Thursday Morning, November 3, 2011

Electronic Materials and Processing Division
Room: 210 - Session EM+TF-ThM

Hybrid Electronic Materials and Interfaces
Moderator: A.J. Muscat, University of Arizona

8:00am EM+TF-ThM1 Chemical Modification of Surfaces for Biological Applications, *W.G. McGimpsey*, Kent State University **INVITED**
The chemical and physical characteristics of surfaces can have profound and useful effects on the behavior of biological systems. We describe here several methods for modifying the surfaces of a variety of biocompatible materials, including metals, glass and polymers, in order to produce desired chemical and physical properties. The effects of surface chemistry and surface morphology on the growth and proliferation of mammalian cells as well as bacteria are also reported. Applications investigated include control of the growth of microbial biofilms, the growth of three-dimensional tissue assemblies, the patterned growth of neurons and other cell types and the functionality of primary neurons deposited on surfaces.

8:40am EM+TF-ThM3 Modification of Oxide-Free Silicon Surfaces with Phosphonic Acid Self-Assembled Monolayers, *P. Thissen*, T. Peixoto, A. Vega, Y.J. Chabal, University of Texas at Dallas
Phosphonic acid self-assembled monolayers (SAMs) are being considered as versatile surface modification agents due to their ability to attach to surfaces in different configurations, including mono-, bi- or even tri-dentate arrangements. Different chemical strategies for grafting SAMs on oxide-free silicon have been developed. Recently, a novel method for preparing OH-terminated, on otherwise oxide-free silicon has been reported [1] and further expanded for this work. This atomically flat surface contains precisely 1/3 OH and 2/3 H termination groups.

Using this model surface, we demonstrate that the phosphonic group of organic molecules can be chemically grafted to the OH group on the surface using a single chemical step, leaving the Si-H termination unaffected, without oxidation of the Si surface. We also show that the nature of solvents is important as they can act as a catalyst. The perfection of the surface (that remains atomically flat throughout the modification) makes it possible to use first principles DFT-based calculations to model the IR and XPS data obtained for this surface. Thus, a detailed structure for the SAMs can be derived on an atomic level. It is found that phosphonic acids are chemically attached to the Si(111) surface as mono-dentate via Si-O-P bond upon reaction with the OH groups. The remaining groups of P=O and P-OH are further oriented by forming a 2D network of hydrogen bonds.

[1] D. J. Michalak, S. R. Amy, D. Aureau, M. Dai, A. Esteve and Y. J. Chabal, Nanopatterning Si(111) surfaces as a selective surface-chemistry route, NATURE MATERIALS, Vol. 9, March 2010

9:00am EM+TF-ThM4 Competing Effects of Interfacial Organic Layers on the Nucleation of Inorganic Thin Films Deposited Via Atomic Layer Deposition, K.J. Hughes, *J.R. Engstrom*, Cornell University
Over the past several years a number of groups have been investigating the use of interfacial organic layers (IOLs) in the form of self-assembled monolayers (SAMs) and/or surface grown or bound oligomers to promote the subsequent growth of inorganic thin films. Work in our group has initially focused on determining the relative importance of the type, density and dimensionality of the organic functional groups present in IOLs on the subsequent growth of the thin film, particularly via ALD[1]. Here we shall report on two perhaps less well-studied aspects concerning the use of SAMs or IOLs to promote nucleation and growth via ALD: (*i*) the effects of the underlying substrate on the IOL, and its ability to promote growth; and (*ii*) given the same IOL|substrate combination, the effects on ALD for a series of inorganic thin film deposition processes. To examine these systems we have made use of a variety of experimental tools, including a conventional viscous flow ALD tool, and also an ultrahigh vacuum (UHV) molecular beam based ALD process, where we employ *in situ* x-ray photoelectron spectroscopy. Concerning the first of these, we have examined the effect of a thin (< 10 Å) organic layer, poly(ethylene-imine) (PEI) on the ALD growth of TaN$_x$, where the underlying substrate is a chemically oxidized SiO$_2$ thin film, or a porous SiO$_2$ based low-κ dielectric thin film. Here we observe essentially the same result from conventional viscous flow, and molecular beam UHV ALD: PEI acts to attenuate TaN$_x$ ALD on SiO$_2$, while it enhances growth on a low-κ dielectric thin film. From a practical point of view, most importantly, we find that PEI stops infiltration/penetration of the TaN$_x$ ALD thin film into the porous low-κ dielectric. Concerning the second major issue, we have examined the effect of PEI on the subsequent growth via ALD of a series of inorganic thin films, namely: Al$_2$O$_3$, HfO$_2$, Ta$_2$O$_5$, and TaN$_x$. Here PEI has the effect of attenuating growth to different degrees depending on the subsequently grown ALD thin film, leading to no attenuation of growth for Al$_2$O$_3$, but significant incubation periods, in increasing order, for Ta$_2$O$_5$, HfO$_2$ and TaN$_x$. The length of the incubation time is found to correlate with both the total enthalpy change of the overall ALD reaction, as well as the net internal energy change of a single ligand exchange reaction representative of the second half of the ALD reaction, suggesting that these factors associated with the ALD process play a key role in determining the length of the incubation period caused by PEI.

