

Tuesday Afternoon, October 30, 2012

Nanometer-scale Science and Technology

Room: 12 - Session NS+EN+GR-TuA

Nanomaterials in Two and Three Dimensions

Moderator: V.P. LaBella, University at Albany-SUNY

2:20pm **NS+EN+GR-TuA2 Nanopatterning of SPRi Sensor Surfaces for Sub-Nanomolar Biomarker Detection**, M.A. Parracino, M.J. Perez Roldan, J. Hanus, V. Spampinato, G. Ceccone, P. Colpo, F. Rossi, Nanobiosciences Unit, JRC, Italy

In this work we report the detection of low-molecular weight biomarkers on two kinds of nanostructured surfaces by using a SPRi sensor. Nanopatterned surfaces are fabricated by combining functionalization and patterning techniques. Two different methods were used for the surface nanopatterning: electro-beam lithography (EBL) and colloidal lithography (CL). Maltose binding protein (MBP) and transthyretin (TTR) are respectively immobilized on the two types of nanopatterns and used as biological recognition elements. Chemical contrast adhesive/non adhesive at nanoscale has been created in order to control protein binding at nanoscale. Plasma deposited (PEO)-like film was used as passivation layer to prevent non-specific binding of protein in between the protein adhesives nano-areas. All the fabrication steps of both surfaces have been carefully controlled and analyzed using several techniques such as AFM, XPS, and SEM. The gold nanostructures were 185 nm width lines, for the patterned created with EBL, and holes of 250 nm in diameters for the pattern fabricated using CL. The gold grating surface made using EBL was functionalized with sugar via a thiol-linker. Maltose Binding Protein (MBP) was bound on sugar modified surface in order to develop a competitive assay for maltose detection. In this competitive assay, the protein binding on the sugar functionalized surface depends on the concentration of his free competitor in solution: by measuring the protein binding, it is possible to evaluate the concentration of the small molecule in solution. In the second methods, NTA functionalized nanoholes in PEO like background were fabricated and subsequently activated with nickel (Ni II) for a selective immobilization of histidines tagged TTR, which underlies to a direct detection of Thyroxine 4 (T4). In both case, the biological intermediates, MBP and TTR, are selectively immobilized onto nanopatterned surfaces. The ligand protein binding on the nanostructure is higher than on the flat surface. The better ligand orientation and immobilization on the nanostructures results in analyte detection at sub-nanomolar concentration. The combination of nanopatterning features with the two different methods of detection presented in this work provides a description for a more generalized approach for the development of stable and reliable biosensor platforms for the detection of different small molecules having an high impact in environmental, and biomedical field.

4:00pm **NS+EN+GR-TuA7 Single Layer of MoS₂ on Close-Packed Metal Surfaces**, D. Le, T.S. Rahman, University of Central Florida

We present results of first principles electronic structure calculations, using van der Waals density functional theory, of the adsorption of a single layer of Molybdenum disulfide (MoS₂) on several close-packed metal surfaces. On Cu(111) we find three energetically equivalent stacking types and a Moiré pattern whose periodicity is in agreement with experimental findings [1]. The layer is found not to be purely physisorbed on the surface, rather there exists a chemical interaction between it and the Cu surface atoms. We also find that the MoS₂ film is not appreciably buckled, while the top Cu layer gets reorganized and vertically disordered. The sizes of Moiré patterns for a single layer of MoS₂ adsorbed on other close-packed metal surfaces are also estimated by minimizing the lattice mismatch between the film and the substrate. The Moiré patterns on Ir(111), Pt(111), and Ru(0001) are particularly interesting as the MoS₂ layer is found to bind more strongly on them than on Cu(111). We compare the nature of the bond in these three substrates with that on Cu(111).

[1] D. Kim, D. Sun, W. Lu, Z. Cheng, Y. Zhu, D. Le, T. S. Rahman, and L. Bartels, *Langmuir* **27**, 11650 (2011).

* This work was supported in part by the U.S. Department of Energy under Grant No. DE-FG02-07ER15842.

4:20pm **NS+EN+GR-TuA8 Chemically Exfoliated Two Dimensional Materials for Energy Applications**, M. Chhowalla, Rutgers University
INVITED

Chemical exfoliation of layered two-dimensional materials such as graphite and transition metal chalcogenides allow access to large quantities of atomically thin nanosheets that have properties that are distinctly different from their bulk counterparts. Although 2D materials have recently become

popular, their fabrication via exfoliation of bulk crystals has been known for decades. For example, Brodie first exfoliated graphite into atomically thin oxidized form of graphene in 1859. In the case of layered transition metal dichalcogenides (LTMDs) such as MoS₂, WS₂, MoSe₂, WSe₂, etc., Frindt et al. performed seminal work in the '70s and '80s. We have revived these techniques to obtain a wide variety of chemically exfoliated two-dimensional nanosheets and utilized these materials in wide variety of electronic and energy applications. In this presentation, I will highlight some of our key contributions with graphene oxide (GO) and LTMD nanosheets. Specifically, I will present their implementation into large area electronics, strategic implementation into solar cells, and as catalyst for hydrogen evolution.

