Molecular and Bio-Magnetism
Room: C-205 - Session MB+BI+OF-TuA

Molecular and Bio-Magnetism
Moderator: M. Grunze, Heidelberg Universität, Germany

2:00pm **MB+BI+OF-TuA1 Single-Molecule Magnets: A Molecular Approach to Nanoscale Magnetic Materials**, ***G. Christou***, *M. Soler, N. Aliaga-Alcalde, S. Bhaduri*, University of Florida, *W. Wernsdorfer*, Laboratoire Louis Neel - CNRS, France, *D.N. Hendrickson*, University of California at San Diego **INVITED**

Single-molecule magnets (SMMs) are molecules that function as single-domain magnetic particles which, below their blocking temperature, exhibit the classical macroscale property of a magnet, namely magnetization hysteresis.[1] SMMs owe their properties to a combination of a large ground state spin value and easy-axis-type anisotropy, which give a significant barrier to magnetization relaxation. SMMs thus represent a molecular (or bottom up) approach to new nanoscale magnetic materials, offering all the advantages of molecular chemistry (room temperature synthesis, purity, solubility in many solvents, a well defined periphery of organic groups, a crystalline ensemble of monodisperse units) as well as displaying the superparamagnetism of a mesoscale magnetic particle. They also display quantum tunneling of magnetization (QTM), emphasizing that they straddle the interface between the classical and quantum regimes. SMMs have many potential applications, but these require that their properties be both understood and controlled, particularly QTM. The Mn12 SMMs are the best understood. Various derivatives have been prepared differing in the organic groups, and it has been discovered that the magnetic properties (including QTM) can be significantly altered. This is also possible by adding additional electrons, and both the [Mn12]- (S = 19/2) and [Mn12]2- (S = 10) versions have been prepared. Mn4 SMMs with S = 9/2 have also been extensively studied. In some cases, two Mn4 SMMs occur as supramolecular dimers, [Mn4]2, and exchange interactions between them lead to interesting modifications of their QTM properties, establishing the feasibility of tuning the QTM in SMMs.[2]

[1] G. Christou, D. Gatteschi, D. N. Hendrickson, and R. Sessoli, MRS Bulletin 25, 66 (2000).

[2] W. Wernsdorfer, N. Aliaga-Alcalde, D. N. Hendrickson, and G. Christou, Nature 416, 406 (2002).

2:40pm **MB+BI+OF-TuA3 Density-Functional-Based Simulation of Molecular Magnets**, ***M.R. Pederson***, *N. Bernstein*, Naval Research Laboratory, *T. Baruah*, Georgetown University, *J. Kortus*, Max-Planck-Institute, Germany **INVITED**

Recently a class of transition-metal containing molecules have attracted significant experimental interest because they retain their magnetic orientation at relatively high temperatures and because they exhibit quantum tunneling of magnetism. These molecular magnets consist of approximately 70-200 atoms and are typically composed of 4-15 transition metal atoms which are held in place by organic ligands and anions. The fundamental figure of merit which governs these phenomena is the magnetic anisotropy which arises due to the spin-orbit interaction and other couplings between spin and spatial degrees of freedom. Recently, a quantum-mechanical method has been developed which allows for the density-functional-based determination of magnetic anisotropies in molecules and clusters.[1] We have used this method to calculate anisotropies in several molecular magnets which include: $Mn_{12}O_{12}(RCOO)_{16}(H_2O)_4$, $Fe_8O_2(OH)_{12}(C_6N_3H_{15})_6$, $Co_4C_5NH_4CH_2O)_4(CH_3OH)_4Cl_4$, and $[Mn_{10}O_4(2,2'\text{-biphenoxide})_4Br_{12}]^{4-}$. Our calculations show that good agreement between experiment and theory can be obtained. While the reorientation barriers and magnetic resonant tunneling fields are primarily determined from the second-order anisotropy hamiltonian,[1] higher-order effects can change these quantities by about ten percent. Further, such effects determine tunnel splittings and play a significant role in tunneling dynamics. Currently the primary source of such splittings is an active area of investigation. We have recently suggested that vibrationally induced changes in the spin-orbit interaction will contribute to higher-order anisotropies.[2] Further, computational results on the 4th-order magnetic anisotropy show that this interaction may provide a dominant contribution to the higher-order barriers and that it partially contributes to tunnel splittings. We discuss these calculations and compare our results to the experimental infrared work of Sushkov et al which shows that certain vibrational intensities are strongly perturbed by applied magnetic fields in the Mn_{12}-Acetate system.[3] A very brief review of the computational method, NRLMOL, used in this work will be included in the talk.

[1] M.R. Pederson and S.N. Khanna, Phys. Rev. B 60, 9566 (1999).

[2] M.R. Pederson, N. Bernstein and J. Kortus, (Cond-mate/0201353).

[3] A.B. Sushkov, B. Jones, J.L. Musfeldt, et al, Phys. Rev B 65,(2002).