[1] K. J. Hughes and J. R. Engstrom, J. Vac. Sci. Technol. A **28**, 1033-1059 (2010)

9:20am EM+TF-ThM5 Towards Molecular Electronics: Solution-Based Methods for Selective Deposition of Metals and Semiconductors, *Z. Shi, J. Yang, P. Lu, A.V. Walker*, University of Texas at Dallas
Robust methods for the chemically selective deposition of metals, semiconductors, biomolecules and other substances are developed and applied in the construction of complex two- and three-dimensional structures. This work has important applications in molecular and organic electronics, sensing, biotechnology and photonics. These methods are easily parallelized, afford precise nanoscale placement and are compatible with photolithography. Two examples are discussed in detail: the chemical bath deposition (CBD) of CdSe on functionalized self-assembled monolayers (SAMs), and the electroless deposition of Ni nanowires on micron-scale patterned surfaces.

CBD is a solution-based method for the controlled deposition of semiconductors. The formation of CdSe nanocrystals are of particular interest for a wide range of applications because their photoluminescence spans visible wavelengths. Using CdSe chemical bath deposition (CBD) we demonstrate the selective growth and deposition of monodisperse nanoparticles on functionalized self-assembled monolayers (SAMs). On – COOH terminated SAMs strongly adherent CdSe nanoparticles form via a mixed ion-by-ion and cluster-by-cluster mechanism. Initially, Cd^{2+} ions form complexes with the terminal carboxylate groups. The Cd^{2+}-carboxylate complexes then act as the nucleation sites for the ion-by-ion growth of CdSe. After a sufficient concentration of Se^{2-} has formed in solution via the hydrolysis of selenosulfate ions, the deposition mechanism switches to cluster-by-cluster deposition. On –OH and –CH$_3$ terminated SAMs monodisperse CdSe nanoparticles are deposited via cluster-by-cluster deposition and they do not strongly to the surface. Thus under the appropriate experimental conditions CdSe nanoparticles can be selectively deposited onto -COOH terminated SAMs. We illustrate this by selectively depositing CdSe on a patterned -COOH/-CH$_3$ terminated SAM surface.

Our approach for the construction of Ni nanowires begins with a single SAM layer deposited and UV-photopatterned using standard techniques. We exploit the different deposition rates of nickel electroless deposition on –CH$_3$ and –OH terminated SAMs to deposit nanowires. The deposited nanowires are long (centimeters) and uniform in diameter, and can be patterned in arbitrary shapes. SAMs are ideal for the construction of nano- and micro- structures since their surface chemistry can be easily tuned to form the needed structures. Further the micron-scale UV photopatterning of SAMs does not require a clean room or expensive lithography equipment.

