

Thursday Afternoon Poster Sessions

Surface Science

Room: 4C - Session SS-ThP

Surface Science Poster Session

SS-ThP1 Amplified Optical Switching of Surface Wettability through Tailored Morphologies, D. Yang, P. Aella, A. Garcia, D. Gust, M.A. Hayes, Arizona State University, S.T. Picraux, Los Alamos National Laboratory

We report the tailoring of surface roughness to significantly amplify light-induced contact angle switching and wettability of surfaces functionalized with the photochromic azobenzene molecules. Potential applications of controlled surface wettability for microfluidic systems include delivering analyses in lab-on-a-chip environments, bio-assay in drug discovery, and chemical analyses. Transporting increasingly smaller volumes of water is an important task in miniaturized microfluidic systems. However traditional mechanical approaches do not scale well to smaller volumes due to the increased importance of interfacial forces relative to inertial forces. Thus alternative methods to control liquid interactions with surfaces and to drive droplet motion are needed. We have previously demonstrated large photo-induced switching of contact angles (10-12 degrees) for water and other fluids on azobenzene-functionalized smooth Si surfaces. With these surfaces we find one can reversibly switch the surface wettability and in cases of sufficiently low hysteresis move liquid droplets by light-induced gradients in the surface tension. In this work, we extend these studies to the design of surface morphologies for increasing the effectiveness of photo-induced switching of surface wetting. We have fabricated ordered arrays of micrometer sized pillars (heights and spacing ~ 5 to $50 \mu\text{m}$) on Si substrates. We also have prepared novel surfaces using CVD vapor-liquid-solid growth to fabrication surfaces with various lengths of Si nanowires (~ 50 - 100 nm in diameter) and combinations of nanowire-micropillar structures to form hierarchical arrays. By combining surface roughness with photochromic azobenzene monolayers, we demonstrate the amplification of the light-induced switching angle by up to a factor of 2 compared to smooth surfaces. Particularly effective amplification is found for hierarchical nanowire-micropillar designed surfaces. We discuss how such amplification enables increased control of surface wettability and droplet manipulation by optical means.

SS-ThP2 Surface Bonding Effects in Nanoparticles, H.H. Farrell, C.D. Van Sielen, D.M. Ginosar, L.M. Petkovic, Idaho National Laboratory, R.D. Parra, DePaul University

The nature of the bonding at surfaces has a profound effect on their properties. Current models for the cohesive energy of nanoparticles generally predict a linear dependence on the inverse particle diameter, $1/r$, for low aspect-ratio (spherical) clusters.¹ Although this is generally true for metals, we have recently found that for the Group IV semiconductors, C, Si and Ge, this linear dependence does not hold.² Instead, using first principles, density functional theory calculations to calculate the binding energy of these materials, we find a roughly quadratic dependence on the inverse of the particle size. Similar results have also been obtained for the metallic Group IV elements Sn and Pb and for Mg, another "poor" metal.³ This result is in direct contradiction to current assumptions. Further, as a consequence of this quadratic behavior, the melting point of these materials will not be linear in $1/r$, but will experience less suppression than experienced by metal nanoparticles with comparable bulk binding energies. Similarly, the vapor pressure of semiconductor nanoparticles will rise more slowly with decreasing size than would be expected. This non-linearity also affects sintering or Ostwald ripening behavior of these nanoparticles as well as other physical properties that depend on the nanoparticle binding energy. The reason for this variation in size dependence involves the covalent nature of the bonding in semiconductors, and even in the "poor" metals. New work on other materials, including compound semiconductors and oxides will also be presented.

¹See, for example, S. C. Vanithakumari, and K. K. Nanda, *J. Phys. Chem. B* 110, 1033 (2006), and references therein.

²See, for example, W. H. Qi, M. P. Wang, M. Zhou, and W. Y. Hu, *J. Phys. D: Appl. Phys.* 38, 1429 (2005), and references therein.

³See, for example, Chang Q. Sun, H. L. Bai, S. Li, B. K. Tay, C. Li, T. P. Chen, and E. Y. Jiang, *J. Phys. Chem. B* 108, 2162 (2004), and references therein.

⁴See, for example, M. Wautelet, J. P. Dauchot, and M. Heq, *J. Phys.: Condens. Matter* 15, 3651 (2003), and references therein.

⁵H. H. Farrell and C. D. Van Sielen, accepted for publication in *J. Vac. Sci. Technol. B*.

SS-ThP3 Initial Adsorption of Yttrium on Si(001) 2X1 Surface, S.Y. Chiam, Imperial College London, Singapore, A.C. Huan, Institute of Materials Research and Engineering, Singapore, W.K. Chim, National University of Singapore, J. Zhang, Imperial College London, Singapore, J.S. Pan, Institute of Materials Research & Engineering, Singapore

Initial adsorption sites of metal on Si is an increasingly important area of research especially for growth of thin films for low dimensional devices. Growth and simulation of heterojunction thin films on Si often require a more detail information about the position and bonding of the adatom. For instance, study of Sr with experimental and theoretical methods have lead to a better understanding of Sr adatom's preferred environment and gave insights into subsequent growth of epitaxial thin film, in particular, SrTiO₃. In this work, we have investigated the initial adsorption of transition metal yttrium (Y) on Si(001). Y although formally a transition metal, have very similar valence electronic properties with the lanthanide family, including lanthanum. In Si based electronics, yttrium silicide, yttrium silicate and yttrium oxide are all potential thin films for source-drain contacts, infrared-detectors, and gate dielectrics. Furthermore, information about Y adsorption sites can aid in the design and growth of ternary or quaternary oxides (eg. LaYAl₂O₃). We have examined the real-time deposition of Y on Si(001) 2X1 by mounting a EFM evaporator source on the STM chamber. Therefore, we have observed the deposition of sub-monolayer coverage of Y atom on the same area of clean Si image thereby reducing any errors that might arise from adsorption of other species in UHV. Our work shows that yttrium adsorbs primarily on dimer bond instead of the cave site as predicted from a theoretical simulation of La on Si(001). We've examine the possible structure for such an adsorption and discuss about its stability and its bonding character using both STM and UPS.

