Nanometer-scale Science and Technology
Room: 311 - Session NS+NC-ThM

Nanoscale Assembly
Moderator: L.E. Ocola, Argonne National Laboratory

8:00am NS+NC-ThM1 Confinement of Electrochemical Metal Deposition on the Nanometer Scale by a Hydrogen-Bonded Network/SAM Hybrid Structure, *C. Silien, M.T. Räisänen*, University of St. Andrews, UK, *R. Madueño,* Universidad de Córdoba, Spain, *M. Buck*, University of St. Andrews, UK

The combination of supramolecular networks with thiol-based self-assembled monolayers (SAMs) offers interesting opportunities as the flexibility in surface functionalisation afforded by SAMs can be carried to an unprecedented level of precision. The scope for nanotechnological applications broadens even further by processing these hybrid systems in an electrochemical environment. Recently we have shown that an extended bimolecular network on Au(111) with a periodicity of 3.5 nm can be prepared from a solution of perylene-3,4,9,10-tetracarboxylic di-imide (PTCDI) and 1,3,5-triazine-2,4,6-triamine (melamine) and that this open hexagonal structure is sufficiently robust to act as template for thiol adsorption.[1] Proper control of the preparation parameters allows filling of the network pores without altering the framework. This leads to patterned self-assembled monolayers that reflect the periodicity and symmetry of the network with islands of thiol molecules kept apart by the PTCDI-melamine backbone. This hybrid structure can then be used as nanoscaled template for the electrodeposition of metal. Using scanning tunneling microscopy the underpotential deposition (UPD) of Cu was investigated where a monolayer of Cu is intercalated at the molecule-substrate interface. In contrast to continuous thiol SAMs where Cu UPD originates at major defects in the SAM and spreads by interfacial diffusion,[2] the hybrid structure acts as a barrier against interfacial diffusion and, thus, confines metal electrodeposition to the thiol-filled cells.[1] As a result a regular pattern forms where metal UPD islands are separated by the PTCDI-melamine framework.

[1] Madueño, R.; Räisänen, M.; Silien, C.; Buck, M. Nature 2008 (in print).
[2] Silien, C.; Buck, M. J. Phys. Chem. C 2008, 112, 3881-3890.

8:20am NS+NC-ThM2 FIB Induced Self-Assembly of InAs Quantum Dots, *M.J. Noordhoek, J.Y. Lee, H. Mckay, A. Dehne, P. Rudzinski, J.M. Millunchick*, University of Michigan - Ann Arbor

The use of various patterning techniques for self-assembly of highly regular and dense quantum dot arrays are being pursued for applications in opto-electronics and quantum computing. In this work, we use a novel in-vacuo focused ion beam and growth system to pattern an array of holes on GaAs for subsequent deposition of InAs quantum dots. Exposure of GaAs(001) substrates to a 30keV 10pA beam of Ga+ ions as a function of pitch 140<L<547nm and dwell time 200<t<1600 microseconds results in well defined arrays of nanometer deep holes. The diameter (20<d<60nm) and depth (0.7<z<4.4nm) of these holes varies somewhat with dwell time and pitch according to atomic force microscopy. The fidelity of the hole array itself depends on dwell time per spot, and not as strongly on the pitch of the pattern. Growth of InAs upon these arrays shows that quantum dots nucleate exclusively at the hole edges. For example, holes spaced 140nm apart and fabricated with a dwell time of 1600 microseconds results in holes that are 38nm in diameter and 4nm deep. Growth of 1.8ML of InAs upon this pattern of holes results in multiple quantum dots that are on average 30nm in diameter nucleated around the edges. Deposition of additional InAs results in coalescence of these dots such that they cover the hole, resulting in quantum dots that are 60nm, much larger than quantum dots assembled without a pattern. Liquid nitrogen temperature photoluminescence studies show that the peak emission varies with deposited thickness and ion dose.