9:40am EM+TF-ThM6 Sensing Mechanism for Peroxide and Hydroperoxide Vapors in Phthalocyanine Thin Film Transistors, *J. Royer*, E. Kappe, W. Trogler, A.C. Kummel, University of California San Diego
Organic thin-film transistors (OTFTs) are promising candidates for selective chemical sensors due to numerous chemical and electrical parameters which govern sensor response. Analyte selectivity can be obtained using multiparameter electrical monitoring of a single OTFT which is sensitive to changes in mobility, I$_{on}$/I$_{off}$ ratio, and/or threshold voltage. The present study demonstrates selective hydrogen peroxide and organic peroxide sensors based on irreversible metal-phthalocyanine (MPc) OTFT threshold voltage shifts. The irreversible threshold voltage shift is not evident with non-oxidizing analytes such as di-methyl methylphosphonate (DMMP) and common background analytes such as water vapor. Furthermore, the threshold voltage shift responds linearly to the dose time which permits dosimetric sensing analysis. A proposed mechanism for peroxide sensing is determined using simultaneous monitoring of mobility and threshold voltage. The data reveal reversible mobility and irreversible threshold voltage response. Mobility response time is fast and saturates

quickly whereas threshold voltage response is dosimetric, and irreversible, suggesting an accumulation of uncompensated positive charge in the MPc film. The results are consistent with a dual response adsorption/decomposition mechanism in which the peroxide reversibly decreases mobility through a molecular chemisorption event and irreversibly shifts threshold voltage due to electron transfer from the MPc to peroxide. The electron transfer from the MPc to peroxide dissociates the peroxide to form hydroxyl products and leaves an uncompensated MPc$^+$. This detection method is exclusive for the OTFT platform and permits high selectivity at low peroxide concentrations.

10:40am EM+TF-ThM9 Organic/Oxide Hybrid Thin-Film Applications for Photo-detector Cells and Complementary Inverters, *S.I. Im*, Yonsei University, Republic of Korea **INVITED**
Due to the distinct advantages and functionalities, oxide and organic devices on glass or flexible substrates have extensively been studied in such basic forms as thin-film transistors (TFTs) and light emitting diodes. As a more revolutionary approach to realize advanced thin-film devices using both oxide and organic layers, organic/inorganic hybrid layer techniques were also employed, so that hybrid p-n diodes, image sensors, nonvolatile memory, and complementary inverters have recently been demonstrated. *These hybrid approaches are an interesting and attractive way to extract a unique device performance which may not be possible with organics or with inorganics alone, compensating some weakness of organics with inorganics or vice versa.* The most representative example among the organic/inorganic hybrid devices may be complementary thin-film transistor (CTFT) inverters with an organic p-channel thin-film transistor (TFT) and an oxide n-channel TFT. In particular, a vertically stacked CTFT (VS-CTFT) inverter for logic operation on a glass substrate is very impressive since the vertical stacking of organic p-TFT on oxide n-TFT improves device integration or device area reduction. For the VS-CTFT inverter for logic and photo-gating, we used a thermally-evapotated p-channel pentacene layer, sputter-deposited n-channel GaZnSn-based oxide (GZTO), and atomic layer deposited (ALD) Al$_2$O$_3$ dielectric. Our VS-CTFT inverter nicely displays effective photo- and electrical-gating with a high voltage gain, dynamically operating in the low-voltage regime of 3, 5, and 8 V (the thin pentacene channel receives blue photons). As a more advanced hybrid approach, we have successfully fabricated transparent image pixels that operate at 3 V as composed of pentacene thin-film transistor (TFT) and semitransparent pentacene/ZnO photodiode with a transparent top electrode in the interest of a light detectable smart functional windows. Our transparent pixels was equipped with an additional 6,13-pentacenequinone phosphor layer as deposited on the pentacene/ZnO photodiode. The organic phosphor transmits most of visible photons but absorbs ultra-violet (UV) photons to convert them to yellow-green photons, so that the emitted yellow-green lights excite the pentacene/ZnO diode under a reverse bias state. Our approach to the transparent pixel adopting such an organic phosphor layer certainly makes the pixel operations efficient under not only visible photons but also UV, protecting the organic pentacene from direct UV.