3:20pm **MB+BI+OF-TuA5 Measuring and Manipulating Single Molecules Inside Living Cells**, ***J.S. Kanger***, *A.H.B. de Vries, J. Greve*, University of Twente, The Netherlands, *B. Krenn, R. van Driel*, University of Amsterdam, The Netherlands **INVITED**

For manipulating single molecules, techniques like AFM or optical tweezers are typically used. However, the actual actuators of these systems are relatively large, and therefore we are not able to manipulate single molecules that are situated deep inside the cell (for example inside the nucleus), without causing massive damage to the cell itself. We describe a conceptual simple arrangement for manipulating ultra small magnetic beads inside living cells using magnetic forces. By using magnetic forces to manipulate the bead, and a low yield HeNe laser to measure its position, we are able to generate a relatively high force, without damaging the cell. The setup is designed to measure the movement of a bead with nanometer precision, and apply picoNewton forces on it. Experimental results combined with model calculations show that a force of 15 pN is feasible for a ferrite bead of 50 nm diameter. If a bead is attached to a functioning protein the movement of this protein in the cell can be monitored and manipulated. We plan to apply this technique to the study of chromatin structure function relations inside the living cell. The magnetic force on a bead is proportional to the magnetization of the bead, and the gradient of the magnetic field. To produce a magnetic field that gives a gradient that is controllable both in direction and strength we constructed a four pole configuration. The tips of these poles (5 µm width and height) are placed 20 µm from each other, which leaves enough space to place a cell, with a magnetic bead in the nucleus, between the poles. The magnetic field is guided from external coils to the poletip that becomes magnetically saturated (1.8 Tesla). The pole tips are produced in the cleanroom facilities of our university. Bead position detection is done by back focal plane interferomtery. A low-yield HeNe laser will is focused on the bead. The combination of the laserbeam and, and the forward scattered light gives a interference pattern on a quadrant detector, which is depended on the position of the bead in the focus.

4:00pm **MB+BI+OF-TuA7 Synthesis and Functionalization of Nanoparticles**, ***A. Ulman***, Polytechnic University **INVITED**

The talk will focus on metal and metal oxide nanoparticles. A one-phase synthesis of thiolate-functionalized metallic nanoparticles will be described, and further chemical reactions, such as surface-initiated polymerization and attachment of DNA bases will be presented. Sonochemical preparation of oxide and mixed oxide nanoparticles will be reported. We have demonstrated, for the first time, that sonication is a very efficient method for coating of γ-Fe_2O_3 and other oxide nanoparticles. The attachment of enzymes to γ-Fe_2O_3 nanoparticles will be described.

Organic Films and Devices
Room: C-102 - Session OF+SS+EL+SC-TuA

Organic Molecular Films
Moderator: H. Fairbrother, Johns Hopkins University

2:00pm **OF+SS+EL+SC-TuA1 Reactivity of Polymers Containing Nitrogen and Oxygen Functional Groups with Vapor Phase Metal Atoms**, ***A.J. Wagner***, *G. Wolfe, D.H. Fairbrother*, The Johns Hopkins University

The surface reactions during the initial stages of polymer metallization are crucial in determining bonding and adhesive characteristics with native and plasma treated polymers. In this study, we have compared the reactivity of different nitrogen and oxygen containing functional groups with a variety of vapor phase metal atoms during the initial stages of metallization. The reactivity of different nitrogen containing functional groups during the vapor deposition of Ti, Fe, Ni, Cu and Au on Nylon 6, containing an amide group (-NH-(C=O)-and nitrogen implanted Poly(ethylene) (N-PE) containing a mixture of C-N, C=N and CN groups was studied. In addition, the reactivity of vapor phase metal atoms with specific functional groups was also investigated using a nitrile (CN) terminated self-assembled monolayer (CN-SAM). For each of the metals studied except Au reaction with Nylon 6 and N-PE resulted in the formation of the metal-nitride (MN), although the extent of reaction increased in the order Ti > Fe > Ni ~ Cu, scaling with the M-N bond strength. Experimental evidence, however, indicated that the different nitrogen containing functional groups present in the nitrogen-modified PE were not equally reactive. Ti and Fe also reacted with the C=O functional group in Nylon 6 to form their respective oxides while Cu, Ni and Au were unreactive with the C=O functional group. Metal nitride formation was also observed during evaporation of Ti and Fe on the CN-SAM although Cu and Au were unreactive towards the CN functional group. In contrast, metal carbide production was only evidenced during reactions with Ti. Results from this investigation will be interpreted in terms of the relative bond strengths associated with specific functional groups within the polymer and potential product species (e.g. metal oxide, nitrides).

2:20pm **OF+SS+EL+SC-TuA2 A New Crystalline Form of Pentacene: pi-stacked Thin Films Grown on Au(111)**, ***J. Kang***, *X.-Y. Zhu*, University of Minnesota

The recent demonstration of pentacene and related molecules in high-mobility field effect transistors (FETs), including superconducting FETs, has attracted great interest in this class of organic semiconductors. Carrier mobility is known to depend intimately on crystalline quality. In order to establish a molecular level understanding of structure-property relationship, we have carried out a scanning tunneling microscopy (STM) and spectroscopy (STS) study of the growth of crystalline pentacene thin films on Au (111). The use of high bias voltage (~ 5 V) and low tunneling current (~ 1pA) has enabled us to image, with molecular resolution, the growth of a new crystalline phase of pentacene well beyond the first a few layers. High resolution imaging shows that pentacene molecules form a pi-stacked crystalline phase with their long-axis parallel to the surface. This is attributed to the strong molecule-surface interaction, which seeds the growth of this new crystalline phase.

