Thin Films
Room Makai - Session TF-TuE

Growth & Characterization of 2D Materials

Moderator: Juan Luis Pena Chapa, CINVESTAV-IPN Unidad Merida, Mexico

5:40pm **TF-TuE1 Characterizing 2D-materials and Hetero-structure of MoS_2 and WSe_2 by Spectroscopic Imaging Ellipsometry**, ***Sebastian Funke,*** Accurion GmbH, Germany*; U. Wurstbauer, E. Parzinger, B. Miller,* Walter Schottky Institute and Physics Department, TU München*; P. Thiesen,* Accurion GmbH, Germany

Characterizing 2D-materials and Hetero-structure of MoS_2 and WSe_2 by Spectroscopic Imaging Ellipsometry

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By stacking different 2D-materials into hetero-structures new optoelectronic devices are formed[1,2]. The advantage of these new hetero-structures compared to conventional devices may be superior material properties and its significant lower height. For the design of efficient hetero-structures the knowledge of the materials properties is essential. We show that spectroscopic imaging ellipsometry (SIE) is capable of measuring the optical properties of different types of 2D-materials. With the lateral resolution down to 1 µm SIE is able to localize and characterize small flakes of e.g. 2D-materials. It also enables the characterization of stacked materials.

In the talk we present spectral investigations on Molybdenum-disulphide from the UV- to NIR. To describe the dispersion for MoS_2 an anisotropic approach is shown[3]. It reveals an anisotropic behaviour in the out-of-plane direction. Further, investigations on a hetero-structure of MoS_2 and WSe_2 are done as seen in Figure 1. All regions can be measured simultaneously, so a comparison of the spectral response of the single 2D-materials can be compared to the stacked response. Spectral investigations around the bandgap of MoS_2 at around 650 nm will be shown and discussed for the overlapping and non-overlapping regions.

Figure 1: Heterostructure of MoS_2 and WSe_2. Green area denotes the overlapping hetero-structure.

References

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6:20pm **TF-TuE3 2D vs. 1D Structures at Stepped Si Surfaces and in Organic Molecules**, ***Franz Himpsel,*** University of Wisconsin Madison, USA*; J.M. García Lastra,* Technical University of Denmark, Denmark*; A. Rubio,* Universidad del Pais Vasco*; I. Boukahil,* University of Wisconsin Madison, USA*; R. Qiao,* Advanced Light Source, LBNL, USA*; S.C. Erwin,* Naval Research Laboratory, USA*; I. Barke,* University of Rostock, Germany **INVITED**

The dimensionality of a structure plays an important role in its electronic properties, as demonstrated recently by a variety of layered compounds who behave very differently as single layer. This raises the question what happens when reducing the dimensionality further to one-dimensional atomic chains - the finest conceivable nanowires. Theory predicts exotic behavior, such as the elusive Luttinger liquid. Strong correlations are established between electrons propagating along an atomic chain, since they are not able to avoid each other. One might also expect reduced dielectric screening and higher chemical activity in 1D structures due to the reduced number of neighbors.

This talk focuses on two types of atomically-precise structures that bridge the gap between 2D and 1D. Both their preparation and their electronic structure are considered. Stepped surfaces can be prepared on vicinal Si with great precision (less than one kink in 10^4 edge atoms), since the high energy cost of a broken Si-Si bond leads to stable surface reconstructions. These can be decorated with a wide variety of metal atoms, frequently leading to metallic wires on a semiconducting substrate. The transition from 2D to 1D is explored by varying the step spacing. A variety of interesting phases have been found in these wires, such as charge density waves [1], spin-polarized energy bands, and an ordered array of spin-polarized Si edge atoms [2].

The other approach uses organic molecules to compare π-bonded carbon sheets and chains [3]. First-principles calculations show that 1D wires exhibit very simple molecular orbitals which mimic the overtones of a vibrating string, while 2D structures form more complex orbital patterns related to the modes of a drum. The dielectric screening is found to scale with the number of atoms in a molecule rather than the number of neighbor atoms, suggesting delocalized screening.

Looking into the future, we discuss molecular complexes combining 2D and 1D structures with atomic precision, such as the donor-π-acceptor complexes used in dye-sensitized solar cells [4]. Computational screening of the energy levels for thousands of dye molecules provides the blueprint for tandem solar cells where two π-absorbers are connected by molecular wires [5].

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7:00pm **TF-TuE5 Probing Atomic Structure of 2D TMDs by High Resolution STEM**, ***Moon Kim,*** *Q. Wang, J. Wang,* The University of Texas at Dallas, USA

As the scaling of various functional devices continues, the future of these devices will rely on new class of materials. Research in graphene and the methodology of preparing ultrathin layers has led to the exploration of other 2D materials. In particular, single layers of transition metal dichalcogenides (TMDs) with lamellar structures similar to those of graphite have drawn significant attention because of their tunable bandgaps. TMDs exhibit diverse properties that depend on their composition: semiconductors, semimetals, metals, or superconductors. TMD properties also strongly depend on the crystalline structure, including the number and stacking sequence of layers. In exploring and developing these emerging materials, nanoscale characterization becomes ever more important. In particular, high resolution electron microscopy-based techniques now are capable of analyzing these 2D nano-materials and devices with better than 0.1 nm resolution. Here, we present our recent studies on the characterization of 2D layered materials by means of Scanning Transmission Electron Microscopy (STEM), specifically High Angle Annular Dark Field (HAADF) imaging and *in-situ* Transmission Electron Microscopy (TEM). We have identified the atomic arrangements and defects in single layer MoS_2, 2H stacked TMDs, 1T stacked TMDs, and distorted 1T stacked TMDs by HAADF STEM imaging . The location and nature of individual atoms, defects, phase transformation, and layer by layer shearing of 2D crystals will be presented and discussed in detail.