SS-ThP4 Site Specific Chemisorption of Cl on Si(114), R.E. Butera, A. Agrawal, J.H. Weaver, University of Illinois at Urbana-Champaign

The dissociative chemisorption of Cl on Si(114) was studied at room temperature using scanning tunneling microscopy (STM). Si(114) is a stable, planar, single-domain, high-index surface composed of rebonded atoms, dimers, and tetramers each aligned in rows along [-110]. STM imaging shows preferential Cl-termination of rebonded atom and dimer sites over tetramer sites. Moreover, the prevalence of specific chlorinated tetramer configurations reveals that dissociation is sufficiently exothermic that Cl can interrogate the potential energy landscape to find a local minimum. A 10 minute anneal at 550 K facilitates diffusion and allows the system to reach the equilibrium configuration. Sequential exposure and annealing cycles reveal a coverage-dependent site occupancy dictated by surface π -bonding. This study provides the necessary starting point for a thorough investigation of the structural implications of halogen etching where we find preferential desorption and novel pattern formation.

SS-ThP5 Irreversible Structural Transformation of Si(114)-2x1 Induced by Subsurface Carbon, G. Duvjir, H. Kim, J.M. Seo, Chonbuk National University, Korea

From the previous STM studies of Si(114)-2x1, it had been reported that its pure and reconstructed surface (A-phase) is composed of rebonded restatom(R), tetramer(T), and dimer(D) rows. Recently, during annealing Si(114) near 1300C, we have found carbon-induced Si(114)-2x1 surface (B-phase) whose reconstruction is composed of T, T and D rows. Such a B-phase turns out to be induced by bulk carbon impurity segregated to surface and trapped at the subsurface. Once the surface changes from A-phase to B-phase, it does not return to A-phase by any kind of annealing process. The portion of B-phase relative to A-phase can also be increased by C₂H₂ adsorption on the clean substrate held at 500 C up to 100 percent. When the surface of B-phase is used as a substrate during Si-homoepitaxy or Ge-epitaxy, the overlayer thickness increases by two layers, differently from one-layer growth mode on the substrate of A-phase. It can be concluded that carbon having a stable subsurface site induces the anisotropic compressive stress on the surface, which results in insertion of Si-dimer to R row to form T row. The potential of this B-phase for application as a template is in its thermal stability and homogeneity since A-phase always has B-phase impurity even in the clean surface.

SS-ThP6 Evidences of Two Commuting Chain Structures Existing on Si(5 5 12)-2x1, H. Kim, H. Li, G. Duvjir, J.M. Seo, Chonbuk National University, Korea

From STM/STS studies of the reconstructed Si(5 5 12)-2x1 surface, it has been found that its atomic structure of the unit-cell consists of four kinds of 1-D structures: honeycomb(H) chain, π -bonded chain, dimer-adatom(D/A) row, and tetramer(T) row. One (5 5 12) period is composed of three

subunits, (337) unit with a D/A row [D(337)], (337) unit with a T row [T(337)], and (225) unit with both a D/A and a T row. Two kinds of adjacent subunits, T(337)/D(337) and D(337)/(225), are divided by H chains, while one kind of adjacent subunits, T(337)/(225), is divided by a π -chain. Existence of two chain structures has been confirmed as follows: (1) In the empty-state topographic image, H-chain has 2x periodicity along the chain due to buckling, while π -chain with missing atom defects has 1x periodicity. (2) From local STS measurement, the empty-state onset of π -chain is 0.5 eV smaller than that of H chain. (3) Exposed benzene molecule adsorbs selectively on π -chain. (4) In the homoepitaxy on Si(5 5 12)-2x1 at 550°C, the first chain grown on D/A row is π -chain. Two chain structures commute with each other depending upon the external stresses perpendicular to the chain, which is the same for two row structures, D/A and T rows. These results indicate that, although numbers of consisting atoms and dangling bonds (DBs) of two different chains are identical, different DB directions induced by tensile stresses perpendicular to the chain result in such a distinct reactivity.

SS-ThP7 In-induced Atomic Chains on the Stepped Si Surface : In/Si(557)1x3. *I. Song, J.H. Nam, M.K. Kim, C.-Y. Park, D.H. Oh, J.R. Ahn,* Sungkyunkwan University, Korea

We have investigated the In-induced one-dimensional (1D) surface reconstruction on the Si(557) surface using low energy electron diffraction (LEED) and scanning tunneling microscopy (STM). One-dimensional electron systems have showed exotic phenomena such as Jahn-Teller distortion, non-Fermi liquid behavior, and Peierls instability.¹ Recently, stepped Si surfaces have attracted much attention as templates for formation of one-dimensional structures. Some examples that have been extensively studied are the Au/Si(553), Au/Si(557), Pb/Si(557) surfaces.² The In-induced 1D structure on the Si(557) surface was prepared by depositing In on the RT Si(557) surface and subsequent annealing at 500 °C. LEED show the In-induced surface reconstruction to have 1x3 phase, where the direction of the x3 period is perpendicular to the step direction. In STM images, we found two kinds of atomic wires located at the step edge and within the terrace, respectively. The atomic chain within the terrace has obviously x3 period along the chain direction, while the atomic chain at the step edge seems to have x1 period along the chain direction. The atomic chains on the In-induced Si(557)1x3 is quite similar with those on the Au/Si(557) surface.³ We will explain the In-induced Si(557)1x3 surface in comparison with the Au/Si(557) surface.