8:40am NS+NC-ThM3 Fabrication and Characterization of Conjugated Organosilicon Nanostructures with UHV STM and X-Ray Spectroscopy, *M.A. Walsh, J.-C. Lin, J.-H. Kim*, Northwestern University, *K.H. Bevan*, Purdue University, *G.Y. Stokes, F. Geiger, S.T. Nguyen, M.J. Bedzyk, M.C. Hersam*, Northwestern University

Functionalized organic nanostructures on silicon present unique opportunities for integrating molecular electronic devices and sensors with conventional microelectronics. Of particular interest are 1-alkyne molecules since they have been shown to retain pi character following covalent attachment to the silicon surface, thus creating fully conjugated organosilicon nanostructures.[1] In an effort to quantify the structure and chemistry of 1-alkyne molecules mounted on silicon surfaces with atomic-

scale spatial resolution, this study probes phenylacetylene and 1-bromo-4-ethynylbenzene adlayers on the Si(100)-2x1:H surface with ultra-high vacuum (UHV) scanning tunneling microscopy (STM) and complementary synchrotron X-ray techniques. UHV STM images reveal well-ordered one-dimensional nanostructures consisting of 1-alkynes that are aligned with the underlying silicon dimer rows. This observed alignment is consistent with the radical mediated chain growth reaction mechanism that has been previously observed for 1-alkenes on silicon. In an effort to provide further evidence in support of this mechanism, a suite of additional surface science techniques and theoretical calculations have been applied to this system. Specifically, the bromine tag on 1-bromo-4-ethynylbenzene can be probed with synchrotron X-ray radiation.[2] For example, X-ray photoelectron spectroscopy confirms that the bromine moiety remains intact following attachment to the silicon surface. Additional X-ray techniques, such as X-ray standing wave (XSW), X-ray fluorescence (XRF), and X-ray reflectivity (XRR), allow the bromine position to be triangulated with sub-angstrom precision. In particular, these X-ray measurements yield a bromine height of 8.85 angstroms above the bulk-like silicon, which agrees well with theoretical values determined by periodic density functional theory. The agreement between the theoretical and experimental results provides strong evidence for the expected sp2 hybridization of the terminal carbon-carbon bond. Overall, this study reveals 1-alkynes as a promising chemistry for forming conjugated organosilicon nanostructures on technologically relevant silicon surfaces.

[1] Cicero, R.L., M.R. Linford, and C.E.D. Chidsey, Langmuir, 2000. 16(13): p. 5688-5695.
[2] Basu, R., et al., Langmuir, 2007. 23(4): p. 1905-1911.

9:00am NS+NC-ThM4 The Driving Forces Underlying the Formation of Chiral Domains of Fluorinated Diacids on HOPG, *S.N. Patole, C.J. Baddeley, M. Schuler, D. O'Hagan, N.V. Richardson*, University of St Andrews, UK

Long chain hydrocarbons were designed and synthesized with carboxylic acid functionalities at each end and two amide linkages in the central region of the molecule. The amide linkages are separated by two –CHF- units. These units are each chiral centres and the molecules were synthesized as a racemic mixture of (R,R) and (S,S) species. We report an STM investigation of the adsorption of these molecules onto highly oriented pyrolytic graphite (HOPG) from phenyloctane solution. There are a number of motivations for this study. Firstly, we are interested in establishing control over 2-D assembly via intermolecular H-bonding interactions. Secondly, we assess the use of fluorine atoms as contrast agents in STM to aid the elucidation of structural aspects of complex molecule adsorption at surfaces. Thirdly, we are interested in the influence of chirality on the ordered adlayers produced on HOPG. The molecules adopt a flat lying geometry on graphite. The conformation of the central (fluorinated) section of the adsorbed molecular species differs significantly from the preferred geometry in the crystal structure. We demonstrate that the ordered molecular assemblies produced are dictated by a combination of effects including the preference of carbon backbones to align along high symmetry directions of HOPG; steric constraints imposed by the C-F bonds at the chiral centres and intermolecular H-bonding. We outline a heirarchy of effects which determine the lateral stacking and head-to-head interactions and explain the influence of stereochemistry on the molecular ordering. We conclude that enantiomerically pure 1-D domains are produced and examine the behaviour at the boundaries between domains of each enantiomer.

