Friday Morning, November 14, 2014

Surface Science
Room: 309 - Session SS+EM-FrM

Semiconductor Surfaces and Interfaces 2
Moderator: Robert Bartynski, Rutgers, the State University of New Jersey, Kurt Kolasinski, West Chester University

8:20am **SS+EM-FrM1 Two Dimensional Supramolecular Ordering of Oligothiophene Molecules on the Si(111) √3×√3-Ag Surface**, *R. Liu,* Lakehead University, Canada*, C. Fu, D.F. Perepichka,* McGill University, Canada*, **Mark Gallagher***, Lakehead University, Canada

The functionalization of semiconductor surfaces with organic molecules is a necessary step in the development of hybrid organic-semiconductor structures. A significant challenge to organic layer formation is the fact that semiconducting surfaces exhibit a large number of dangling bonds, which suppress the diffusivity of adsorbed molecules and can even break the molecules apart via the formation of Si-C bonds. Recently it has been shown that these problems can be obviated by depositing the organic molecules onto a passivated surface [1].

We have studied the adsorption of brominated π conjugated tetrathienoanthracene molecules (TBTTA) onto the Si(111)-√3×√3-Ag surface. Thiophene based molecules like TBTTA are of considerable interest in organic semiconductor research due to their efficient conjugation and the chemical stability [2]. The Si(111) √3×√3-Ag surface has no Si dangling bonds and should provide a high mobility surface suitable for TBTTA adsorption. Scanning Tunneling Microscopy images reveal that at low coverage the molecules readily migrate to step edges and defects in the √3 overlayer, in fact many images show direct evidence of molecular mobility. With increasing coverage the molecules eventually form compact supramolecular structures. In terms of the √3 lattice vectors ($\boldsymbol{a}$ and $\boldsymbol{b}$), the oblique unit cell of these structures is $\boldsymbol{a_m} = 3\boldsymbol{a} + \boldsymbol{b}$, and $\boldsymbol{b_m} = \boldsymbol{a} + 2\boldsymbol{b}$. The structures are quite fragile and can decompose under repeated STM imaging. Our results suggest that TBTTA is weakly bound to the √3 surface at room temperature and that the supramolecular structures are held together by weak van der Waals forces.

1. T. Suzuki et al., Phys. Chem. Chem. Phys. 11, 6498 (2009).

2. R. Gutzler et al., Nanoscale 6, 2660-2668 (2014).

8:40am **SS+EM-FrM2 Interface Formation between a Self-Assembled Monolayer and an Organic Semiconductor**, ***Sujitra Pookpanratana****, H.-J. Jang, A.N. Brigeman, J.I. Basham, O.A. Kirillov, D.J. Gundlach,* National Institute of Standards and Technology (NIST)*, O.D. Jurchescu,* Wake Forest University*, C.A. Richter, C.A. Hacker*, NIST

Organic-based electronics are attractive because they have potential manufacturing advantages such as mechanical flexibility and simpler processing (solution-based, low temperature, and atmosphere conditions). Molecular-based semiconductors offer a nearly limitless range of possibilities in tailoring the chemical composition and structure for a desired electronic, optical, or film-processing property. Probing and understanding molecular surfaces and interfaces is essential for the further development of organic-based photovoltaics, light emitting diodes, and field-effect transistors. Organic-organic interfaces are key in some of those devices, and understanding the impact of a self-assembled monolayer (SAM) has when an organic semiconductor is on top of it, is a complex issue.[1] This strategy is commonly implemented as a way to modify the hole injection barrier between an organic material and an inorganic substrate.