¹ J. R. Ahn, J. H. Byun, H. Koh, E. Rotenberg, S. D. Kevan, and H. W. Yeom, Phys. Rev. Lett. 93, 106401 (2004)

² J. N. Crain, J. L. McChesney, Fan Zheng, M. C. Gallagher, P. C. Snijders, M. Bissen, C. Gundelach, S. C. Erwin, and F. J. Himpsel, Rhys. Rev. B 69, 125401 (2004)

³ M. Krawiec, T. Kwapiński, and M. Jalochocki, Phys. Rev. B 73, 075415 (2006).

SS-ThP8 Ozone Oxidation of Self-Assembled Monolayers on Silicon Surfaces. *T.M. McIntire,* University of California, Irvine, *A.S. Lea, P.L. Gassman,* Pacific Northwest National Laboratory, *Q. Li,* KLA-Tencor Corporation, *O.S. Ryder, B.J. Finlayson-Pitts,* University of California, Irvine

Airborne particles have well-documented effects on human health, visibility and the chemistry of the atmosphere. A major area of concern, but also largely uncertain, is the impact of particles on global climate. A significant part of this uncertainty is the lack of understanding of the nature of the organic component. This deficiency includes the chemical speciation and the distribution of the organics between the surface and the bulk of liquid particles, as well as changes due to oxidation during transport in the atmosphere. In this work, the formation of large organic aggregates has been observed from the ozone oxidation of unsaturated alkene self-assembled monolayers (SAMs) on solid silica surfaces. Ozonolysis of terminal alkene SAMs of 3- and 8-carbon lengths, as proxies for organic-coated airborne dust particles, leads to the formation of large hydrophobic aggregates which do not increase the uptake of water as previously assumed. These SAMs were generated on silicon substrates and reacted at room temperature with gaseous ozone. A combination of experimental techniques, atomic force microscopy, scanning electron microscopy, Auger microprobe, time-of-flight secondary ion mass spectrometry, and transmission FTIR, were used to study the surface composition and morphology after oxidation. Large (micron-size) organic aggregates formed on the surface while the surrounding substrate became depleted of carbon and exposed the original substrate. This highly unusual result establishes that the mechanism of ozonolysis of alkene SAMs involves polymerization, likely induced by secondary reactions of the Criegee intermediate (CI). For that reason, formation of polymers under atmospheric conditions may be more common than previously recognized. The uptake of water was not increased upon oxidation of these films, in contrast to current expectations. Implications for SAM reactions and stability in air, ozonolysis of alkenes on surfaces, and for the oxidation of alkenes on airborne dust particles are discussed.

SS-ThP9 Thermal and Non-thermal Interactions of MEA on Si(100). *B. Forster, S. Yeninas, J. Thompson, J.H. Craig, Jr., J. Lozano,* Bradley University

We have used several surface analysis techniques to study the adsorption dissociation, and desorption of monoethylamine (MEA) on Si(100) surfaces. Thermal processes were studied using high resolution electron energy loss spectroscopy (HREELS) and temperature programmed desorption (TPD). Non-thermal processes using electron irradiation of MEA/Si(100) at 100 K were studied using HREELS TPD, x-ray photoelectron spectroscopy (XPS), and electron stimulated desorption (ESD). Our data indicated low temperature electron-induced dissociation of MEA, deposition of nitrogen, and formation of silicon nitride.

SS-ThP10 Adsorption Studies of Trisilylamine on the Si(100) Surface. *B. Bush, A. Marquis, O. Egwu, J.H. Craig, K. Roos, J. Lozano,* Bradley University

Trisilylamine (SiH₃)₃N is the silicon analog to the carbon-containing molecular species trimethylamine (CH₃)₃N. The fundamental structural difference between these amines is the planar backbone exhibited by TSA. The Si₃N backbone is the same structure which occurs in silicon nitride Si₃N₄. Little fundamental work has been reported on the adsorption properties of TSA on the Si(100) surface. We report on the results of a series of adsorption studies of TSA on the Si(100) surface at 100K using XPS, UPS, HREELS, and TPS to elucidate the dissociation pathways and bonding of the TSA molecule on the surface. Results of electron bombardment studies to remove hydrogen ligands from the adsorbed species will also be discussed. Preliminary STM images of very low coverage adsorption of TSA on the Si(100) surface will also be presented and discussed.

SS-ThP11 STM Study of Niobium Deposited on Si(111) Surface. *H. Suh, Y. Kuk,* Seoul National University, Korea

Superconductivity in low dimensionality has been attracting attentions of many researchers due to its technological and scientific importance. While it is well known that superconductivity is suppressed as the dimensionality is reduced, the conditions and criteria for the dimensionality still remain questionable. Scanning Tunneling Microscopy is a powerful tool for studying both topographies and local electronic structures in nanometer scale. To explore superconductivity at reduced dimensionality, we studied Nb deposits on Si surfaces. Nb, which has the highest superconducting transition temperature among elemental superconductors and has various compounds with even higher transition temperatures, was e-beam evaporated onto Si(111) surface and annealed. The surface was characterized with Scanning Tunneling Microscope (STM) and local electronic structures of the deposited Nb was studied with Scanning Tunneling Spectroscopy (STS).