9:20am NS+NC-ThM5 Potential-Controlled Force Curve Measurements between Electroactive Self-Assembled Monolayers, *Y. Yokota, T. Yamada*, RIKEN (The Institute of Physical and Chemical Research), Japan, *M. Kawai*, RIKEN and The University of Tokyo, Japan

It has been known that atomic force microscopy (AFM), in addition to providing topographic information, can be used to discriminate surface functional groups.[1] One of the most established methods is based on the surface sensitivity of the adhesion force between the tip and sample. Several groups have tried to electrochemically modify the interfacial properties by applying the appropriate potential.[2] We present the force curve measurements between electroactive ferrocene (Fc)-terminated Self-assembled monolayers (SAMs) under independent control of the tip and sample potentials. From the cyclic voltammetry of Fc SAM, the electronic states of Fc moieties in each force curve measurement were characterized.[3] The adhesion force of Fc SAM was drastically changed with the oxidation state of the Fc moieties (Fc or Fc^+). According to the previous wettability measurements, hydrophobicity of the Fc-terminated SAMs is decreased with the oxidation of Fc moieties.[4] Because the adhesion force in aqueous solutions is largely determined by hydrophobicity, the oxidation-state dependence of the hydrophobicity is responsible for the adhesion force change. We performed two control experiments using methyl (CH_3) and

amino (NH_3^+)-terminated SAMs. Unlike in the case of Fc SAM, the force curves, both the approach and retraction curves, did not change with the applied potential. This indicates that the force curve measurements in this study are largely regulated by the effects of surface functional group rather than charging of double layer. Although Fc^+ and NH_3^+ SAMs contain almost the same amount of functional groups, their repulsive forces between the tip and sample considerably differed depending on the surrounding environment of counter anions. These results demonstrate that this AFM-based technique can be a powerful tool for investigating the ion pair formations.

[1] A. Noy et al., Annu. Rev. Mater. Sci. 27, 381 (1997).
[2] H.-C. Kwon et al., J. Phys. Chem. B 109, 10213 (2005).
[3] Y. Yokota et al., J. Phys. Chem. C 111, 7561 (2007).
[4] N. L. Abbott et al., Langmuir 10, 1493 (1994).

9:40am NS+NC-ThM6 Self-Assembly of Nanostructures and Nanocomposites using De Novo Designed Helix- Loop- Helix Polypeptides, *D. Aili, K. Enander,* Linköping University, Sweden, *L. Baltzer,* Uppsala University, Sweden, *B. Liedberg*, Linköping University, Sweden

Self-assembly has emerged as a promising and powerful technique for fabrication of complex hybrid materials and nanocomposites. This contribution will discuss how folding of a set of de novo designed polypeptides can be utilized for the assembly of fibers, fibrous nanostructures and gold nanoparticles. The 42-mer polypeptides fold into four-helix bundles upon dimerization. The peptides are rich in either Glu or Lys which render them a high negative or positive net charge, respectively. Charge repulsion prevents homodimerization at neutral pH while promoting heterodimerization through the formation of stabilizing salt bridges. For the Glu rich polypeptide, homodimerization can be induced at acidic (pH<6) or by addition of certain metal ions, such as Zn^{2+}.[1] The polypeptides have a single Cys in the loop region to facilitate directed immobilization onto gold substrates. The Cys can also be utilized to connect two polypeptides via a disulphide bridge. The disulphide-linked polypeptides spontaneously and rapidly assemble into micrometer long fibers with a diameter < 5 nm as a result of a propagating association mediated by folding. In addition, the fibers have been observed to assemble into highly symmetric nano-rings. Furthermore, the polypeptides enable reversible, folding induced assembly of gold nanoparticles with defined interparticle distances.[1] Aggregation of polypeptide functionalized nanoparticles can be induced in a number of ways utilizing the highly specific interactions involved in both homodimerization and hetero-association. Furthermore, particle aggregation can be utilized to induce folding of the immobilized polypeptides. Helix-loop-helix polypeptides can also be utilized as a robust scaffold, or synthetic receptor, for biosensor applications.[2] The sensor scaffold was, as a proof of concept, site-selectively modified with a benzenesulfonamide moiety that provides a specific recognition site for Human Carbonic Anhydrase II (HCAII). Gold nanoparticles functionalized with the sensor polypeptide enabled simple colorimetric detection of HCAII.

[1] D. Aili, K. Enander, J. Rydberg, I. Nesterenko, F. Björefors, L. Baltzer, B. Liedberg, J. Am. Chem. Soc. 2008, 130, 5780-5788.
[2] K. Enander, G. T. Dolphin, L. Baltzer, J. Am. Chem. Soc. 2004, 126, 4464.

