

Monday Morning, November 9, 2009

Biomaterial Interfaces

Room: K - Session BI+NS-MoM

Nanoparticles and Self Assembly

Moderator: A. Chilkoti, Duke University, V. Perez-Luna, Illinois Institute of Technology

8:20am **BI+NS-MoM1 Self-assembling and Biofunctionalization of Plasmonic Gallium and Gold Nanoparticles on Semiconductors for Label Free Bio- and Chemo-sensing.** *M. Losurdo*, IMIP-CNR, Italy, *P.C. Wu*, Duke University, *G.V. Bianco*, *M. Giangregorio*, IMIP-CNR, Italy, *T.H. Kim*, Duke University, *G. Bruno*, IMIP-CNR, Italy, *A.S. Brown*, Duke University

Biorganic functionalization of gold thin films and nanocluster mesoscale assemblies and their resulting optical properties have immense applications ranging from biosensing to nanomedicine. The appealing property is the surface plasmon resonance of those bio-metal ensembles that can be tailored not only by the metal nanoparticles geometry but also by the nature of the biomolecules and the chemistry of the interface. This characteristic is being exploited for realizing nanoscale optical chemosensors and biosensors based on localized surface plasmon resonance of metal nanoparticles.

In this contribution we present and discuss bio- and chemo-functionalization of a novel system based on plasmonic gallium (Ga) nanoparticles (NPs) self-assembled on a large variety of semiconductor substrates including Si, SiC, GaN and GaAs. The advantages of this system for a plasmonic metal/semiconductor sensing platform are presented and compared to the standard gold (Au) nanoparticles system.

The Ga and Au NPs are directly deposited on semiconductors by evaporation and/or plasma sputtering.

For both systems Ga (NPs)/semiconductor and Au(NPs)/semiconductor we discuss semiconductor surface treatments affecting the interface chemistry and the dynamics of interface phenomena playing a role in tailoring the surface plasmon resonance.

Those systems have also been functionalized by bio-molecules, e.g., antigens and antibodies for biosensing and by porphyrins for gas sensing to nitric oxide (NO).

The peculiarity of our study is the exploitation of Plasmonic spectroscopic ellipsometry (HORIBA UVISEL, Jobin Yvon) for the optical monitoring of the plasmon resonance tuning in real time during the nanoparticles deposition on semiconductor surfaces and for the functionalization of metal nanoparticles by anchoring biomolecules to the semiconductor nanostructures.

For these plasmon-enhanced semiconductor nanoscale sensors, the degree of coverage by the porphyrin and/or protein, the aggregation, the type of binding and orientation of biomolecules on a semiconductor nanostructures surface is important for the sensing activity. Therefore, plasmonic ellipsometry is used to investigate the interplay among the nanostructures size and shape, the functionalizing solution concentration and dipping time, the mechanism of anchoring of the functionalizing molecules.

Data are corroborated by atomic force and electrical force microscopies.

This work is supported by the 7FP European Project NanoCharM_Multifunctional NanoMaterial Characterization exploiting ellipsometry and polarimetry

8:40am **BI+NS-MoM2 Geometry and Interactions: How Shape and Intermolecular Interactions Direct the Self-Assembly of Cage Molecules on Au{111}**, *J.N. Hohman*, *M. Kim*, *P. Zhang*, *E.I. Morin*, The Pennsylvania State University, *V.E. Balema*, The Sigma Aldrich Corporation, *P.S. Weiss*, The Pennsylvania State University

The self-assembly of cage molecules on metal surfaces enables the manipulation of interface chemistry while eliminating an entire class of defect modes commonly associated with straight-chain molecules such as the n-alkanethiols. The adamantanethiols and carboranethiols have similar geometries and unit cells on Au{111}, but exhibit striking differences in their behavior. We attribute these differences to their contrasting electronic structures and consequent intermolecular interactions. We have characterized the SAMs of positional isomers of several carboranethiols and adamantanethiols by scanning tunneling microscopy, cyclic voltammetry, grazing-incidence Fourier transform infrared spectroscopy, Kelvin probe microscopy, and contact-angle goniometry. We discuss how geometry and intermolecular interactions play competing roles in determining monolayer assembly and stability.

9:00am **BI+NS-MoM3 On the Role of Supramolecular Nanostructure in determining Interfacial Energy and Biological Interactions.** *F. Stellacci*, Massachusetts Institute of Technology **INVITED**

It is known that specific molecules can spontaneously arrange on various surfaces forming two-dimensional poly-crystalline mono-molecular layers called self-assembled monolayers (SAMs). These organic coatings are used to impart targeted optical, electronic and biological properties to surfaces. Very often SAMs composed of more than one type of molecule (mixed-SAMs) are used to simultaneously impart multiple properties. Scanning tunneling microscopy (STM) studies have shown that, in mixed SAMs, molecules phase-separate in domains of random shape and size.