SS-ThP12 STM Study of Submonolayer of Au Adsorption on Si (111)-(7x7) Surface and Influence of Substrate Temperature. *H. Shim, L. Zhang, Y. Kim, G. Lee,* Inha University, South Korea

Adsorption of submonolayer Au on Si (111)-(7x7) surface at different substrate temperature was investigated using STM. At room temperature deposition, the Au adsorption on Si (111)-(7x7) typically features coexistence two species, high-lighted triangles and clusters confined within half-unit cells. The high-lighted triangles are dominant at a very low coverage, but give way to clusters with various sizes as the coverage increases. Slightly heating the substrate (below 150 C) during deposition also decreases the number of the highlighted triangles. The clusters, mostly confined within half unit cells for the deposition at substrate temperatures below about 350 C, coalesce to cover the borders of the half unit cells when substrate temperature increases. Vacancies and disorders are created near the clusters, suggesting the incorporation of Si atoms into the clusters at the heated substrate. At about 550 C deposition, the Au adsorption leads (5x2) reconstruction in the form of characteristic island-hole pairs on terrace or only (5x2) islands at the step edge. The evolution of the Au-adsorbed surfaces with substrate temperature during deposition will be discussed and compared with that of the room temperature deposition and post annealing.

SS-ThP13 Controlling and Probing Molecular Orientation and Differential Conductivity in Solid Films of Ionic Perylenebis(dicarboximide)s. *A. Jeewandara, S.M. Casey,* University of Nevada, Reno

We report the control of molecular orientation and differential conductivity in solid films through self-organization and induced orientation processes. We synthesized water-soluble cationic 3,4,9,10-perylene diimide and derivatives and formed chromonic N phases (nematic lyotropic liquid crystalline phases) at room temperature upon solution concentration. Upon induced alignment (by shearing) of the chromonic N phase on a substrate and removal of solvent, anisotropic solid films of the dichroic dyes were

produced. By use of a combination of polarized UV-vis and FT-IR spectroscopies, the orientation of the average molecular plane in these films was determined to be perpendicular to both the shearing direction and the substrate plane. The effect of molecular orientation on the differential conductivities in the films will be discussed.

SS-ThP14 The Molecular Scale Origins of the Surface Memory Effect, K. Buřkin, R. Adams, B.L. Johnson, D.L. Patrick, Western Washington University

The behavior of liquid crystals (LC) at interfaces has been an important area of research for many years because of its relevance to LC device applications such as LCDs. In this research ordered monolayer films of the LC 4'-octyl-4-biphenyl-carbonitrile (8CB) on highly oriented pyrolytic graphite were investigated by scanning tunneling microscopy (STM) in order to study their disordering kinetics and to develop a better understanding of a phenomenon known as the surface memory effect. The surface memory effect occurs when a LC film retains a degree of remnant orientational order even after being heated above its isotropic transition temperature. Using STM we studied molecular-scale ordering in 8CB films heated to varying temperatures and for varying lengths of time. The results are compared to large-scale Monte Carlo simulations of a 2-dimensional Ising Model, which suggests for the first time that nearest-neighbor interactions in the isotropic phase play an important role in producing surface memory effects.

SS-ThP15 Chiral Control in Organic Monolayer Films Using Liquid Crystal Solvents, C. Reinhart, A. Morris-Cohen, D.L. Patrick, Western Washington University

Many important chemical and physical properties of organic thin films are affected by molecular-scale order. We present investigations of a method for controlling the orientation of molecules and their chirality in monolayer films using thermotropic liquid crystal (LC) solvents and magnetic fields. Two different methods of chiral and orientational control will be discussed. The first involves an achiral set of organic compounds that, when deposited on a graphite surface, produce crystalline monolayers with non-superimposable left and right handed domains; the second set involves 3-dimensionally chiral compounds and is aimed at controlling enantiomeric excess through selective adsorption. Molecular ordering, 2D chirality and enantiomeric excess are analyzed by scanning tunneling microscopy.

SS-ThP16 Organic Semiconductor Film Growth Using Liquid Crystal Solvents, B.B. Ohlson, F.S. Wilkinson, D.L. Patrick, Western Washington University

Organic semiconductor (OS) thin films have attracted widespread interest for their potential use in electronics, optics, information storage, photovoltaics and many other applications. Since properties such as charge transport are known to be anisotropic in most crystalline structures, having control of crystallite orientation should lead to improvements in the tunability of devices such as organic thin film transistors (OTFTs) and organic light emitting diodes (OLEDs). Furthermore, by creating films that are highly crystalline, with large grain size, and thus less potential for charge trapping at the grain boundaries, charge transport characteristics can be optimized. We present a new approach for growing OS thin films using thermotropic nematic liquid crystal (LC) solvents to deposit tetracene films with long-range uniaxial order. The LC solvent imprints its directionality onto the crystalline tetracene film as it grows, resulting in larger, highly oriented crystals. Films were deposited via atmospheric-pressure sublimation onto substrates coated by a LC layer oriented using mechanically rubbed polyvinyl alcohol (PVA). This poster will describe the effects of different processing conditions, such as LC layer thickness, substrate temperature and flux rate on film morphology and crystallinity.