Here, we have investigated the interaction between a pi-conjugated organic semiconductor (tris-(8-hydroxyquinoline) aluminum, Alq_3) on SAM's of different tail and backbone composition. We have used ultraviolet and X-ray photoelectron spectroscopies to monitor the energy level alignment and chemical structure at the interface. The SAM's strongly interact with the Au substrate, where an interface dipole can down shift or up shift the surface work function. After Alq_3 is deposited onto the SAM-coated substrates, we find that the highest occupied molecular orbital of Alq_3 is relatively constant (with respect to the substrate Fermi level) on all surfaces, suggesting Fermi level pinning.[2] However, the composition of the SAM's did strongly influence the growth and chemical structure of the Alq_3 at the interface. The photoemission signal arising from the Au substrate is least attenuated when the SAM/Au surface is hydrophobic when compared to a hydrophilic SAM/Au or bare Au surface. The difference in substrate attenuation suggests that that the early growth of the Alq_3 layer strongly depends on this surface property. This finding is corroborated with microscopy of the same samples. In addition, Alq_3 chemically reacts with a fluorinated SAM at the organic-organic interface as indicated by the shifting and asymmetric broadening of Al and N core levels. These results will be discussed in context of painting a comprehensive picture of the organic-organic interface formation that influences the chemical composition, electronic structure and physical structure at the interface.

[1] F. Rissner *et al*, *ACS Nano* 3, (2009) 3513.

[2] L. Lindell *et al*., *Appl. Phys. Lett*. 102, (2013) 223301.

9:00am **SS+EM-FrM3 Reactions of Benzoquinone with Hydrogen Terminated Silicon Surfaces***, R.L. Opila, **Meixi Chen**, N.A. Kotulak, N.J. Schreiber*, University of Delaware

Quinhydrone dissolved in methanol has long been know to react with hydrogen terminated silicon surfaces to passivate electronic defects where photo-excited carriers recombine non-radiatively. The mechanism of this passivation is not well understood. We have shown that benzoquinone, $C_6O_2H_4$ rather than hydroquinone, $C_6O_2H_6$, both components of the quinhydrone mixture, is the active component. Benzoquinone reacts to abstract a hydrogen and then itself bonds with the surface. We have shown that the hydrogen can be abstracted from the solvent and that incident light is necessary for this reaction to take place. X-ray photoelectron spectroscopy and Fourier Transform Infrared Spectroscopy were used to show that the benzoquinone reacted with the surface. Photo-excited carrier lifetime is a good measure of the extent of the passivation of the surface. Density functional theory supports the proposed reaction mechanism.

9:20am **SS+EM-FrM4 High-Quality Monolayers Derived from Short Alkyne Chains on Si(111) Surfaces**, ***Sidharam Pujari****, A. Filippov, S. Gangarapu, H. Zuilhof*, Wageningen University, Netherlands

Hydrosilylation has been a key reaction in preparing monolayers on silicon surfaces. This process involves the reaction of a terminally unsaturated reactant with the Si surface. Over the past 20 years, several advances have been accomplished to obtain better (i.e. denser and more stable) monolayers with various reactants (alkenes, alkynes, dienes, etc.) under different reaction conditions (e.g. thermal initiation, ultraviolet light, etc.).[1,2] Such a higher density is advantageous for the structural ordering, stability and a wide range of applications. The procedure used in our lab (as well as labs around the world) involves wet-chemical techniques for the surface modifications. As the name implies, the reactants with these techniques must be available as liquids under the reaction conditions. Due to this constraint, only monolayers of relatively long chain lengths have been made, because shorter chains evaporate under thermal conditions (or are even a gas). In the current project, we have prepared and characterized a new class of monolayers with (short) chain lengths that were previously inaccessible.

H-Si(111) surfaces were modified with gaseous alkynes in a pressure-resistant PARR reactor. This novel method in silicon-carbon chemistry allows the chemisorption of compounds that were previously unusable in surface modification due to its volatility. Si–C-bonded monolayers derived from propyne, 1-butyne and 5–functionalized-pent-1-ynes (-COOH, -Cl, & -NH_2) were prepared and characterized using various surface-sensitive techniques. Si(111)–propenyl and butenyl silicon-monolayers display a higher packing density (up to 75%) than any wet-chemically prepared alkyne-derived monolayer. Furthermore, a combination of experimental and theoretical data shows that propyne chemisorption happens in a temperature-dependent manner, not observed for any other alkyne studied up to now: through addition of the second carbon (-*iso*) at temperatures below 90 ° C, and of the terminal carbon (-*lin*) above 90 ° C. Finally, 5-chloro-1-pentyne and 4-Pentynoic acid were shown to bind at high surface densities and (near-)exclusively via the terminal carbon of the triple bond. These end groups allow for further functionalization of the monolayer.