2:40pm **OF+SS+EL+SC-TuA3 Vapor Deposition and Polymerization of Low-k Polycyanurate Films**, ***J.N. Russell, Jr.***, *V.J. Bellitto, B. Bartlett, MJ Brooks, P.G. Santangelo, A.W. Snow*, Naval Research Laboratory **INVITED**

Future microelectronics will require advanced materials and processes for smaller, faster and more robust devices. Polymers address these needs and range from ultra-low permittivity materials to molecular semiconductors. Developing and understanding solventless deposition processes such as vapor deposition polymerization is important for producing conformal, voidless polymer films. One class of low-k polymers, polycyanurates, shows promise as a vapor depositable material. Yet little is known about the surface chemistry of the cyanate functionality and the conditions required for surface polymerization. Initially the surface chemistry of key functionalities in the monomer and polymer are examined using model compounds such as phenyl cyanate and triazine on Al(111). Aluminum was chosen because it is used for interconnects in microelectronics. Then, the in situ vacuum deposition and polymerization chemistry of NCO-CH2(CF2)6 CH2-OCN (F6Cy) is studied on Al, Cu, and Si surfaces. The vapor deposited F6Cy monomer film undergoes a photo-induced cyclotrimerization process to form cross-linked cyanurate networks with a permittivity of 2.1 at 1 GHz.

3:20pm **OF+SS+EL+SC-TuA5 Formation of Chemically Patterned Surfaces using Gas-Phase Oxalyl Chloride**, ***M.C. Asplund***, *G. Husseini, M.R. Linford, E.T. Sevy*, Brigham Young University

Optical lithography is a common technique for the formation of electronic devices on semiconductor substrates. Here we show an analogous technique that allows the introduction of a reactive functional group (-COCl) onto an alkylated Si substrate, or onto any substrate that contains C-H groups. The importance of the -COCl group stems from its high reactivity with amino and hydroxyl groups. Our new method consists of exposing a C-H containing surface to a gaseous mixture of N2 and oxalyl chloride ($(COCl)_2$) and then illuminating with 355 nm light. The UV photons form free radicals from the oxalyl chloride that then react with the C-H containing surface. We have shown using wetting, XPS, elipsometry and FT-IR spectroscopies that we have been able to form acid chloride functional groups on surfaces. By using simple optical masks we have shown that this functionalization occurs only where the sample is exposed to light. The key step to understanding the reaction mechanism for the surface reaction is understanding the formation and subsequent reaction of the radicals formed from the oxalyl chloride. Previous liquid phase reaction studies of oxalyl chloride with adamantane led to the suggestion that at 266 Cl is the primary radical formed, while at 355 nm the primary radical is the COCl radical. We have looked at the formation of radicals as a function of wavelength to analyze dissociation mechanism, and product energy distributions as well as the effect of pressure on radical formation. The minimum feature size which can be made using this method is given by the diffusion length of the radical. Thus the quenching must be understood and optimized to have controlled patterning of surfaces.

3:40pm **OF+SS+EL+SC-TuA6 Characterization of Ultrathin Organic Films via Near-edge X-ray Absorption Fine Structure Spectroscopy**, ***T.M. Willey***, University of California Davis and Lawrence Livermore National Laboratory, *A.L. Vance, T. van Buuren, C. Bostedt, A.J. Nelson, L.J. Terminello,* Lawrence Livermore National Laboratory, *C.S. Fadley*, University of California Davis and Lawrence Berkeley National Laboratory

Self-assembled monolayers (SAMs) and other thiol compounds adsorbed on Au(111) surfaces have become increasingly important for achieving surface attachment and orientation of complex molecules. Surface-attached molecular species containing catenanes and rotaxanes promise to play a vital role in achieving molecular-scale electronics and other devices.[1] Only through a rigorous understanding of the structure and properties of such molecular monolayer species can a rational synthesis of these hybrid materials be realized. Orientation of chemical bonds and thus the orientation of molecules can be precisely determined with near-edge x-ray absorption fine structure (NEXAFS) spectroscopy. Here, we present NEXAFS results on the configuration of surface-attached fundamental building-blocks of such systems, including a simple surface-attached rotaxane and its constituents. This rotaxane consists of a crown ether ring, threaded by a molecule bound to the gold at one end and providing an athracene stopper at the other.[2] Investigating films of the stopper molecule only vs. the complete rotaxane we confirm the presence of the crown ether in the complete molecule. We present the orientation of the anthracene stopper and crown ether ring with respect to the surface by deconvoluting their respective features in the NEXAFS.

Acknowledgements: This work is supported by the U.S. Department of Energy, BES Materials Sciences under contract W-7405-ENG-48, LLNL; at the ALS under contract number DE-AC03-76SF00098 at LBNL; and at the SSRL under contract number DE-AC03-76SF00515 at SLAC.