SS-ThP17 Analyte Binding to CoPc: A Comparison of Analyte Binding Strength and Basicity, N.L. Tran, A.C. Kummel, University of California at San Diego

A recent study has shown a strong correlation between analyte electron donor ability and chemiresistive Cobalt phthalocyanine (CoPc) sensor response.¹ The $-H_{BF_3}$ scale method was used as a measure of the electron pair donor ability of the 10 analytes investigated.² It is speculated that sensor response is dictated by the degree of charge transfer in CoPc-analyte complexes as opposed to analyte binding strength. To investigate this hypothesis, the binding strength of these electron donating analytes (acetonitrile being the weakest and triethylamine the strongest electron donor) to the Co metal of CoPc was calculated using density functional theory. Subsequently, the atomic charges of the CoPc and CoPc-analyte complex will be analyzed to measure the degree of charge transfer between the analyte and Co metal. The interaction of a neurotoxin analogue, dimethyl methylphosphonate (DMMP) with CoPc is also being investigated to determine the potential for use of CoPc sensors to detect

organophosphate neurotoxins. Preliminary DFT simulations show that although O₂ binding to the Co metal is weak (less than -0.1 eV exothermic), a large effect on the CoPc electronic structure and charge transfer is observed. Weak analyte-MPC binding with a large change in electronic structure are the key properties of a good sensor because a reversible absorption will result in a large change the conductivity of the MPC film.

¹ F. Bohrer, A. Sharoni, C. N. Colesniuc, J. Park, I. K. Schuller, A. Kummel, and W. C. Troglor, *Journal of the American Chemical Society* submitted (2007).

² P. C. Maria and J. F. Gal, *Journal of Physical Chemistry* 89 (7), 1296 (1985).

SS-ThP18 Ablation of Polyvinylidene Fluoride at 157-nm¹, J.A. Leraas, S.R. John, S.C. Langford, J.T. Dickinson, Washington State University

Polyvinylidene fluoride [PVDF—(CH₂CF₂)_N] is a piezoelectric polymer employed in a variety of sensors. PVDF also possesses excellent thermal and chemical stability, which complicate the manufacture of parts with complex geometries. Structure formation by energetic radiation is potentially important to the broader application of this material. In this work, we characterize the products produced by exposing PVDF to 157-nm radiation from an F₂ excimer laser. In the early stages of irradiation, the dominant neutral product is HF, produced by photochemical excitation of side chain bonds. HF production is accompanied by the conjugation of C-C bonds and cross-linking. Given sufficient laser fluences, prolonged exposure produces bursts of positive and negative charge, neutral particles, and light. We attribute burst formation to the accumulation of conjugated carbon bonds in the near surface region. When the peak temperatures generated by successive laser pulses reach a critical level, a burst results. This unusual behavior is associated with the chemistry of the PVDF molecule. In polytetrafluoroethylene, for instance, 157-nm radiation cleaves the polymer backbone to produce small fragments that are continuously removed from the target. Side chain cleavage in PVDF allows damaged material to accumulate until conditions produce a large burst of emission. The charged products accompanying a burst are strongly coupled to form a tenuous plasma, or charge cloud. The positive ions in the charge cloud have kinetic energies of 7-10 eV, consistent with electrostatic ejection from the polymer surface. We show evidence for high electron densities in the charge cloud—sufficient to neutralize most (but not all) of its positive charge. These electrons are largely confined to the charge cloud, and play an important role in generation of negative ions by dissociative electron attachment to neutral species. The relatively high velocity of the charge cloud is matched only by the fastest neutrals. Therefore only the fastest neutral particles are vulnerable to attachment. The spatial and temporal distribution of the product species have important consequences on product evolution prior to deposition. The unsteady emission intensities, with occasional large bursts, provide challenges and opportunities for the growth of PVDF films by laser ablation at 157 nm.

¹ This work was supported by the US Department of Energy under Grant DE-FG02-04ER-15618.

SS-ThP19 Ablation Mechanism In Polytetrafluoroethylene (PTFE) under 157-nm Irradiation¹, S.R. John, J.A. Leraas, S.C. Langford, J.T. Dickinson, Washington State University

Polytetrafluoroethylene (PTFE) (C₂F₄)_n is a model organic polymer with unique properties. In this work, we explore the mechanisms responsible for the superior etching others have demonstrated using 157-nm F₂ excimer lasers. At fluences well below the threshold for plasma formation, the major neutral products are (CF₂)_x units. Thus decomposition is primarily from backbone scission. Mass selected time-of-flight signals for these neutral products show a fast component with energies on the order of 1.2 eV, as well as a slower, thermal component. We attribute the fast component to products formed from scission of C-C bonds due to electronic excitations along the surface. We attribute the slower component to products produced in the bulk, which then diffuse to the surface and desorb. The clean etching of PTFE at 157 nm is the result of dissociative electronic excitations. Nevertheless, analysis of the slow component indicates high surface temperatures. The F₂ laser significantly heats the surface. Intense electron, positive and negative ion emissions are also observed. The high positive ion kinetic energies (3-10 eV) are consistent with an electrostatic emission mechanism. The negative ion signals are an order of magnitude weaker than the positive ions, but display similar kinetic energies (3-5 eV). We attribute negative ion formation to dissociative electron attachment of neutral monomers. This process requires high electron densities, which are observed in the cloud of positive ions. The presence of both positive and negative ions, in addition to reactive (CF₂)_x units, would promote the growth of high quality PTFE films by laser ablation deposition. We will briefly describe the ablation of a another fluorocarbon polymer, polyvinylidene fluoride (PVDF) (C₂H₂F₂)_n, at 157-nm. Initial exposure yields intense emissions of neutral HF due to side chain scission-in contrast to PTFE, where fragmentation is predominately due to backbone scission. The presence of hydrogen in the PVDF renders side chain bonds especially vulnerable. During prolonged irradiation, especially intense bursts of charged and neutral products accompany some laser pulses and not others.

The bursts are presumably due to the accumulation of damaged material in the intervening laser pulses.

[†]This work was supported by the U.S. Department of Energy under Grant DE-FG02-04ER-15618.