(1) Rijksen, B.; Pujari, S. P.; Scheres, L.; van Rijn, C. J. M.; Baio, J. E.; Weidner, T.; Zuilhof, H. *Langmuir* **2012**, *28*, 6577-6588.

(2) Li, Y.; Calder, S.; Yaffe, O.; Cahen, D.; Haick, H.; Kronik, L.; Zuilhof, H. *Langmuir* **2012**, 9920-9929.

9:40am **SS+EM-FrM5 Surface Modification of Antimonide-Based Compound Semiconductor Superlattices using ALD**, ***Erin Cleveland****, J. Nolde, C. Canedy, E. Aifer*, Naval Research Laboratory

The use of dielectric films in device passivation is complicated by the fact that they are typically deposited on processed material surface that bear little resemblance to that of the virgin growth surface. This is particularly evident in technologically important device structures employing antimonide-based compound semiconductor (ABCS) superlattices, where the exposed mesa sidewalls may be comprised of four or more atomic species and their complex oxides. Physically, the etched surface presents a different crystallographic orientation, and may have additional structure due

to variation in etch rate of superlattice layers. Since the nature of the dielectric/semiconductor interface directly impacts the density of surface states, it is critical to understand how processed, multilayer semiconductor surfaces may be modified during the initial phase of the atomic layer deposition (ALD) process.

A significant effort has been focused on surface preparations prior to ALD that removes the native oxide and passivates the III-V atoms in order to ensure the best possible interface. Current approaches typically rely upon wet-chemical etches to remove the defect-prone native oxide layer prior to dielectric deposition; however, this technique typically suffers from a lack of reproducibility, as well as potential interface contamination between processing steps. Therefore, we studied the effectiveness of using the ALD precursor, TMA, in conjunction with wet and dry pre-treatments, in removing carbon and etch precipitates, scavenging the various oxide species, and residues of excess group III and V elements on (100) surfaces of ABCS superlattices as a function of precursor choice, sequence (i.e. TMA vs oxidizer first), exposure time, as well as substrate temperature. Furthermore, surface passivation stability was investigated as a function of temperature and time. Surfaces were analyzed using XPS, AFM, and SEM both before and after ALD treatments. Results indicate that a completely oxide free surface may not be necessary to produce a good electrical interface.

10:00am **SS+EM-FrM6 Mechanism Changes Caused by Metal Catalyst During Silicon Etching in V_2O_5 + HF Solutions**, ***Kurt Kolasinski**, W.B. Barclay*, West Chester University

Etching of Si in oxidant + HF solutions can lead to a self-limiting reaction that spontaneously produces nanocrystalline porous Si – a process known as stain etching. The presence of a metal catalyzes and localizes etching such that ordered arrays of pores or nanowires can be formed depending on the structure of the metal – a process known as metal assisted etching (MAE). Ag, Au, Pd and Pt were deposited from solution onto H-terminated Si to act as catalysts for MAE. The metals all catalyzed the injection of holes into the Si. They all increased the rate of hole injection by approximately a factor of 5. The stoichiometry of MAE in V_2O_5 + HF solutions depended on the chemical identity of the metal. The stoichiometry when etching with Ag and Au was the same as for stain etching in V_2O_5 + HF solutions. However, for Pd and Pt, the stoichiometry differed significantly, consuming more V_2O_5 and producing less H_2 per mole of Si etched. This indicates that the metal catalyst can change the mechanism of etching. Etching in V_2O_5 + HF solutions was well behaved and gave consistently reproducible kinetic results. The behavior is much different when HOOH is added instead of V_2O_5. In the absence of deposited metal, no reaction occurs with HOOH. When HOOH was added to metal-coated Si samples immersed in HF(aq), etching was immediate in all cases. In contrast to V_2O_5, we were unable to obtain well-behaved stoichiometric results for HOOH + HF solutions. This is related to heightened sensitivity on reaction conditions compared to the V_2O_5 system as well as nonlinearities introduced by side reactions.