10:40am NS+NC-ThM9 Non-IPR C_{60} Solids, *D. Löffler,* Universität Karlsruhe, Germany, *N. Bajales,* Universidad Nacional del Litoral-CONICET, Argentina, *M. Cudaj, P. Weis, A. Böttcher, M.M. Kappes*, Universität Karlsruhe, Germany

Thin monodisperse films consisting of primarily non-IPR C_{60} isomers (IPR = Isolated Pentagon Rule) have been generated by depositing vibronically excited C_{60} ions on HOPG and subsequently sublimating the undesired IPR $C_{60}(I_h)$ isomer from the deposited mixture. The deposition procedure is based on UHV-compatible soft-landing of mass-selected carbon cluster ions on substrates (Low Energy Cluster Beam Deposition, LECBD). Beams of non-IPR C_{60} cations were produced by electron-impact mediated heating and ionization of various buckminsterfullerenes. The associated excitation processes activate the Stone-Wales rearrangement of carbon atoms in the cage (S-W), which creates non-IPR sites on C_{60} cages. The relative amount of these S-W isomers, C_{60} (S-W), deposited from the beam of hot C_{60} ions scales with the kinetic energy of electrons used for excitation/ionization. Essentially pure C_{60}(S-W) films were obtained simply by heating as deposited (mixed isomer) films up to ~600 K. This results in the thermal desorption of most IPR cages, $C_{60}(I_h)$. The topography of the resulting films, as studied by means of AFM, is governed by the aggregation of the C_{60}(S-W) cages and reflects intercage bonds constituted by non-IPR sites. These covalent intercage bonds are responsible for the higher stability of the C_{60}(S-W) films as mirrored by a sublimation offset at ~1100 K (compared to $C_{60}(I_h)$ which sublimes at ~ 550 K). In contrast to the characteristic doublet structure of the HOMO-derived band in C_{60} (I_h) films, the valence band of the C_{60}(S-W) films exhibits a triplet with a well distinguishable additional peak at a binding energy of ~2.6 eV. This results from electronic modifications induced by intercage bonds. The C_{60}(S-W) films exhibit a narrower HOMO-LUMO gap than found for $C_{60}(I_h)$ films.

11:00am NS+NC-ThM10 Plasma Functionalized Surfaces for Chemically Directed Assembling of Luminescent Nanocrystals for Sensing and Optoelectronic Application, *E. Sardella,* CNR-IMIP, Italy, *F.D. Liuzzi,* University of Bari, Italy, *R. Comparelli, N. Depalo,* CNR-IPCF, Italy, *A. Agostiano,* University of Bari, Italy, *M.L. Curri, M. Striccoli,* CNR-IPCF, Italy, *P. Favia, R. d'Agostino*, University of Bari, Italy

Nanotechnology is increasingly oriented towards the fabrication of devices based on colloidal inorganic nanocrystals (NCs) arranged on a surface. Such interest is justified by the expectation that the controlled assembly of NCs, with relevant size-, shape-, and composition-dependent properties, will open access to unusual collective phenomena relevant to novel technological applications. The chemically-directed assembly of NCs onto substrates allow to obtain functionalities on multiple locations and levels. This approach requires the introduction of suitable functionalities at the NC surface, in order to tune their reactivity without altering the original structural and the chemical-physical properties, also at the interface with substrate, where the NC assembly will take place.[1,2] Several strategies are currently employed to drive NCs assembly onto different substrates, with some limitations. In this work alternative plasma based routes are considered in order to fabricate functionalized substrates with an accurate control on the surface treatment depth. Plasma technology is used to produce customized surfaces irrespectively to the material composition, also to define patterns for the subsequent NC immobilization.[3] The obtained functionalized surface are then exploited to assembly red emitting CdSe@ZnS core shells NCs. The results have successfully demonstrated the effectiveness of such an assembling approach, thus envisioning promising application for the nanostructured materials in optoelectronic and sensing field.[4] Acknowledgements: PRISMA-INSTM 05MADA1 and EC NaPa-NMP4-CT-2003-500120 projects are acknowledged for the financial support.