[1] Collier et al., Science 289, 1172-5

[2] Kolchinski et al., Chem. Commun., 1998, 1437-8

4:00pm **OF+SS+EL+SC-TuA7 Interfaces with Evaporated Short Chain Polyaniline**, ***B. Xu****, *A.N. Caruso, M. Bai, Y. Ovchenkov, S. Ducharme, B. Doudin, P.A. Dowben*, University of Nebraska-Lincoln

The interface properties of evaporated short chain polyaniline (PANI) were investigated by X-ray photoemission spectroscopy (XPS), inverse photoemission spectroscopy (IPES), as well as angle integrated photoemission spectroscopy (UPS). With sodium doping, the valence bands, conduction bands as well as the characteristic core levels show consistent shifts to the higher binding energy. Sodium, as an electron donor, when added to the polyaniline system, results in increased electron populations in the polyaniline bands --- effectively filling the almost completely filled band. In the case of iodine doping, all the states shifted to lower binding energy. Iodine, as an electron acceptor, effectively depletes the electron population in the occupied bands polyaniline. There is no abrupt interface formed between sodium or iodine and polyaniline, as demonstrated by the angle-resolved XPS. By comparison, the interface between polyaniline and another polymer poly(vinylidene fluoride with trifluoroethylene) copolymer (PVDF-TrFE) is quite abrupt. A P-N diode was made by evaporating PANI (p type) on the top of PVDF-TrFE (n type). The results presented here should apply to the problems associated with improving heterojunction polymer devices.

4:20pm **OF+SS+EL+SC-TuA8 Controlled p-Doping of Organic Molecular Films**, ***W. Gao***, *A. Kahn*, Princeton University

We investigate the controlled electrical p-doping of the hole-transport organic molecular material α-NPD with the strong electron acceptor tetrafluoro-tetracyano-quinodimethane (F_4-TCNQ) using ultraviolet and inverse photoelectron spectroscopies (UPS/IPES), and in-situ I-V measurements. We previously examined p-doping of ZnPc co-evaporated with F_4-TCNQ,[1] and found an excellent energy match between the ionization energy (IE) of ZnPc (5.28eV) and the electron affinity (EA) of F_4-TCNQ (5.24eV), demonstrating host HOMO-to-guest LUMO charge transfer. The ZnPc thickness dependence of I-V data further demonstrated a 7 orders of magnitude increase in hole current injected from Au due to tunneling through the doping-induced narrow depletion region at the metal/organic interface.[2] In the present study, we show that α-NPD (IE=5.52eV) is also efficiently doped with F_4-TCNQ. The hole injection current increases by almost 5 orders of magnitude when only the first 80Å of α-NPD away from the metal/organic interface is doped, and increases by another factor of 10 when the entire organic film is uniformly doped. However, the doping-induced movement of E_F toward the HOMO appears to be more restricted than in ZnPc. Having excluded extrinsic effects like surface photovoltage, we propose that the substantial (~0.2 eV) ionization-induced relaxation of molecular energy levels moves the "doped" α-NPD HOMO upwards, and thus pins E_F deeper into the gap than for ZnPc, which is a planar molecule with a negligible relaxation energy (< 0.05eV). This

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***** Morton S. Traum Award Finalist

interpretation is further confirmed with UPS study of the host material growth on a film of the dopant molecules. We also show that molecular level alignment at organic/organic interfaces is controllable by doping-induced dipole. Work supported by the NSF (DMR-0097133).

[1] W. Gao and A. Kahn, Appl. Phys. Lett., 79, 4040 (2001)
[2] W. Gao and A. Kahn, Organic Electronics (in press).

4:40pm **OF+SS+EL+SC-TuA9 Processable Optically Transparent Thin Films of Conducting Polymers**, ***B.D. Martin***, *N. Nikolov, R. Shashidhar*, Naval Research Laboratory

A major problem in the area of electronically conducting polymers is that attempts to enhance their electrical conductivity by adding ionic dopants are always accompanied by a decrease of optical transparency. In this study we show how molecular self-assembly of small carbohydrate molecules can decouple the optical transparency and electrical conductance of conducting polymer films. When a carbohydrate such as glycerol, which is essentially a non-ionic hydrogen bonding dopant, is added to a commercially available conducting polymer suspension (Baytron P), the carbohydrate forms an intercalated, hydrogen bonded sandwich between the ionic pairs of the conducting oligomer unit and its supporting polymer suprastructure. This results in a pronounced increase of the distance between the ion pairs, and hence, to decreased electrostatic interaction. As a consequence there is an enhanced mobility of the ions and hence an increased conductivity without an accompanying increase in optical absorption. This behavior, which is in striking contrast to the normally observed trends in conducting polymers doped with traditional ionic dopants, is very important to the development of plastic liquid crystal displays (LCDs) and organic light emitting diode (OLED) displays.