SS-ThP20 Solid-Liquid Interface Engineering: Static and Dynamic Hydrophobicities on Self-assembled Monolayer Surfaces, *N. Yoshida*,

The University of Tokyo, Japan, *S. Suzuki*, Tokyo Institute of Technology, Japan, *M. Sakai*, *A. Hashimoto*, Kanagawa Academy of Science and Technology, Japan, *Y. Kameshima*, *A. Nakajima*, Tokyo Institute of Technology, Japan, *T. Watanabe*, The University of Tokyo, Japan

Wettability of solid surface has attracted much attention in many fields, from basic surface science to practical uses. Up to now, numerous studies have sought to interpret the static hydrophobicity (contact angle of a droplet and surface energy/surface tension of solid surface) in terms of the interaction between liquid and solid surface. The static hydrophobicity has been well-clarified (controlled by surface energy and morphology), however, the dynamic hydrophobicity (sliding angle and velocity of a droplet), a measure of dynamic adhesive property against water, is still in controversy. Practically, dynamic hydrophobicity does not simply depend on static hydrophobicity. Thus far, no one could completely explain a fact that hydrophobic surfaces of similar water contact angles often show quite different adhesive property against water. In this study, we successfully prepared various hydrophobic surfaces using alkyl and fluoroalkyl silanes with various adhesive properties against water in terms of solid-liquid interface engineering. We will demonstrate that the dynamic hydrophobicity, a measure of the adhesive property against water, depended on the surface morphology (even of the order of a few nanometers) and surface composition (small amount of polar groups on the surface) and that we could control it independent of static hydrophobicity.

SS-ThP21 Structural, Mechanical and Electronic Properties of Stilbene and Pentathiophene Based Molecular Monolayers, *Y. Qi*,

University of California, Berkeley, *B. Hendriksen*, *V. Navarro*, *D. Esteban*, *J.Y. Park*, *I. Ratera*, *J. Klopp*, Lawrence Berkeley National Laboratory, *C. Mauldin*, University of California, Berkeley, *C. Edder*, Lawrence Berkeley National Laboratory, *J. Frechet*, University of California, Berkeley, *M. Salmeron*, Lawrence Berkeley National Laboratory

The incorporation of molecules in electronic devices is promising for technological applications and a new direction in fundamental research. The structural, mechanical and electronic properties of monolayers of two molecules containing pi-systems have been studied with conducting probe atomic force microscope (CP-AFM), X-ray photoemission spectroscopy (XPS) and near edge X-ray fine structure spectroscopy (NEXAFS). One is *w*-(trans-4-stilbene)alkylthiol, and the other is decyl-pentathiophenyl butyric acid. We found that the *w*-(trans-4-stilbene)alkylthiol molecules self-assemble on Au (111) with the thiol group covalently bond to Au surfaces as confirmed by X-ray photoemission spectroscopy. The molecular film undergoes a slow structural change from a tilted to a more upright geometry, a process that can be accelerated by thermal annealing. In all cases *w*-(trans-4-stilbene)alkylthiol molecules show poor electrical conductivity in the vertical direction. Molecular monolayers of decyl-pentathiophenyl butyric acid were deposited on heavily doped Si (100) by the Langmuir Blodgett technique. The orientation of the molecules has been studied by NEXAFS. Current versus voltage measurements and conductivity mapping reveal a higher conductivity than that of *w*-(trans-4-stilbene)alkylthiol self-assembled monolayers. The friction and the conductivity were observed to strongly depend on the molecular arrangement.

SS-ThP22 Characterization of Chemically Etched Poly(tetrafluoroethylene), *T.R. Richardson*, *F.A. Donate*, *C.L. Gentry*, *D.D. Hawn*, *B.J. Kern*, *G.E. Mitchell*, *G.E. Potter*, *C.W. Reinhardt*, *R.J. Wachowicz*, The Dow Chemical Co., *S. Marsh*, *M.E. Yevich*, Acton Technologies

Chemical etching solutions are typically employed to prepare the surface of poly(tetrafluoroethylene) for bonding to a surface. These etching solutions are based on sodium-naphthalene complexes in an aprotic organic carrier such as a glycol diether. The use of such etchants produces a chemically modified surface suitable for bonding. We employed X-ray photoelectron spectroscopy, static secondary ion mass spectrometry, and atomic force microscopy in order to understand the chemical properties of these etched surfaces. Key to this work was a procedure which utilizes macrotopomy to remove thin layers of material from the surface, but these sections are obtained at a very low angle relative to the surface plane (1° or 1/2°). Using this procedure, the thickness of a layer could be "magnified" 60 or 120 times. This facilitated the use of XPS and SIMS to analyze the surface composition as a function of depth. The procedure developed produced surfaces and thin sections with no measurable smearing or contamination. The design of the apparatus resulted in production of sections or surfaces

with reproducible and accurate appearance and chemistry. In this presentation we will discuss the results obtained from these low angle macrotopomed surfaces, highlighting the chemistry of the surface and the modified zone. The results discussed apply to molded industrial poly(tetrafluoroethylenes).