[1] E. Fanizza et al., (2007) Advanced Functional Materials, 17, 201
[2] N. Depalo et al., J. Phys. Chem B (2006), 110, 17388
[3] E. Sardella et al, Plasma Process. and Polym. (2006) 3, 456
[4] R. Comparelli et al. in: Nanomaterials for Biosensors Vol. 8 Nanotechnologies for the Life Sciences; WILEY-VCH, 2006, 123

11:20am NS+NC-ThM11 Insertion of Block Copolymers Into the Lithographic Process, *P.F. Nealey, J.J. de Pablo*, University of Wisconsin-Madison **INVITED**

Self-assembling materials spontaneously form structures with well-defined dimensions and shapes at length scales of interest in nanotechnology. In the particular case of block copolymer materials, the thermodynamic driving forces for self-assembly are small and low-energy defects can get easily trapped. At issue is the extent of direction or guidance required to meet criteria related to perfection and registration for use of such materials in nanofabrication. We explore and develop new materials and processes for advanced lithography in which self-assembling block copolymers are integrated into and advance the performance of the patterning process for semiconductor manufacturing and data storage applications. Through fundamental understanding of the physics and chemistry of interfacial phenomena associated with equilibrating block copolymer films in the presence of lithographically defined chemically nanopatterned substrates, we synthesize and assemble materials to enable fabrication at length scales (3-20 nm) currently not possible. Essential attributes of existing manufacturing practices must be retained, including pattern perfection, registration and overlay, and the ability to pattern device-oriented geometries, but with additional qualities including resolution enhancement and precise control over the shapes and dimensions of patterned features.

Authors Index

Bold page numbers indicate the presenter

— **A** —

Agostiano, A.: NS+NC-ThM10, 2
Aili, D.: NS+NC-ThM6, **2**

— **B** —

Baddeley, C.J.: NS+NC-ThM4, **1**
Bajales, N.: NS+NC-ThM9, 2
Baltzer, L.: NS+NC-ThM6, 2
Bedzyk, M.J.: NS+NC-ThM3, 1
Bevan, K.H.: NS+NC-ThM3, 1
Böttcher, A.: NS+NC-ThM9, **2**
Buck, M.: NS+NC-ThM1, 1

— **C** —

Comparelli, R.: NS+NC-ThM10, 2
Cudaj, M.: NS+NC-ThM9, 2
Curri, M.L.: NS+NC-ThM10, 2

— **D** —

d'Agostino, R.: NS+NC-ThM10, 2
de Pablo, J.J.: NS+NC-ThM11, 2
Dehne, A.: NS+NC-ThM2, 1
Depalo, N.: NS+NC-ThM10, 2

— **E** —

Enander, K.: NS+NC-ThM6, 2

— **F** —

Favia, P.: NS+NC-ThM10, 2

— **G** —

Geiger, F.: NS+NC-ThM3, 1

— **H** —

Hersam, M.C.: NS+NC-ThM3, 1

— **K** —

Kappes, M.M.: NS+NC-ThM9, 2
Kawai, M.: NS+NC-ThM5, 1
Kim, J.-H.: NS+NC-ThM3, 1

— **L** —

Lee, J.Y.: NS+NC-ThM2, 1
Liedberg, B.: NS+NC-ThM6, 2
Lin, J.-C.: NS+NC-ThM3, 1
Liuzzi, F.D.: NS+NC-ThM10, 2
Löffler, D.: NS+NC-ThM9, 2

— **M** —

Madueño, R.: NS+NC-ThM1, 1
Mckay, H.: NS+NC-ThM2, 1
Millunchick, J.M.: NS+NC-ThM2, 1

— **N** —

Nealey, P.F.: NS+NC-ThM11, **2**

Nguyen, S.T.: NS+NC-ThM3, 1
Noordhoek, M.J.: NS+NC-ThM2, **1**

— **O** —

O'Hagan, D.: NS+NC-ThM4, 1

— **P** —

Patole, S.N.: NS+NC-ThM4, 1

— **R** —

Räisänen, M.T.: NS+NC-ThM1, 1
Richardson, N.V.: NS+NC-ThM4, 1
Rudzinski, P.: NS+NC-ThM2, 1

— **S** —

Sardella, E.: NS+NC-ThM10, **2**
Schuler, M.: NS+NC-ThM4, 1
Silien, C.: NS+NC-ThM1, **1**
Stokes, G.Y.: NS+NC-ThM3, 1
Striccoli, M.: NS+NC-ThM10, 2

— **W** —

Walsh, M.A.: NS+NC-ThM3, **1**
Weis, P.: NS+NC-ThM9, 2

— **Y** —

Yamada, T.: NS+NC-ThM5, 1
Yokota, Y.: NS+NC-ThM5, **1**