5:00pm **OF+SS+EL+SC-TuA10 Optical Properties of Ordered Ultrathin Films of PTCDA**, ***R. Nitsche***, *H. Proehl, S. Mannsfeld, T. Dienel, T. Fritz*, TU Dresden, Germany

Research activity on molecular solids has gathered pace in recent years as these materials have a wide range of interesting properties, emerging industrial interest with real applications at the horizon, and possible future applications that will enable electronics to move into the nanoscale. High quality samples, precise structural data, and a detailed understanding of the physical properties is essential, with special emphasis on thin films and interfaces. In this respect, the use of highly controlled growth techniques like Organic Molecular Beam Epitaxy (OMBE) is becoming more and more important, aiming at high quality thin films with controlled crystal structure and morphology, therefore displaying well defined physical properties. In our contribution we will discuss the special optical properties of ultrathin films of an archetypal organic material, namely PTCDA (perylene-3,4,9,10-tetracarboxylic-3,4,9,10-dianhydride). Highly ordered organic thin films on a gold single crystal have been prepared by means of OMBE with submonolayer to multilayer coverage. All films were structurally characterized by combining Scanning Tunneling Microscopy (STM) with Low Energy Electron Diffraction (LEED), clearly indicating epitaxial growth in the point-on-line mode. Differential Reflection Spectroscopy (DRS, a variant of reflection absorption spectroscopy) both ex situ and in situ has been applied to measure the optical characteristics of those films. The results clearly show that ultrathin layers have different optical properties as compared to thicker films, which in turn match the results known for long from polycrystalline samples. The results are further compared to thin films grown on mica to discuss the influence of different substrates.

Organic Films and Devices
Room: C-102 - Session OF+EL+SS+SC-WeM

Metal-Organic Interfaces
Moderator: L.J. Guo, University of Michigan

8:20am **OF+EL+SS+SC-WeM1 Interfaces between Metals and Conjugated Organic Materials: From Physisorption to Covalent Bonding**, ***N. Koch***, Princeton University, *J. Ghijsen*, Facultes Universitaires Notre-Dame de la Paix, Belgium, *A. Rajagopal*, Rutgers University, *C. Chan*, Princeton University, *J.J. Pireaux*, Facultes Universitaires Notre-Dame de la Paix, Belgium, *J. Schwartz*, *A. Kahn*, Princeton University **INVITED**

The electronic properties of interfaces formed between conjugated organic materials (polymers and small molecules) and other organic and inorganic materials are of paramount importance in terms of the performance of organic-based devices (e.g., light emitting diodes, thin film transistors). The alignment of energy levels at such interfaces is a direct consequence of the physical and chemical interactions between the materials. Using mainly photoemission spectroscopy (PES), we show that the nature of interaction between low work function metals and phenylene-based electroluminescent oligomers and polymers covers the whole range from physisorption (aluminum and samarium) to chemical reduction (calcium), and to charge transfer reactions (alkali metals). Although PES is a very powerful experimental tool to determine electronic properties of interfaces, great care must be taken in the interpretation of the data when wide band-gap materials, such as conjugated organic materials, are being investigated. We demonstrate that the observation by PES of a finite density of occupied states at the Fermi-level on an organic film in which alkali metal atoms have been intercalated does not necessarily imply metallicity nor the presence of negative polarons (radical anions), as previously proposed. From a combination of ultraviolet PES and Kelvin probe measurements, evidence is obtained that the substrate and the surface of the organic film are not necessarily in thermodynamic equilibrium, leading to potential misinterpretations of the Fermi level position at the surface of organic films.

9:00am **OF+EL+SS+SC-WeM3 Structural and Electronic Properties of the Interfaces between Au(111) and the Organic Semiconductors Pentacene and p-sexiphenyl**, ***C.B. France***, *P.G. Schroeder*, *B.A. Parkinson*, Colorado State University

Thorough understanding of the interface between organic semiconductors and metal contacts is important because of charge transfer events that take place in new devices based on organic semiconductors. Transistors[1] and photovoltaic devices[2] have been fabricated using pentacene as the organic semiconductor. In the interest of understanding the structural and electronic environments of these interfaces we have investigated thin films of pentacene and p-sexiphenyl on the Au(111) surface in ultrahigh vacuum using multiple characterization techniques. The entergetics of these heterojunctions have been measured using photoemission spectroscopy. Large interfacial dipole barriers exist at the interface of both systems. Temperature programmed desorption has been used to investigate the binding environment of the organic semiconductors on the metal substrate. Two different binding environments have been uncovered for both molecular semiconductors on the Au(111) substrate. Scanning tunneling microscopy has been used to investigate the coverage dependant structures that are formed by thin films of semiconductor molecules on the Au(111) surface. Pentacene was found to generate many overlayer structures at differing film thickness. Structures found on low coverage, monolayer and multilayer films will be discussed.

[1] Schön, J. H.;Berg, S.;Kloc, C.;Batlogg, B. Science 2000, 287, 1022.

[2] Schön, J. H.;Kloc, C.;Bucher, E.;Batlogg, B. Nature 2000, 403, 408. .

9:20am **OF+EL+SS+SC-WeM4 Growth of Organic Molecules on Ferromagnetic Substrates for Hybrid Organo-metallic Spintronic Devices**, ***M.V. Tiba***, *O. Kurnosikov*, *B. Koopmans*, *J.T. Kohlhepp*, *C.F.J. Flipse*, *W.I.M. de Jonge*, *U.S. Schubert*, Eindhoven U. of Technology, CNM, The Netherlands

Motivated by the success of polymer based- and molecular electronics, a challenging new field is emerging. Recent work has demonstrated the feasibility of hybrid organo-metallic spintronics, in which the spin degree of freedom is explicitly being used. Application in future magnetic sensor and memory technology has been proposed. Improved characteristics of such devices require very clean interfaces, therefore deposition of organic molecules in UHV environment is desirable. A severe complication of growing ordered structures of organic molecules on transition metal ferromagnetic substrates is their high reactivity. In this work we investigate the influence of substrate passivation on the bonding to the substrate (and hence the molecular ordering) for different organic molecules. Selection of the molecules is based on their electronic properties as well as their tendency to form well ordered layers. In the particular case of PTCDA molecules deposited on a Ni(111) substrate we show that quarter monolayer of oxygen reduces enough the reactivity of Ni to enable the molecules to form an ordered structure.[1] Current activities aiming at the fabrication of organo-metallic hybrid magnetic tunnel junctions having polycrystalline Co electrodes and organic barriers will be addressed as well.