5:00pm **NS+EN+GR-TuA10 Isolation and Surface Structure of Ultrathin Nanosheets formed by Atomic Layer Deposition**, K.M. Lee, D.H. Kim, G.N. Parsons, North Carolina State University

Ultrathin nanosheets are two-dimensional structures that are often exfoliated from layered compounds. The nanosheets are flat with large surface area (100's of nm²) but with very small thickness in several nm scale. A common example of a nanosheet is graphene which is exfoliated from graphite. Other nanosheet materials that are chemically exfoliated from layered crystals include MoS₂, VS₂, and many oxide materials such as MnO₂, TiNbO₅, or LaNb₂O₇. These materials show unique capabilities for nanoelectronic devices, photocatalysts, and electrochemical sensor applications. For our work, we explore atomic layer deposition (ALD) as an effective technique to fabricate metal oxide nanosheets with precisely controlling thickness and chemical composition. To form nanosheets, we spin-coated a substrate with polymer such as polymethylmethacrylate (PMMA), polyvinyl alcohol (PVA), or polyacrylic acid (PAA) as a sacrificial layer, then deposited TiO₂, Al₂O₃ or ZnO on polymer layer by ALD. Dissolving the polymer in solvent releases nanosheets from the substrate. We successfully attained two dimensional TiO₂ nanosheets with several hundred μm in lateral size and less than 10 nm in thickness. Attaining nanosheets with thickness near 1nm proved to be rather challenging. For Al₂O₃ and TiO₂, nanosheets with thickness of ~1 nm can be isolated by two-immiscible liquid separation process. For ZnO, the thinnest nanosheet obtained to date is closer to 15 nm. We characterized nanosheets using AFM to confirm their thickness and found that the surface structure and roughness depends on the materials and thickness. We also examined the functionality of TiO₂ nanosheets as an agent for photocatalytic degradation of organic dyes. This work demonstrates and defines the capabilities and limits for functional nanosheets fabrication by atomic layer deposition.

5:20pm **NS+EN+GR-TuA11 All Solution Processed InGaO₃(ZnO)_m Thin Films with Layered Structure and their Thermoelectric Properties**, J.H. Kim, H.K. Cho, Sungkyunkwan University, Republic of Korea

As the materials currently in use have been reached terminal and showed low productivity in a few field, the development of advanced materials are demanded. In the middle of atmosphere, low-dimensional nanostructures have been introduced in recent studies such as 1-D nanowire and 2-D superlattice. Among them, a multi-layered structure shows unique properties originating from the confinement of carriers in the two-dimensional layer. For example, LaFeO₃-LaCrO₃ superlattice structures fabricated by pulsed layer deposition (PLD) have shown enhanced ferromagnetism [1] and InGaO₃(ZnO)_m superlattice structure grown by sputtering method has improved thermoelectric properties [2].

These homologous series of RAO₃(MO)_m (R=In or rare earth elements; A=Ga, In, Al, or Fe; M=Mg, Co, Cu, or Zn; m=integer) comprise alternating stacks of RO₂⁻ and AO⁺(MO)_m layers and are candidate to exhibit the quantum effect due to its natural superlattice [3]. Despite these materials being widely investigated, the fabrication of RAO₃(MO)_m thin film with layered structure is limit due to their fabrication which requires expensive high-vacuum equipment and shows low productivity.

In this study, all solution process (an epitaxial ZnO buffer layer growth on sapphire substrate, amorphous IGZO layer on ZnO buffer layer by composition controlled solution process, and post-annealing at 900°C for 9hours) enables us to fabricate InGaO₃(ZnO)_m thin film with periodic superlattice structure. Crystallinity of thin film was analyzed by X-ray diffraction and TEM results. And also, TE properties such as Seebeck coefficient, electrical conductivity, thermal conductivity were evaluated to identify the degree of crystallization of superlattice with layered structure.

Reference

[1] K. Ueda, H. Tabata and T. Kawai, *Science*, 1998, **280**, 1064

[2] D. K. Seo, B. H. Kong and H. K. Cho, *Cryst. Growth Des.*, 2010, **10**, 4638

[3] J. L. F. Da Silva, Y. F. Yan and S. H. Wei, *Physical Review Letters*, 2008, **100**, 255501.

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