40am **2D+EM+NS+SS+TF-WeM6 Synthesis and Properties of Large Scale, Atomically Thin Tungsten Diselenide (WSe<sub>2</sub>), Sarah Eichfeld, Y.C. Lin, L. Hossain, The Pennsylvania State University, A. Piasecki, The Pennsylvania State University, A. Azcatti, University of Texas, Dallas, S. McDonnell, R.M. Wallace, University of Texas at Dallas, J.A. Robinson, The Pennsylvania State University**

Transition metal dichalcogenides (TMDs), such as tungsten diselenide (WSe<sub>2</sub>) are of interest due to their intriguing properties including the transition from indirect gap to direct gap as the material is thinned to a single atomic layer. Stacking of these layered TMDs also allows for the possibility of bandgap tuning. These properties can suit a large range of flexible and low temperature electronic and optoelectronic devices. Current methods of WSe<sub>2</sub> research involve exfoliation or vaporization of WO<sub>3</sub> and Se powder, which limits industrial scalability. This work is focused on development of a metal-organic chemical vapor deposition process that can controllably produce highly-crystalline, atomically thin WSe<sub>2</sub> on large area substrates.

Growth of controlled monolayer tungsten diselenide (WSe<sub>2</sub>) was carried out using chemical vapor deposition in a cold wall vertical reactor. Tungsten hexacarbonyl (W(CO)<sub>6</sub>) and dimethylselenium (DMS<sub>e</sub>) served as the tungsten and selenium precursors, respectively. Use of MOCVD precursors provides a means to independently control the W and Se precursors allowing for more precise control of the individual species during growth. Process variables including temperature (500-950°C), pressure (100-700 Torr), and carrier gas, which were correlated with grain size, growth rate, and nucleation density of the WSe<sub>2</sub> to identify optimal parameters for atomically controlled synthesis. Increasing the growth pressure from 100-700 Torr results in a decrease in growth rate and nucleation density, leading to a >50x increase in grain size. Increased growth temperatures yield an increase in grain size, however, it was found that above temperatures of 800 °C the sapphire substrate begins to decompose in the growth environment, resulting in a degradation of WSe<sub>2</sub> above 800°C. Synthesis using 100% hydrogen, and also hydrogen/nitrogen mixtures was carried out. It was found that 100% hydrogen was necessary in order to achieve low carbon incorporation in the WSe<sub>2</sub> films. Characterization of these samples via Raman and photoluminescence spectroscopy verified that high quality, monolayer WSe<sub>2</sub> is readily achievable. Additional characterization (i.e. scanning electron microscopy, atomic force microscopy, etc.) verify the quality, grain size, and nucleation density of the atomic layers. Finally, we will discuss the impact of substrate choice on the quality of the WSe<sub>2</sub> atomic layers, as well as providing direct evidence that synthesis on graphene results in highly textured films, with nearly 100% commensurability to the underlying graphene.

11:00am **2D+EM+NS+SS+TF-WeM10 Growth of Transition Metal Dichalcogenides and their Alloys and on Flat and Patterned Substrates.** *E. Preciado, A. Nguyen, D. Barroso, V. Klee, S. Bobek, I. Lu, S. Naghibi, G. Von Son Palacio, T. Empante, K. Brown, K. Yang, A. Nguyen, J. Mann, Ludwig Bartels*, University of California - Riverside

The use of organic chalcogen precursors permits the CVD growth of  $\text{MoS}_{2(1-x)}\text{Se}_{2x}$  alloys of any composition between pure  $\text{MoS}_2$  and  $\text{MoSe}_2$  on  $\text{SiO}_2$ . Spatially resolved vibrational and photoluminescence (PL) spectroscopy is used to characterize our samples: while we observe a continuous transition of the PL maximum with S: Se ratio, the vibrational modes behave in a more complicated, 2-mode fashion. Depending on growth conditions, compositional homogeneous and heterogeneous films can be prepared.

We present details of our growth processes and show to which extend patterns on the substrates can affect the resultant structures. The patterns range from simple hole and pillar arrays to complex waveguide structures. We find that holes to an underlying reducing substrate (silicon) are effective in seeding growth. In contrast, protrusions on the substrate have little effect, so that complex devices can be overgrown.