[1] M.V.Tiba et al. Surf. Sci. 498 (2002) 161.

9:40am **OF+EL+SS+SC-WeM5 Controlling Metallic Contacts to Molecular Electronic Devices**, ***A.V. Walker***, *T.B. Tighe*, *O. Cabarcos*, *B.C. Haynie*, *D.L. Allara*, *N. Winograd*, Pennsylvania State University

In the development and design of molecular electronic devices, it is vital to understand the nature of the metal-organic monolayer interaction. To fully characterize these interactions, we employ a multi-technique approach using time-of-flight secondary ion mass spectrometry (ToF SIMS), infrared spectroscopy (IRS), x-ray photoelectron spectroscopy (XPS) and density functional theory (DFT) calculations. Using an unfunctionalized molecular wire (4-[4?-(phenylethynyl)-phenylethynyl]-benzenethiol) monolayer on Au, we demonstrate that the metal-monolayer contact can be varied from complete destruction of the monolayer to contact formation at the monolayer terminus to complete penetration through the layer. For example, we show that upon deposition of Cu or Ag, the Cu and Ag atoms simultaneously interact with the terminal phenyl ring and penetrate to the Au/S interface. In contrast, Au penetrates through the monolayer at all coverages studied. By using metals specifically tailored for the chemistry of the device molecule as well as for electronic states, the characteristics of the metal-molecule contact can also be controlled. These types of data provide a foundation for rational design of contacts in molecular electronic devices.

10:00am **OF+EL+SS+SC-WeM6 DLC Thin Film as Electron Injection Layer in Organic LEDs**, ***M. Cremona***, Pontificia Universidade Catolica do Rio de Janeiro, Brazil, *R. Reyes*, Universidad Nacional de Ingeniería, Perú, *C.A. Achete*, *P.I. Guimarães*, *S.S. Camargo, Jr.*, Universidade Federal do Rio de Janeiro, Brazil

Recently, there has been an increased interest in organic light emitting diodes (OLEDs) due of their potential applications to color flat panel displays and in new optoelectronic components. These devices are assembled using three organic molecular materials: an electron injection layer, the emitting one and finally the hole injection layer. However, in most cases the electron injection is more difficult to achieve than hole injection. In this work two different diamond like carbon (DLC) thin films cathode were used to decrease the electron injection barrier. The first kind were nitrogen-doped amorphous hydrogenated hard carbon films deposited by rf glow discharge from methane-nitrogen mixtures onto the TPD/Alq$_3$ layer structure thermally deposited. DLC films were obtained for different N_2 partial pressures (bias voltage V_b=â€“370 V and total pressure P=8 Pa). Next, amorphous carbon nitride thin films (a-CN$_x$) have been deposited using a rf diode sputtering system onto the same organic structure. In this case the DLC films were deposited in reactive nitrogen-argon atmospheres. The partial pressure of nitrogen ranged from 0% to 100% at two different deposition pressures (P = 2 Pa and P = 8 Pa). In both cases a thick (150 nm) aluminum electrode were deposited onto the whole structure. The deposition process for the organic compounds is performed in high vacuum environment (6x10^{-6} Torr) on glass substrates coated with an hole injecting ITO transparent layer. A preliminary investigation was conducted on the properties of the OLED device with the two DLC intermediate layers. The relationship between the properties of the DLC deposited films on the electroluminescent characteristics of the different devices are investigated. The refractive index of the DLC film deposited, their conductivity and optical absorption, the OLED I-V curves, a preliminary photoluminescent and electroluminescent OLED results are presented and discussed.

10:20am **OF+EL+SS+SC-WeM7 Self-assembly of Molecular 1D wires on Cu(110)**, ***Y. Naitoh***, *F. Rosei*, *P. Thostrup*, *M. Schunack*, *F. Besenbacher*, University of Aarhus, Denmark

The adsorption of a large organic $C_{90}H_{98}$ molecule, known as the Lander molecule, is studied by Scanning Tunneling Microscopy (STM) on a Cu(110) surface.[1] By exposing the surface to low doses of oxygen at elevated temperatures, we form a nanopattern of alternating bare Cu(110) regions and (2x1)-O reconstructed regions aligned parallel to the [001] direction. The oxygen-induced reconstruction reveals a long-range ordering of Cu-O rows 20-50 Å wide. When deposited on this template, Lander molecules adsorb preferentially on bare Cu regions. By tuning the oxygen dosing, thereby adjusting the lateral periodicity of the template, and by varying molecular coverage in a controlled manner we can form long 1D rows of molecular wires. This type of assembly opens new possibilities for ordering organic molecules on surfaces.