11:20am EM+TF-ThM11 Near-ideal Schottky-Mott Behavior of n-Si / Hg Diodes with Hydroquinone-Alcohol Monolayers, *A. Vilan*, R. Har-Lavan, O. Yaffe, P. Joshi, R. Kazaz, D. Cahen, Weizmann Institute of Science, Rehovot Israel
The Schottky-Mott model predicts that the eventual energy barrier formed when metal and semiconductor are brought into intimate contact, will be equal to the difference between the metal work function and the semiconductor's electron affinity (for n-type). 60 years of extensive experiments have clearly shown that this ideal picture, that seems to hold for wide bandgap ionic semiconductors such as ZnO, GaS etc., is far from being adequate for the more covalent narrow bandgap Si, Ge, InP, and GaAs. Following Bardeen, who attributed this deviation from the model to surface states energetically located within the semiconductor's forbidden gap, different explanation were raised as for the source of those surface states.

One commonly used model for surface states formation at the interface of semiconductor and metal is the intrinsic Metal Induced Gap State (MIGS) model, stating that gap states are inevitably formed due to the decay of metal electronic states' wavefunction into the semiconductor's bandgap.

We have examined the presence of such MIGS using Hg, which is one of the few metals that doesn't interact chemically with Si, as an electrode. Furthermore, in order to eliminate surface states which are just due to Si dangling bonds, we have used state of the art mixed molecular monolayers of hydroquinone and alcohols that were shown to be the best chemical passivation for Si surfaces.

Using alcohols of different alkyl chain lengths we succeeded to effectively change the electron affinity of the Si over 400 mV range while maintaining firm surface passivation. Current-voltage measurements of diodes formed

that way, with Hg on organically modified n-Si surface, demonstrated near ideal Schottky-Mott characteristics with index of interface behavior S=0.9 (compared to a common value for Si S=0.1).

11:40am EM+TF-ThM12 Electroless Deposition of Metals on SiO$_2$ Surfaces Modified by a Self-Assembled Monolayer, *R. Jain*, A. Ng, A.J. Muscat, University of Arizona
Self-assembled monolayers (SAMs) are used to both chemically activate and deactivate semiconductor surfaces. For instance, octadecyltrichlorosilane prevents atomic layer deposition of high-k films, and 3-aminopropyltriethoxysilane promotes metal deposition. The formation of a uniform and defect free monolayer is essential for nano-scale device fabrication. SAMs could serve as an adhesion layer, which is required for the electroless deposition of metals on some dielectric surfaces. Electroless deposition processes in particular are known to be sensitive to the surface termination and are not robust. In this work, the thickness and density of an aminosilane SAM formed on a SiO$_2$ surface were monitored as a function of solvent, concentration, and time, and the metal to N ratio was quantified.

A 3-aminopropyltrimethoxysilane (APTMS) SAM was formed on a well-hydroxylated SiO$_2$ surface. SAM formation was studied as a function of solvent (methanol and toluene), APTMS concentration (5.72 mM and 57.2 mM), immersion time, solution agitation (stirring and sonication), and post-deposition rinsing in methanol or chloroform depending on the solvent used. The thickness of the APTMS SAM using ellipsometry was 7.8±0.2 Å after 15 min when prepared by stirring an APTMS-methanol solution. This thickness corresponds to the expected length of an APTMS molecule. The roughness was 0.3±0.1 nm measured over 2×2 µm^2 regions using atomic force microscopy. These thickness and roughness values indicate that thin, uniform layers were formed using this method. The absence of a peak for methoxy groups in the high resolution C 1s x-ray photoelectron spectroscopy (XPS) spectrum suggests that all of the methoxy groups were hydrolyzed on the APTMS molecules that reacted with the surface. A single peak in the N 1s spectrum at 399.7 eV indicates the presence of a primary amine when the SAM was prepared in methanol. A second peak was also observed at 400.4 eV corresponding to a hydrogen-bonded amine when the SAM was prepared in toluene. These results suggest that all the SAM molecules were bonded to the surface by siloxane (Si-O-Si) linkages and that amine groups were directed away from the surface with the methanol solvent. Based on XPS peak areas, the molecular density in the SAM layer was 5.4±1.9 molecules/nm^2. A layer of Pd atoms was successfully deposited by immersing the APTMS SAM surfaces in an 80 mM PdCl$_2$-HCl solution for 2 min, yielding one Pd atom bonded to two amine groups based on XPS peak areas. These results demonstrate that an adhesion layer can be formed that will bind metal. Future work will be done to determine how strongly the metal layer adheres to the SAM.

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