7:40pm **TF-TuE7 Synthesis of Transitional Dichalcogenide Films by Chemical Transformations of Thin Films**, ***Shaul Aloni,*** Lawrence Berkeley National Laboratory, , USA*; C.T. Chen, T.R. Kuykendall,* Lawrence Berkeley National Laboratory, USA*; C. Kastl,* Lawrence Berkeley National Laboratory, USA*; T.P. Darlington, P.J. Schuck, N.J. Borys,* Lawrence Berkeley National Laboratory, USA*; A.M. Schwartzberg,* Lawrence Berkeley Lab, USA

The promising properties of transition metal chalcogenides (TMD's) continue to inspire great deal of research on optical and electronic devices. However, the progress in this field is limited by challenges in materials synthesis and device fabrication. In this work we present a new approach for the synthesis of TMD's with digital control of layer thickness. This method utilises chemical transformation of solid thin films of oxides deposited with submonolayer precision by ALD. Following their deposition the films are exposed to a chalcogen containing gas resulting in smooth and continuous TMD films whose thickness is defined by the thickness of the ALD deposited oxide film.

Typical experiments involve deposition of metal oxide, WO3 or MoO3, followed by a short conversion procedure involving annealing of the oxide film in presence of a chalcogenation agent, *e.g.* hydrogen disulfide gas or organochalcogen vapor. Typical composition of the gas phase is equivalent to 1% of H2S in argon. However, precise control of water content in the gas phase composition provides means for controlling the reaction mechanism. At low water vapor content (2-10 ppm) metal oxide films are chalcogenized in place with the thickness of the continuous TMD film defined by the thickness of the oxide layer. The resulting WS2 thin films are nanocrystalline, and moderately luminescent . At higher water concentrations (> 200 ppm) the process is dominated by vapor transport. Under these conditions, the volatility of the oxide species is significantly enhanced, resulting in minimal residual metal disulfide after growth. Under optimized conditions, highly luminescent, triangular monolayer WS2 and MoS2 islands with good island-to-island uniformity can be grown directly on the previously metal-oxide-coated substrate or onto a bare substrate placed downstream of a source. Carefully controlled humidity (~ 100 ppm) consistently produces high quality highly luminescent triangular WS2 and MoS2 islands.

The chemical transformation of solid films by a gas phase precursors offers additional benefits. In addition to precise control of thickness and compatibility with many transition metals, it is also compatible with any substrate that is not adversely affected by the chalcogenation agent. We present deposition of WS2 on variety of substrates including amorphous SiO2 and Si3N4 as well as SiC, TiO2 and GaN. Moreover, we suggest that the use of controlled amounts of water vapor is a new knob by which to tune growth of these materials, and these results demonstrate a route to improved material quality and unprecedented reproducibility of chemical vapor transport of many transition metal dichalcogenides.

8:00pm **TF-TuE8 Growth and Characterization of hBN/Graphene Heterostructures on Metal Substrates***, **Boris Feigelson**,* U.S. Naval Research Laboratory, USA*; K. Sridhara,* Texas A & M, USA*; J.K. Hite,* U.S. Naval Research Laboratory, USA*; A. Nath,* George Mason University*; J.A. Wollmershauser,* U.S. Naval Research Laboratory, USA

The development of 2D hBN/graphene heterostructures is still in the early stages and largely depends on possibility to grow these heterostructures as well as on rapid and accurate characterization of the grown hBN/graphene layers. Along with graphene, atomically thin two dimensional hexagonal boron nitride (2D hBN) is one of the key materials in the development of new van der Waals heterostructures due to its outstanding properties including an atomically smooth surface, high thermal conductivity, high mechanical strength, chemical inertness and high electrical resistance.

In this work, hBN/graphene films were grown by atmospheric-pressure CVD on metal substrates (mainly Cu, but also Cu-Ni alloys). A vertical custom-made CVD reactor was used to grow 2D hBN/graphene films. The design of the vertical reactor allows the simultaneous growth of a few samples of hBN/graphene layers on different substrates in the same run.

As it was shown in our previous work [1], Fourier transform grazing-incidence infrared reflection absorption spectroscopy (FT-IRRAS) can be used to characterize monolayer and few-layer h-BN films directly on metal substrates. Two sub-bands of the A_{2u}(LO) vibrational mode were found for thin 2D h-BN films in contact with Cu and Ni. The lower-energy A_{2u}(LO)1 sub-band around 819 cm^{-1} is related to 2D h-BN coupled with Cu substrate, while the higher energy A_{2u}(LO)2 sub-band around 824 cm^{-1} is related to decoupled (essentially free standing) 2D h-BN.

The IR-active out-of-plane vibrational mode was exploited to identify and characterize 2D hBN in grown heterostructures directly on metal substrates, while graphene was characterized by micro Raman spectroscopy. Combining FTIR and Raman spectroscopy allows express and in-depth characterization of hBN/graphene heterostructures directly on metal substrates used for growth.

The approach also provides an opportunity to determine which growth conditions lead to the absorption of foreign species on the substrate prior to the heterostructure deposition. Such interfacial layers were shown to result in easily-recognizable shifts in the A_{2u}(LO) peak. The degree to which the interaction of the hBN layer with the substrate is uniform and homogenous can also be assessed easily by examining the width and fine structure of the A_{2u}(LO) band.

B. N. Feigelson, V. M. Bermudez, J. K. Hite, Z. R. Robinson, V. D. Wheeler, K. Sridhara, and S. C. Hernandez, Nanoscale **7,** 3694 (2015)

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