The mechanism of Si etching changes based on the presence of a metal catalyst during metal assisted etching and depends on the chemical identity of the metal. A valence 2 path dominates the formation of photoluminescent nanoporous Si in stain etching as well as MAE with Ag and Au. A valence 4 path dominates the formation of photoluminescent nanoporous Si in MAE with Pt. However for MAE with Pd, no nanoporous Si is formed initially and a mixture of valence 4 and valence 2 processes is observed. The nature of the electron transfer process and its dependence on the electronic structure of the metal/Si interface will be discussed.

10:40am **SS+EM-FrM8 Selective Wet Etching of III-V Semiconductors with HCl, H_2O_2, and α-Hydroxy Acid Mixtures**, ***Pablo Mancheno-Posso**, R. Jain, A.J. Muscat*, University of Arizona

The higher electron mobility of III-V semiconductors makes them suitable for NMOS devices in CMOS transistor technology. A clean, smooth and well-defined semiconductor surface is needed for epitaxial growth of heterostructures and atomic layer deposition of dielectrics. Device fabrication also requires selective etching and smooth finishing of layers composed of different materials. Wet chemical treatments enable batch processing, and aqueous mixtures containing an oxidizing agent and an etchant (acid or base) have been developed for III-V materials. The (100) face of the binary III-V semiconductors contains both group III (electron-deficient) and V (electron-rich) atoms. HCl solutions favor the removal of the latter. The addition of α-hydroxy acids (citric and tartaric acids) to the etching mixture is expected to promote a more uniform etch by chelating the group III atoms. In this study, we compare the etching rates of the (100) faces of GaAs, InAs, InP, InSb and GaSb, using aqueous solutions of HCl (0.01-4 M), H_2O_2 (0.01-8 M), and tartaric and citric acids (0.1-1.5 M). The etching rate was determined by profilometry measurements of the step height on patterned substrates. The chemical composition of the surface was studied using XPS, and the surface topography and roughness were characterized with AFM. The etching rate of GaAs in HCl-H_2O_2 mixtures was independent of HCl concentration (0.1-4 M) and showed a linear dependence on H_2O_2 concentration (0.1-8 M). Etching was limited by the removal of water-soluble Ga and As chlorides formed from GaAs oxides. InP etching was independent of HCl concentration (1-5 M), but sharply increased for 6-7 M. H_2O_2 concentration showed no significant effect on InP etching. The GaSb etching rate depended linearly on H_2O_2 concentration but in a narrower range (0.1-0.5 M). The etching of InP and GaSb is limited by the removal of the group III atoms. Etching of GaAs and InAs is limited by the removal of the group V atom. The strong bond that As makes with O drives etching. The etching selectivity of GaAs to InP increased from about 15 to 250 when the H_2O_2 concentration was raised from 1 to 8 M at a fixed 1.76 M HCl concentration. The addition of tartaric or citric acid to HCl and H_2O_2 mixtures yielded no change in the etching rate of GaAs when compared to solutions containing HCl and H_2O_2 only, but preferentially removed Ga atoms, yielding smoother surfaces at low concentrations. Using a chelator etched InAs with high selectivity relative to InP without as much roughening as with HCl. Selective etching will be discussed in the context of a set of proposed mechanisms based on the data.

11:00am **SS+EM-FrM9 Lanthanum Quantification for Optimization of Advanced High-k/Metal Gate Stacks using Low Energy Electron X-ray Emission Spectrometry**, *E. Martinez,* CEA, LETI, MINATEC Campus, France, *C. Trouiller,* STMicroelectronics, France, *M.P. Moret, N. Morel,* CAMECA, France, ***Andrew Davis***, CAMECA Instruments Inc, *P. Caubet,* STMicroelectronics, France, *F. Bertin*, CEA, LETI, MINATEC Campus, France

We report about accurate monitoring of ultra-low La doses inserted in advanced high-k/metal gate stacks for threshold voltage tuning purposes. Three characterization techniques are implemented for precise and reproducible lanthanum quantification. LEXES (Low energy Electron X-ray Emission Spectrometry) capabilities are highlighted in terms of sensitivity and accuracy thanks to a comparison with reference results obtained by Rutherford Backscattering Spectrometry (RBS). The capabilities of state-of-the-art Auger nanoprobes for depth profiling in the sub-nanometer range are also illustrated.

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