We will show that when mixed SAMs are formed on surfaces with a radius of curvature smaller than 20 nm they spontaneously phase-separate in highly ordered phases of unprecedented size. The reason for this supramolecular phenomenon is purely topological and can be rationalized through the "hairy ball theorem". In the specific case of mixed SAMs formed on the surface of gold nanoparticles, the molecular ligands separate into 5 Å wide phases of alternating composition that encircle or spiral around the particle metallic core. This new family of nano-structured nanomaterials shows new properties solely due to this novel and unique morphology. For example, we will show that the cell uptake of these particles strongly depends on the particle's composition and the ligand shell morphology.

9:40am **BI+NS-MoM5 Can We Make Alkanethiol SAM's on Surface of Gold Nanorods?**, *S. Chakraborty*, *S. Lee*, *V. Perez-Luna*, Illinois Institute of Technology

Gold has been a fascinating element that drew the interest of people since early origins of human history. However, it is just over the last two decades that it gained a resurgence of interest, in conjunction with the advent and development of nanotechnology. Gold nanoparticles have a wide variety of bio-applications such as labeling, sensing, and targeted drug delivery. A directed assembly of gold nanoparticles in the form of nanowires or networks is extensively used as nanodevices. Nanoparticles come in a variety of shapes; spheres, rods and cubes being the frequently observed ones. Surface functionalization facilitates tailoring of the gold surface for various applications. The objective here is to investigate the surface modification of gold nanorods by chemisorption of alkanethiols.

An important property of gold nanorods is their *aspect ratio*, which is defined as the width-height ratio. The lateral surface and edge surface mostly comprise of [100] and [111] surfaces respectively. By appropriate choice of capping agents, the anisotropic surfaces can be tailored for different applications. One of the most-successful methods for synthesis of gold nanorods relies on the use of cationic surfactant Cetyltrimethyl Ammonium Bromide (CTAB). CTAB provides stability, size and shape control. The displacement of CTAB allows functionalization with other molecules. In this work, the displacement of CTAB is carried out with alkanethiols of varying chain length, viz. 16-mercaptohexadecanoic acid, 11-mercaptoundecanoic acid, 3-mercapto propionic acid. An indirect investigation method is used to analyze the behavior of gold nanorods. Planar surfaces with the same crystalline structures as gold nanorods (111 and 110) are selected for the experiment. Surface modification of planar surfaces is conducted in two steps: formation of CTAB bilayers by immersing planar substrates followed by displacement of CTAB bilayers with alkanethiols.

The experimental studies are characterized by contact angle measurements, Fourier transform infrared spectroscopy and cyclic voltammetry. The displacement of CTAB is confirmed by decrease in the contact angle upon formation of carboxyl terminated surfaces and concomitant appearance of stretching band of carboxyl groups. Cyclic voltammetry studies are carried out to calculate the free energy of adsorption of the alkanethiol layers on gold surfaces. Results indicate that longer chain alkanethiols perform better in terms of displacing the CTAB layer from the gold surfaces. The displacement of CTAB is possible on both the lateral and edge surfaces.

10:00am **BI+NS-MoM6 Size-selective Placement of Nanoparticles on a Single Particle Level**, *P. Bhadrachalam*, *S.J. Koh*, University of Texas at Arlington

We present a new nanoparticle placement technique in which single nanoparticles of different sizes recognize different target positions on a substrate and exactly one nanoparticle of specific size is placed on each target position in a self-limiting way. We demonstrate this by using ~50nm and ~20nm colloidal Au nanoparticles (AuNPs) as a model system, where the ~50nm particles are first electrostatically guided onto targeted substrate locations and then the ~20nm particles to different target locations on the

same substrate. The electrostatic guiding structure was defined using CMOS-compatible fabrication processes and subsequent functionalization of surfaces using self-assembled monolayers (SAMs) of organic molecules. Using appropriate guiding structure, we present >90% success rate of ~50nm AuNPs placement onto substrate locations targeted for ~50nm AuNPs only. Theoretical calculations for ~20nm AuNPs, which was carried out by solving the non-linear Poisson-Boltzmann equation, revealed that the self-limiting single-particle placement is due to an increase of the free energy barrier after the placement of one nanoparticle onto a targeted substrate location, which prevents the approach of other nanoparticles to the already occupied position. The size-selective placement of single nanoparticles can be explained by dependence of the free energy barrier changes upon the sizes of nanoparticles and guiding structures. The same approach may also be useful for size-selective and single-entity-level placement of other nanoscale building blocks such as nanowires, proteins, and DNA. (Supported by NSF CAREER (ECS-0449958), ONR (N00014-05-1-0030), and THECB (003656-0014-2006))

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