Surface Science
Room: C-110 - Session SS-FrM

Self-Assembly at Surfaces
Moderator: D.H. Fairbrother, The Johns Hopkins University

8:20am **SS-FrM1 Structure of Nitrile-functionalized Alkanethiolate Monolayers on Gold and Silver**, ***A. Shaporenko***, *S. Frey,* Universität Heidelberg, Germany, *Ph. Harder, D.L. Allara,* Pennsylvania State University, *M. Zharnikov, M. Grunze,* Universität Heidelberg, Germany

Self-assembled monolayers (SAMs) formed from nitrile-functionalized alkanethiols (AT) are perspective candidates for SAM-based lithography and the fabrication of surfaces with low protein affinity. In addition, the polar nitrile group with a relatively large dipole moment is well-suitable to explore to what extent the structure of a non-substituted AT SAM can be affected by strongly interacting tail groups. We used several complementary experimental techniques, such as X-ray photoelectron spectroscopy and near-edge X-ray absorption fine structure spectroscopy at the C1s and N1s absorption edges to get an information on the chemical identity, packing density, and orientational order in SAMs formed from $CN(CH_2)_{16}SH$ (CN-C16) on (111) gold and silver substrates. The results imply that the substitution of the weakly interacting methyl groups by the nitrile entities has a strong influence on the molecular orientation, packing, and the structure of AT SAMs on both gold and silver. A strong dipole-dipole interaction between the polar nitrile groups is assumed to disturb a balance between the headgroup-substrate and interchain interactions, which is responsible for the SAM structure and packing density. In contrast to the methyl-functionalized AT SAMs, only a slight difference in the orientation of the alkyl chains in CN-C16/Au and CN-C16/Ag is observed. The nitrile groups in both CN-C16/Au and CN-C16/Ag are oriented almost parallel to the film surface, which is beneficial to minimize the dipole-dipole interaction between these moieties, but different from the "standard" orientation of the functional groups in ω-functionalized AT SAMs of the same chain length.

8:40am **SS-FrM2 Self-assembled Monolayers on Aluminium: The Role of Oxide Surface Chemistry**, *T.A. Lewington, I. Liakos, G.E. Thompson, R.C. Newman,* UMIST, UK, *E. McAlpine,* Alcan International, UK, ***M.R. Alexander***, UMIST, UK

Application of self-assembling organics molecules on oxide-covered, metal surfaces is of growing interest in areas ranging from medical implants[1] to adhesion promotion pre-treatments.[2] In the latter application area, legislation is driving industry to explore environmentally friendly pre-treatments for aluminium. Corrosion protection has been obtained using di-functional alkyl-phosphonic acids assembled on aluminium as a paint pre-treatment. It has been shown that one of the phosphonic acid head-groups form a phosphonate bond with the hydroxylated oxide film at the surface of the aluminium.[3] In addition to coupling of the resin and surface, it has been proposed that hydration is inhibited at the phosphonate-aluminium interface.[4] In contrast to the stable gold surface utilised in the assembly of alkane-thiols, the oxide at the aluminium surface is readily hydrated on exposure to ambient conditions.[5] It is proposed that this instability causes the inconsistent self-assembly often obtained on the aluminium surface. Thus, the oxide surface chemistry of magnetron sputtered aluminium has been controlled using solution and atmospheric conditioning; the effect on self-assembly of alkane-phosphonic acids is reported. XPS has been used to provide oxide thickness and surface hydroxyl concentration while contact angle and FTIR measurements have been used to probe the SAM coverage and order. Evidence for hydration inhibition by phosphonic acids SAMs is presented.

[1] G. L. KENAUSIS et al. J Phys Chem B 104 (2000) 3298.
[2] I. MAEGE et al Prog Org Coatings 34 (1998) 1.
[3] R. D. RAMSIER et al. Surf Sci 203 (1988) 72.
[4] A. DAVIS et al. J Mater Sci 20 (1985) 975.
[5] M. R. ALEXANDER et al. Surf Int Anal 29 (2000) 468.