[1] F. Rosei et al., Science 296, 328 (2002).

10:40am **OF+EL+SS+SC-WeM8 Dip Pen Nanolithography on Insulating Substrates**, ***S.E. Kooi***, *P.E. Sheehan*, *L.J. Whitman*, Naval Research Laboratory

Methods of assembling nanoscale components at chosen locations on a surface are needed to produce nanoscale electronic and sensor devices. Dip pen nanolithography (DPN) has been successful in producing such features as small as ~10 nm wide and one monolayer thick in several different molecule - surface combinations. The most studied systems have been alkyl and aryl thiol depostion on gold surfaces; however, DPN has also been demonstrated for inorganic salts on silicon, biomolecules on gold, and silazanes on semiconductor surfaces. We explore the application of DPN to write functional molecules on a technologically important insulating surface, namely silicon oxide. We have written several different trichlorosilane molecules directly onto thermally-grown silicon oxide substrates. By choosing an appropriate trichlorosilane and post-deposition chemical modification of the written molecules, we can direct the deposition of other nanostructures (such as carbon nanotubes, semiconducting nanowires, or nanoparticles). For example, by writing 10-undecenyltrichlorosilane onto silicon oxide, we can create a terminal carboxylic acid group with a post-deposition chemical oxidation. Subsequent deprotonation of the patterned carboxylic acid groups produces a negative charge that directs the deposition of positively-charged nanostructures. The ability to place nanoscale components at chosen locations on a surface, in combination with traditional (e-beam) lithographic techniques, opens up the possibility of interfacing nanoscale components with traditional devices.

Organic Films and Devices
Room: Exhibit Hall B2 - Session OF+EL-WeP

Organic Films and Devices

OF+EL-WeP1 Cycloaddition of Silyl-disila-cyclopentene on Si(001) Surface, ***B.-Y. Choi***, *Y.-J. Song, Y. Kuk*, Seoul National University, South Korea

It is known that π bonds of unsaturated organic molecules can easily react with Si=Si dimers of the reconstructed Si(001)-2x1 surface, resulting in two new Si-C σ bonds. Through such a cycloaddition, densely-packed molecules on hybridized Si(001) surface are highly ordered both translationally and rotationally over macroscopic length scale. However, in spite of much effort, the mechanism of cycloaddition on surface is not known clearly. We investigated the reaction of 2-silyl-1,3-disilacyclopent-4-ene (SDC) with the Si(001) surface using scanning tunneling microscopy. STM images show that the SDC molecules are slightly elongated parallel to the dimer direction, suggesting that the molecules bond in a manner of typical [2+2] cycloaddition. It can be noted that there exists a preferred bonding site of SDC molecule. However, the analysis of the observed structure suggests that there is more than one way for SDC to bond to the Si(001) surface. Some molecules place perpendicular to dimer direction and even complex absorbates are shown. We suggest that the several reactions occur nearly as frequently.

OF+EL-WeP2 Nanolithography Technique Based on Dynamic Mode Atomic Force Microscopy and Organosilane Self-Assembled Monolayers, ***K. Hayashi***, *N. Saito, H. Sugimura, O. Takai*, Nagoya University, Japan

Organosilane self-assembled monolayer (SAM) is a candidate for resist material in future nanolithography techniques. Although several techniques have been applied to patterning of the SAMs, scanning probe lithography using an atomic force microscope (AFM) is promising since the method has a high potential in archiving nanometer scale resolution. However, there has been a serious problem, that is, damages of the AFM-tip, when the AFM is operated in the contact mode. Here we report on nanopatterning of organosilane SAMs using a dynamic mode AFM in which tip damages are expected to be reduced. We observe AFM-tip induced chemical changes on the SAM surfaces by Kelvin-probe force microscopy (KFM) working in the dynamic mode as well. Onto cleaned silicon (Si) substrates covered with native oxide (SiO_2), a SAM was formed from n-octadecyltrimethoxysilane [ODS: $CH_3(CH_2)_{17}Si(OCH_3)_3$]. Thickness of this ODS-SAM was ca. 1.8 nm. While scanning a AFM-tip (Au coated Si tip), operated in the dynamic mode, on an ODS-SAM/Si sample, a DC bias voltage was applied between the conductive tip and the sample. After the patterning, the sample surface was characterized by KFM. Due to electrochemical reactions induced by the injected current, the modified region where current had been injected from the tip was found to show a more positive surface potential than the surrounding unmodified region. Through the surface potential images acquired by KFM, chemical changes of ODS-SAM could be detected, while such changes could hardly be confirmed in topographic images. KFM is a powerful means to characterize nanoscale patterns on the SAMs drawn by scanning probe lithography.