SS-ThP23 Surface Chemistry of (2,4-dimethylpentadienyl)(ethylcyclopentadienyl)Ru on Polycrystalline Ta, *K.M. Thom*, *J.G. Ekerdt*, University of Texas at Austin

As device dimensions in integrated circuits scale down, there is a need to deposit ultra-thin, conformal, continuous films for various microelectronic applications. Ruthenium (Ru) thin films are promising candidates for applications such as diffusion barriers in copper metallization and capacitors in dynamic random access memories. Chemical vapor deposition and atomic layer deposition have been used to deposit Ru thin films using a variety of precursors, but the surface chemistry of these precursors is largely unexplored. This work examines the surface chemistry of (2,4-dimethylpentadienyl)(ethylcyclopentadienyl)Ru [DER] on polycrystalline tantalum (Ta) foil, with and without the presence of methyl iodide. X-ray photoelectron spectroscopy (XPS) and temperature programmed desorption (TPD) were used to study the adsorption and desorption behavior. Because DER was found to dissociate negligibly at room temperature and above, low temperature experiments were used to examine the interaction of the DER with the Ta foil. The DER was dosed onto Ta at 140 K and then desorbed during the TPD process; XPS spectra were taken both before and after TPD. The DER adsorbs and desorbs molecularly, although a small amount of dissociation occurs during TPD. Both XPS and TPD results indicate that the DER saturates on the surface at an exposure of about 4 Langmuir (L); no multilayers are formed. For exposures up to 0.5 L, a single TPD desorption state is observed at 272 K. As coverage increases, the single state splits into two desorption features which are centered at 264 K and 297 K at saturation. The two states are attributed to different physical states of the molecules; possibly two different molecular orientations occur on the surface. The Ru 3d_{3/2} XPS feature shifts from 286.2 eV to 287.3 eV as exposure is increased from 0.1 L to saturation, a binding energy (BE) change of about 1 eV; the Ru 3d_{5/2} XPS feature also shifts up by 1 eV. The BE shift with increasing coverage is consistent with the presence of two adsorbed states. Because other research has shown alkyl iodides enhance the nucleation of Ru films, methyl iodide was co-dosed into the chamber along with the DER in an attempt to promote dissociation at room temperature and above. The addition of methyl iodide enhanced the dissociation of DER as compared with the molecule alone. This talk will discuss the surface reactions of DER in the presence and absence of adsorbed iodide.

SS-ThP24 X-Ray Photoelectron Spectroscopy for Impedance Measurements, *S. Suzer*, *H. Sezen*, *G. Ertas*, *A. Dana*, Bilkent University, Turkey

A new technique is introduced for probing charging/discharging dynamics of dielectric materials, in which X-ray photoemission data is recorded while the sample rod is subjected to 10.0 V square-wave pulses with varying frequencies in the range of 0.001 to 1000 Hz. This technique allows us to probe electrical impedance of dielectric materials. Accordingly, for a conducting graphite sample the C1s peak appears at correspondingly -10.0 eV and +10.0 eV binding energy positions (20.0 eV difference) with no frequency dependence. However, the corresponding C1s and O1s peaks of polymeric materials (PS, PMMA, and PS/PMMA blends) appear with less than 20.0 eV difference and exhibit strong frequency dependence due to charging of the polymeric films, which are faithfully reproduced by a theoretical model.^{1,2} Information can be obtained from the frequency dependence of the positions, as well as the widths of the peaks. Various applications of this technique for characterization of organic (polymeric) and inorganic homogeneous and heterogeneous materials and surface structures will be presented and discussed.

¹S. Suzer, and A. Dana, J. Phys. Chem. B 110, 19122 (2006).

²H. H. Sezen, G. Ertas, A. Dana, and S. Suzer, Macromolecules (in press).

SS-ThP25 Sliding Behavior of a Water Droplet between Two Hydrophobic Coatings by Self-assembled Monolayer, *A. Nakajima*, *S. Suzuki*, Tokyo Institute of Technology, Japan, *M. Sakai*, *A. Hashimoto*, Kanagawa Academy of Science and Technology, Japan, *N. Yoshida*, The University of Tokyo, Japan, *Y. Kameshima*, *K. Okada*, Tokyo Institute of Technology, Japan

Self-assembled monolayer (SAM) coatings of organosilanes have been widely used for surface modification of inorganic materials. We studied the sliding behavior of water droplets sandwiched between Si substrates treated by octadecyltrimethoxysilane (ODS) and fluoroalkylsilane (FAS) by changing the plates' distance (D) and droplet mass (m). The sliding angle depended on D, m, and the upper and bottom combination of the coating. The droplet between FAS coatings exhibited larger sliding angle than the

ODS coating when $D=1.0$ mm although the FAS coating possesses higher water contact angle. The sliding behavior of water droplets sandwiched between ODS and FAS coatings was observed using a high speed camera system on a declined surface (35 degrees). The larger droplet mass and plate distance, the larger sliding acceleration. The internal fluidity in the droplet visualized by particle image velocimetry method revealed that the droplet slid down with twin flows between plates and that their border was almost the center of the plates. The water droplet sandwiched between FAS/ODS exhibited heterogeneous rolling fluid: the border of the twin flow was not the center between the plates. The magnitude of the rolling fluid depended on the surface chemical composition and the distance between two plates.

SS-ThP26 Characterisation of Self-Assembled Monolayers Using Angle Resolved XPS. *J. Wolstenholme*, Thermo Fisher Scientific, UK, *D.J. Graham*, Asemblon, Inc., *R.G. White*, Thermo Fisher Scientific, UK

Self assembled monolayers (SAMs) are increasingly important as a means to functionalise surfaces and to control surface properties or reactivity. The length of many of the molecules used in these layers and, therefore, the thickness of the monolayers formed by them is often less than the attenuation length of the photoelectrons emitted in the XPS process. This means that the XPS technique is ideal for characterising the layers. The additional benefits coming from ARXPS are also important for the determination of layer orientation and thickness. For this work, the ARXPS data was collected in parallel over a 60 degree range, without the need to tilt the samples. This means that it is possible to collect angle-resolved XPS maps of the surface to examine the uniformity of the layers. If the layers are uniform, data can be collected as a map over a large area to minimise the X-ray flux density used in the analysis. By examining a number of samples having the same SAM at the surface, the precision of the measurements can be determined. Obviously, high precision is required if the two-dimensional uniformity is to be investigated. It will also be shown, using a range of SAM's, that the techniques developed for extracting non-destructive depth profiles from ARXPS data can be successfully applied to these materials. Results will be reported from SAMs formed from alkane thiols and from molecules containing additional functional groups.