9:00am **SS-FrM3 A Thermodynamic Perspective on Self-Assembled Monolayer Growth**, ***D.K. Schwartz***, *J. Mellott,* University of Colorado, *I. Doudevski,* University of California, Santa Barbara, *W. Hayes,* Crompton Corp., *C. Messerschmidt,* Infinion Corp. **INVITED**

Self-assembled monolayers form spontaneously at the solution/solid interface as a consequence of molecular adsorption and two-dimensional self-organization. The self-organization process can be viewed from the perspective of the nucleation and growth of a dense 2D phase (solid) from a less dense phase. In particular, the nucleation and growth kinetics of solid clusters in coexistence with a 2D "vapor" phase agree quantitatively with models of vapor phase epitaxial growth that predict growth regimes and scaling exponents. Other growth mechanisms are found, however, when the adsorbate/substrate interaction is varied. In fact, one can observe a qualitative change in the growth mechanism for a single system as a function of temperature. These mechanisms can be classified into three classes which can be viewed in a 2D thermodynamic context as occurring (1) below the liquid-vapor triple point, (2) above the liquid-vapor triple point, and (3) above the liquid-"solid" critical point, respectively.

9:40am **SS-FrM5 pH-Dependence of the Interaction Between Functionalized Probes and Tri(Ethylene Glycol)-Terminated Self-Assembled Monolayers on Gold Studied with Force Spectroscopy**, ***C. Dicke***, *G. Haehner*, University of St Andrews, UK

The understanding of protein adsorption on ultrathin synthetic surfaces has attracted considerable interest in recent years. In particular, the understanding of non-specific interactions is one of the major concerns. Functionalized self-assembled monolayers (SAMs) represent a class of ultrathin model surfaces that allow it to study the resistance to protein adsorption. Several recent investigations demonstrated the outstanding protein repelling properties of SAMs formed by oligo(ethylene glycol) (OEG) terminated alkanethiols on gold. Different suggestions have been made in order to explain this observation. Due to the strong hydration of the EG units in aqueous solutions an extended net-like structured water layer has been proposed to be responsible for the observed behaviour. The possibility of a specific incorporation of ions from solution into the self-assembled structure has also been suggested. Furthermore, it has been speculated that interactions of hydroxyl and/or hydronium ions with the synthetic interface play a major role. In order to elucidate the nature of the forces underlying the protein resistance in more detail, SAMs of methoxy-tri(ethylene glycol)-terminated undecanethiolates (EG3-OMe) adsorbed on polycrystalline gold were investigated by chemical force spectroscopy under liquids. Measurements with differently functionalised probes were performed under aqueous solutions with various ionic strengths and pH-values.

10:00am **SS-FrM6 Extraordinary Properties of the C 1s Photoemission Line of n-alkanethiolates on Gold and Silver**, ***K. Heister***, *M. Zharnikov,* University Heidelberg, Germany, *L.S.O. Johansson,* University Karlstad, Sweden, *M. Grunze,* University Heidelberg, Germany

The investigation of the C 1s photoemission line for n-alkanethiolate SAMs by synchrotron-based high resolution x-ray photoelectron spectroscopy (HRXPS) shows surprising properties. The energetic position of the C 1s emission line varies significantly by changing the substrate from Au to Ag. The analysis of this effect suggests that the observed shift of about 0.3-0.4 eV is only indirectly related to the substrate. Instead it seems to resemble the details of the film structure which change with the substrate. Besides we have observed that the C 1s peak shape alters with increasing alkyl chain length. The course of the peak shape evolution suggest a deconvolution of the C 1s emission line in several constituents. They can be attributed partly to intrinsic energy losses and partly to the influence of the close SAM-substrate interface on the innermost carbon atoms.