Ref: Mann et al., 2-Dimensional Transition Metal Dichalcogenides with Tunable Direct Band Gaps:  $\text{MoS}_{2(1-x)}\text{Se}_{2x}$  Monolayers, *Advanced Materials* 26, 1399 (2014)

11:20am **2D+EM+NS+SS+TF-WeM11 Synthesis, Characterization and Radiation Response of Boro-Carbon-Oxy-Nitride: A Heterogeneous 2D Material.** *GaneshRahul Bhimanapati, M. Wetherington, M. Kelly, J.A. Robinson*, The Pennsylvania State University

Since graphene, there have been many other two-dimensional materials systems (e.g., boron nitride (hBN), borocarbon nitride (BCN), transition-metal dichalcogenides) that provide an even wider array of unique chemistries and properties to explore future applications. In fact, these other 2D materials, are sometimes far better suited for many optoelectronic and mechanical applications. Specifically, tailoring graphene/boron nitride heterostructures, which retain the character of single-atom thick sheets that can withstand large physical strains, are easily functionalized, and have entirely different optical and mechanical properties compared to graphene can provide the foundation for entirely new research avenues. In recent years, it has been shown that because of the similar crystal structure, carbon, boron, and nitrogen can coexist as atomic sheets in a layered structure. Thus, combining these materials to form a new heterogeneous material system known as boro-carbon-oxy-nitride (BCON) for potential nano-mechanical and electronic applications and to study its fundamental property relations is necessary. Here, we present the fundamental property relations of BCON and its structural response to various radiation sources such as alpha, beta and gamma particles thereby providing a means for potential radiation sensing applications.

We have developed a facile method of integrating boron nitride and graphene oxide (GO) via chemical exfoliation. Chemical exfoliation of graphene oxide and boron nitride powders is accomplished via oxidation in strong acids, as we find previous methods of sonication in polar solvents does not yield stable solutions of hBN. Upon exfoliation, GO and hBN are mixed, and the resulting BCON material can be suspended in DI water, with suspension stability depending on the pH of the GO. The study of the stability of this material at different pH conditions indicates a stable and a uniform solution is achievable at pH 4-7. Fourier transform infrared spectroscopy (FTIR) indicates the B-N-B bending in the BCON is decreased as an effect of parent GO. Further, radiation response of this material to various radiation sources such as alpha, beta and gamma radiation are studied using In-Situ X-Ray Photoelectron Spectroscopy (XPS). The structural changes of carbon 1s peak in the BCON even for very low doses of radiation energy indicate potential applications in radiation sensing.

11:40am **2D+EM+NS+SS+TF-WeM12 The Structure of 2D Glass.** *Christin Büchner*, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany, *L. Lichtenstein*, Lawrence Berkeley National Laboratory, *M. Heyde, H.-J. Freund*, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany **INVITED**

For the first time, the structure of an amorphous network is imaged in real space.[1] Through a thin film approach, silica is made accessible for investigation with scanning tunneling microscopy (STM) and atomic force microscopy (AFM). Physical vapor deposition with subsequent annealing is employed to create an atomically flat bilayer of  $\text{SiO}_2$ , supported on a Ru(0001) single crystal. Atomic positions of oxygen and silicon can be visualized, as well as ring structures with their distributions and local neighborhoods. All atomic species on the surface can be directly assigned with chemical sensitivity imaging.[2] This allows for statistical analysis of the building units, comparing amorphous to crystalline regions, as well as experiment to theory. Pair correlation functions of the 2D film structure are

set against diffraction data of bulk silica, revealing very similar bond distributions.

Coexisting crystalline and amorphous areas allow imaging of a topological transition region.[3] The understanding of glassy structures gained from these experiments is the starting point for more in-depth structural investigations[4], but also for investigating thin films with modified composition. Al-doping or Fe-doping can be employed to create 2D-Aluminosilicates or 2D-Clays, respectively.[5] Adsorption properties of the film can be probed using single metal atoms which migrate through the film, exhibiting ring-size-selectivity.[6]

[1] L. Lichtenstein, et al., *Angew. Chem., Int. Ed.* 51, 404 (2012)

[2] L. Lichtenstein, et al., *J. Phys. Chem. C* 116, 20426 (2012)

[3] L. Lichtenstein, et al., *Phys. Rev. Lett.* 109, 106101 (2012)