SS-ThP27 Study of the Interplay between PDMS and Surfaces Modified with Monolayers and Small Molecules. *L. Yang, F. Zhang*, Brigham Young University, *N. Shirahata, T. Nakanishi*, National Institute for Materials Science, Japan, *M.R. Linford*, Brigham Young University

Here we describe a method for probing the surface free energies of materials by stamping them with polydimethylsiloxane (PDMS) stamps that have also been wet with low molecular weight PDMS. Hydrophobic surfaces, e.g., alkyl monolayers with high advancing water contact angles, resist adsorption of PDMS, while PDMS adsorbs effectively onto hydrophilic or even moderately hydrophobic surfaces. For example, PDMS transfers to thin films of C60, while it does not transfer to thin films of molecules that contain long alkyl chains. In addition, PDMS transfers to hydrophilic spots patterned onto hydrophobic monolayers, but not onto the background. The degree of PDMS transfer can be used to monitor processes such as the contamination of a clean metal surface in the ambient. The PDMS transferred in these cases is easily detected by spectroscopic and imaging time-of-flight secondary ion mass spectrometry (ToF-SIMS) because of the sensitivity of this technique for this species. Wetting, X-ray photoelectron spectroscopy, and principal components analysis of the ToF-SIMS data are also employed to study this problem.

SS-ThP28 Direct Polymer Growth on Hydrogen-Terminated Silicon. *M.R. Linford*, Brigham Young University, *N. Shirahata*, National Institute for Materials Science, Japan, *R.B. Blake, M.V. Lee*, Brigham Young University

When hydrogen-terminated silicon is immersed in a solution of an unsaturated monomer and a free radical initiator, a very thin, ca. 2 nm, thin polymer film grows on the surface, provided the temperature of the reaction mixture is raised to the decomposition point of the initiator. Changing the nature of the monomer, the initiator, and reaction conditions do not seem to lead to the production of significantly thicker polymer layers. However, addition of appropriate chemical reagents allows ca. 10 nm polymeric layers to be directly grown on hydrogen-terminated silicon. This method can be used in conjunction with photopatterning of hydrogen-terminated silicon, which removes hydrogen termination in certain areas on the surface and thus prevents polymer growth in these regions. Surface reactivity and patterning are confirmed by X-ray photoelectron spectroscopy, spectroscopic ellipsometry, and atomic force microscopy.

SS-ThP30 In Situ Real-Time Grazing Incidence Study of Organic Thin Film Growth. *A. Amassian, V.A. Pozdin, S. Bhargava*, Cornell University, *D.-M. Smilgies*, CHESS, Cornell University, *A. Papadimitratos, S. Hong*, Cornell University, *A.R. Woll*, CHESS, Cornell University, *G.G. Malliaras, J.R. Engstrom*, Cornell University

We have performed in situ, real-time grazing incidence X-ray synchrotron measurements during the growth of organic thin films of pentacene. Experiments were carried out on films deposited from both thermal and supersonic sources on a variety of substrates (e.g., SiO₂, photoresists, polymers) and over a broad range of process parameters (e.g., growth rate, temperature, beam kinetic energy). A CCD detector captured both in-plane Bragg peaks and out-of-plane Bragg sheets, allowing us to solve the 3D structure of pentacene crystals. We reveal the formation of new polymorphs of the so-called "thin film" and bulk phases of pentacene, while in situ measurements (video to be shown) provide new insights into the initial growth of organic crystals.

SS-ThP31 Self-Assembled Monolayers of Aromatic Tellurides on Gold and Silver Substrates. *M.T. Weidner*, University of Washington, *A. Shaporenko*, Universität Heidelberg, Germany, *J. Müller, M. Höltig, A. Terfort*, University of Marburg, Germany, *M. Zharnikov*, Universität Heidelberg, Germany

Self-assembled monolayers (SAMs) of tellurolates are promising alternatives to most frequently used thiolate-based systems. In this study we present first experimental data on SAMs of aromatic tellurolates. These SAMs were fabricated on Au(111) and Ag(111) substrates from a ditelluride precursor, bis(4'-methylbiphenyl-4-yl) ditelluride (BBPDTe) and characterized by high resolution X-ray photoelectron spectroscopy and near-edge X-ray absorption fine structure spectroscopy. BBPDTe was found to adsorb dissociatively on both substrates, resulting in the formation of well-defined, densely packed, and ordered BPTe SAMs, with a larger molecular inclination, a lower packing density, and inferior crystallinity on Au than on Ag. However, both BPTe/Au and BPTe/Ag were not stable under ambient conditions, but underwent a rapid autooxidation, which affected exclusively the tellurolate headgroups. The BPTe molecules in the oxidized films remained, however, bound to the substrate by the terminal O atoms coordinated to the Te moieties, and the quality of the films, given by parameters such as packing density, degree of the orientational order, and average tilt angle of the SAM constituents was not noticeably affected by the autooxidation. In addition, the BPTe SAMs were compared with the analogous thiol- and selenol-based systems, and common tendencies for the different chalcogen headgroups, ranging from Te to O, were derived.

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