10:20am **SS-FrM7 Temperature-Programmed Desorption and Scanning Tunneling Microscopy Studies of n-Alkane Derivatives on Graphite: Desorption Energetics and the Influence of Functional Groups on Adsorbate Self-Assembly**, ***T. Müller***, *K.T. Rim, G.W. Flynn,* Columbia University, *A.V. Teplyakov*, University of Delaware

While carbon materials have found many practical applications ranging from sorption and catalyst support to the protection of magnetic storage media, numerous further uses may follow from the more recently discovered allotropes, fullerenes and carbon nanotubes. Alkane derivatives on the inert support provided by graphite can serve as model systems to study organic thin films and two-dimensional self-assembly. In the present study, Temperature Programmed Desorption (TPD) and Scanning Tunneling Microscopy (STM) are utilized to examine the influence of functionalization on the adsorption energetics and self-assembly of n-alkanes on Highly-Oriented Pyrolytic Graphite (HOPG). For adsorption of 1-bromoalkanes, alkanoic acids, and 2-bromoalkanoic acids, full activation of the substrate surface required annealing temperatures of approximately 700 K. Molecular desorption from physisorbed mono- and multilayers was found to exhibit first and zeroth-order kinetics, respectively. A Redhead analysis of monolayer desorption signals uncovered a profound influence of alkane functional groups. As compared with unfunctionalized n-alkanes, the desorption energies of all derivative species studied here exhibit a reduced chain length dependence in conjunction with an increased adsorption energy in the limit of zero chain length. Both effects reach their maximum for 2-bromoalkanoic acids, where (up to 2-bromooctanoic acid) the adsorption energy is nearly independent of the number of methylene units. The presence of functional groups is seen to introduce additional interactions, causing added configurational constraints and a competition with alkyl chain interactions in determining self-assembly patterns. These trends will be discussed in the context of molecular self-assembly information provided by ambient (liquid/solid) and UHV STM studies.

10:40am **SS-FrM8 Nanomolecular Motion Induced by Molecular Rectificator in the Self-Assembled Monolayers**, ***T. Ishida***, National Institute of Advanced Industrial Science and Technology (AIST), Japan, *H. Fukushima*, JRCHMM -JCII and TPRC, SEIKO EPSON Corporation, Japan, *T. Tamaki, H. Tokumoto*, National Institute of Advanced Industrial Science and Technology (AIST), Japan

Nanoscale molecular motion induced by polarity change of the electric field was observed by scanning tunneling microscopy (STM), when small amounts of asymmetrical disulfides containing terphenyl moieties were embedded into pre-assembled dodecanethiol self-assembled monolayers (SAMs). The class of disulfide was specifically designed to perform the large dielectric anisotropy in the terphenyl moiety. At the positive tip bias, few of protrusions were observed. When the STM tip bias turned to negative, many protrusions appeared on the binary monolayer surface. Scanning tunneling spectroscopy (STS) revealed the higher rectification property at the area of the terphenyl terminated monolayer where also showed the higher electrical conduction at the negative tip bias compared to positive one. The higher electrical conduction at the negative tip bias was likely to retract the STM tip, showing the apparent nanomolecular motion by the polarity change. Our observed nanomotion (about 1 min) is much faster than previously observed switching time (at least 20 min).[1] Also, the apparent molecular motion can be observed in the case of nanometer scale domains as well as single molecule.

[1] Z.J. Donhauser et al., Science 292 (2001) 2303-2307.

11:00am **SS-FrM9 Conductance Switching in Single Molecules**, ***Z.J. Donhauser****, *T.P. Pearl, P.S. Weiss*, The Pennsylvania State University