[4] C. Büchner, et al., *Z. Phys. Chem.*, DOI: 10.1515/zpch-2014-0438 (2014)

[5] J. A. Boscoboinik, et al., *Angew. Chem. Int. Ed.* 51, 6005 (2012)

[6] W. E. Kaden, et al., *Phys. Rev. B* 89, 115436 (2014)

# Authors Index

**Bold page numbers indicate the presenter**

## — A —

Altman, E.I.: 2D+EM+NS+SS+TF-WeM4, **1**  
Azcatl, A.: 2D+EM+NS+SS+TF-WeM6, **1**

## — B —

Barroso, D.: 2D+EM+NS+SS+TF-WeM10, **2**  
Bartels, L.: 2D+EM+NS+SS+TF-WeM10, **2**  
Bhimanapati, G.R.: 2D+EM+NS+SS+TF-WeM11, **2**

Bobek, S.: 2D+EM+NS+SS+TF-WeM10, **2**  
Brown, K.: 2D+EM+NS+SS+TF-WeM10, **2**  
Büchner, C.: 2D+EM+NS+SS+TF-WeM12, **2**

## — E —

Eichfeld, S.M.: 2D+EM+NS+SS+TF-WeM6, **1**  
Empante, T.: 2D+EM+NS+SS+TF-WeM10, **2**

## — F —

Fisher, B.L.: 2D+EM+NS+SS+TF-WeM3, **1**  
Freund, H.-J.: 2D+EM+NS+SS+TF-WeM12, **2**

## — G —

Gonzales, J.M.: 2D+EM+NS+SS+TF-WeM5, **1**  
Götzen, J.: 2D+EM+NS+SS+TF-WeM4, **1**  
Guisinger, N.P.: 2D+EM+NS+SS+TF-WeM3, **1**

## — H —

Hersam, M.C.: 2D+EM+NS+SS+TF-WeM3, **1**  
Heyde, M.: 2D+EM+NS+SS+TF-WeM12, **2**  
Hossain, L.: 2D+EM+NS+SS+TF-WeM6, **1**

## — K —

Kelly, M.: 2D+EM+NS+SS+TF-WeM11, **2**  
Király, B.T.: 2D+EM+NS+SS+TF-WeM3, **1**  
Klee, V.: 2D+EM+NS+SS+TF-WeM10, **2**

## — L —

Le Lay, G.: 2D+EM+NS+SS+TF-WeM1, **1**  
Lichtenstein, L.: 2D+EM+NS+SS+TF-WeM12, **2**  
Lin, Y.C.: 2D+EM+NS+SS+TF-WeM6, **1**  
Lu, I.: 2D+EM+NS+SS+TF-WeM10, **2**

## — M —

Mann, J.: 2D+EM+NS+SS+TF-WeM10, **2**  
Mannix, A.J.: 2D+EM+NS+SS+TF-WeM3, **1**  
McDonnell, S.: 2D+EM+NS+SS+TF-WeM6, **1**

## — N —

Naghibi, S.: 2D+EM+NS+SS+TF-WeM10, **2**  
Nguyen, A.: 2D+EM+NS+SS+TF-WeM10, **2**

## — O —

Oleynik, I.I.: 2D+EM+NS+SS+TF-WeM5, **1**

## — P —

Piasecki, A.: 2D+EM+NS+SS+TF-WeM6, **1**  
Preciado, E.: 2D+EM+NS+SS+TF-WeM10, **2**

## — R —

Robinson, J.A.: 2D+EM+NS+SS+TF-WeM11, **2**;  
2D+EM+NS+SS+TF-WeM6, **1**

## — S —

Schlaf, R.: 2D+EM+NS+SS+TF-WeM5, **1**  
Schwarz, U.D.: 2D+EM+NS+SS+TF-WeM4, **1**  
Sonnenfeld, A.: 2D+EM+NS+SS+TF-WeM4, **1**

## — V —

Von Son Palacio, G.: 2D+EM+NS+SS+TF-WeM10, **2**

## — W —

Wallace, R.M.: 2D+EM+NS+SS+TF-WeM6, **1**  
Wetherington, M.: 2D+EM+NS+SS+TF-WeM11, **2**

## — Y —

Yang, K.: 2D+EM+NS+SS+TF-WeM10, **2**

## — Z —

Zhu, X.: 2D+EM+NS+SS+TF-WeM4, **1**