We have studied functionalized phenylene ethynylene oligomers as candidate molecular electronic devices using scanning tunneling microscopy (STM). A simple self-assembly strategy has been demonstrated that allows us to control monolayer structure, placement of individual molecules, and switching activity of individual molecules. Alkanethiolate self-assembled monolayers (SAMs) were used as host matrices to isolate and to insulate individual candidate molecular electronic devices. The isolated molecules were individually addressed and electrically probed using STM imaging and spectroscopy. The guest molecules exhibit reversible conductance switching, manifested as a change in the topographic height in STM images. High and low conductance states are visible when the molecules are inserted in dodecanethiolate SAMs, but the low conductance states are of the same height or lower than the host matrix. Using thin alkanethiolate matrices (as low as octanethiolate) reveals that the molecules can occupy at least three discrete conductance states. The amount and rate of active switching can be mediated by the structure of the host matrix. Poorly ordered SAMs were produced using a short deposition time; molecules inserted in these monolayers have a high switching activity. Well-ordered SAMs were produced using a vapor annealing procedure, which has been demonstrated with mixed alkanethiolate monolayers. Guest molecules inserted in vapor annealed SAMs have a low switching activity.

11:20am **SS-FrM10 Metastable Nanopattern Formation during Pb/Cu(111) Self-Assembly**, *R. van Gastel, R. Plass*, Sandia National Laboratories, Albuquerque, *N.C. Bartelt*, Sandia National Laboratories, Livermore, ***G.L. Kellogg***, Sandia National Laboratories, Albuquerque

Competing inter-atomic interactions on surfaces can lead to the spontaneous formation of ordered 2-D domain patterns in widely varying systems. The potential use of such patterns as templates for the fabrication of nanostuctures has fostered considerable interest in the underlying self-assembly process. Recently, it has been discovered that two phases of Pb on Cu(111) (a surface alloy and a Pb overlayer) self-assemble into nanoscale domain patters.[1] As the Pb coverage increases, the equilibrium patterns progress from islands of the overlayer (droplets) to stripes to islands of the alloy (inverted droplets). These equilibrium patterns are not the only patterns that can be constructed, however. Here, we use low energy electron microscopy to investigate metastable patterns that can be created by varying the temperature and deposition sequence. These include a stripe phase formed at low Pb coverages, and metastable droplet and inverted droplet phases, in which the island sizes are larger than those of the equilibrium structures. Both the droplet and inverted droplet metastable structures can develop into "froth" patterns -- the 2-D analog of soap bubbles. These patterns evolve in a deterministic manner. If the droplet phase from which a froth phase is created is ordered, a stable array of ordered hexagonal domains results. If the initial droplet phase is not ordered, the froth phase coarsens by a well-defined set of rules.[2] Thus, Pb on Cu(111) provides a model system both to explore the type of metastable patterns that can be formed for nano-template applications and to determine the laws that govern the formation, evolution and stability of nanometer-scale, 2-D patterns. Work supported by the U. S. DOE under Contract DE-AC04-94AL85000.

[1] R. Plass, J. A. Last, N. C. Bartelt, and G. L. Kellogg, Nature 412, 875 (2001)

[2] D. Weaire and N. Rivier, Contemp. Phys. 25, 59 (1984)

11:40am **SS-FrM11 Buffer-Layer-Assisted Nanostructure Growth Via Two-Dimensional Cluster-Cluster Aggregation**, *C.L. Haley*, ***V.N. Antonov***, *J.H. Weaver*, University of Illinois at Urbana-Champaign

Physical vapor deposition of metals onto Xe multilayers at 20 K produces three-dimensional clusters. Warming to room temperature desorbs the Xe and causes coalescence. The net motion, and hence the extent of coalescence, depends on the buffer layer thickness. Using transmission electron microscopy, we determined the spatial distribution of these nanostructures as a function of Xe thickness. Using the scaling concepts of cluster-cluster aggregation, we found a fractal dimension ranging from 1.42 to 1.72 for initial fractional coverages of 0.04 to 0.20, consistent with Monte Carlo simulations of two-dimensional diffusion-limited cluster aggregation (DLCA). Both the number density and the weighted average nanostructure size show a power law dependence on the Xe layer thickness, where the latter plays the role of time in DCLA modeling. These relationships facilitate the design of nanostructure arrays generated by desorption-assisted coalescence.

***** Morton S. Traum Award Finalist

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