OF+EL-WeP3 Photoemission Study of Dodecanthiol on Au (111), *H. Geisler, S. Sales*, Xavier University of Louisiana, ***J.M. Burst***, *S.N. Thornburg, C.A. Ventrice Jr.*, University of New Orleans, *Y. Losovyj, P.T. Sprunger*, Louisiana State University

The adsorption of alkanethiols on various single-crystal metal surfaces results in the formation of self-assembled monolayers (SAMs). Typically, SAMs are grown on surfaces that are immersed in aqueous solutions, and adsorption times of 15 hours or more are necessary to obtain well-ordered, defect free structures. In this study, 1-dodecanethiol was vapor deposited on Au (111) in ultra high vacuum, which produces a SAM in a period of only a few minutes. Angle-resolved ultraviolet photoelectron spectroscopy (ARUPS) was used to determine the orientation and the electronic structure of the thiol. Deposition at room temperature gave no signature of thiol adsorption at the surface with either ARUPS or low energy electron diffraction (LEED). Deposition at ~100 K resulted in an ordered monolayer, as indicated by the dispersion of the thiol valence band emissions. A comparison between clean gold and the SAM spectra indicate that the 1-dodecanethiol adsorbs upright at a 20° angle to the surface normal. Deposition of multilayers of thiol at ~100 K produced a disordered overlayer with no dispersion of the valence band emissions. The onset of emission from the thiol valence band for the multilayer films was measured to be 3.5 eV below the Fermi level.

OF+EL-WeP4 XPS Studies of Brilliant Green Doped Conducting Polymer Polythiophene Films, ***H.K. Kato***, *S.T. Takemura, M.H. Hirayama*, Kanto Gakuin University, Japan, *H.M. Makihara*, Kansai Research Institute, Japan

Conducting polymer polythiophene (PT) films incorporated with dye molecule brilliant green (BG) prepared by electrochemical doping and diffuse injection methods were investigated by XPS. Polymeric structure, charge transfer and interaction between the dye molecule and PT backbone in the hybrid films were closely investigated by analyzing the core-level energies and spectral profiles of the atomic components. XPS core-level analysis of N 1s showed that BG molecules were injected into polymer matrix in the hybrid films prepared by electrochemically reduced method and BG diffused method. S 2p lines were observed split indicates simultaneous doping of BG cation and HSO4-. The higher binding energy peak corresponds to HSO4- while lower binding energy peak can be assigned to the S sites of polymer backbone. Synthesized film samples were categorized into two types, A-type and B-type by the difference of S 2p core-level energy shift. In the sample of A-type, the energy shift of the lower peak of S 2p suggest the charge transfer between BG molecules and polymer backbone creating a n-type polymer backbone state. In the case of electrochemically as-grown films, both BG and HSO4- doping were not observed because S 2p line was single and no N 1s signal was observed.

OF+EL-WeP5 XPS Studies of Initial Stage of Conducting Polymer Film Growth on Si Substrate, *H.K. Kato*, ***S.T. Takemura***, Kanto Gakuin University, Japan, *H.M. Makihara*, Kansai Research Institute, Japan

Conducting polymer polythiophene (PT) film growth on Si substrate was investigated by XPS. PT/Si interface fabricated by electrochemical method was closely investigated by analyzing the core-level energies and spectral profiles of the atomic components. At the initial stage of electrochemical polymer growth, affinity between a deposited polymer PT film and Si substrate was strong compared with the case of PT film growth on ITO substrate expecting bondings between polymer chains and Si substrate layers. Spectral profiles of Si core-level spectra showed that both Si 2s and 2p spectra were basically composed of different Gaussian components correspond to different valence states of Si in contrast to the core-level spectra of non-deposited Si substrate. The lower binding energy peaks (LS1 and LS2) observed in Si 2p spectra of PT/Si correspond to the Si states with strong interaction between Si and PT. The peak height of LS1 slightly increases and LS2 drastically grows in the case of PT polymer growth on Si substrate. The C 1s core-level spectrum was composed of a higher energy component and a lower energy component originated from the polymer backbone and oxidized Si layers, respectively. Strong affinity between a deposited polymer PT film and Si substrate and variation of the XPS spectral profile suggest that Si-C and Si-F bondings are created at the PT/Si interface.

OF+EL-WeP6 Formation and Characterization of Ferrocene and Porphyrin Monolayers on Si and Ge Surfaces : Towards a Hybrid Molecular/CMOS Electronic Device, ***A.A. Yasseri***, *Z. Liu, R. Dabke*, University of California Riverside, *V. Malinovskii, K.H. Schweikart, J.S. Lindsey*, North Carolina State University, *W.G. Kuhr, D.F. Bocian, K.M. Roth*, University of California Riverside

Construction of a novel hybrid molecular based device may provide the most tractable approach in bridging the gap between modern day semiconductor materials and molecular based devices. Toward this goal, we have examined functionalized monolayers of ferrocene and porphyrin terminated alcohols and thiols covalently linked to mono-crystalline Si and Ge (100) and (111). Electrochemical communication with the surface immobilized molecules was achieved through a covalently anchored Si-O, Si-S or Ge-O and Ge-S tether to photlolithographically patterned surfaces. Silicon microelectrodes were fabricated on heavily doped silicon masked with a thermally grown oxide to define the active electrode area for monolayer assembly. Surfaces were activated via a two-step process. Chemically stable hydride-terminated surfaces, using HF or ammonium fluoride, were reacted with a solution of iodine yielding an iodide functionalized surface. XPS measurements confirm the mechanism for the displacement of surface iodine atoms via a base catalyzed reaction with alcohol terminated iron and zinc-centered ferrocene and porphyrin respectively. Iodide derivitization prior to film deposition chemically facilitates the formation of more densely packed monolayer of porphyrins. Fast scan voltammetry performed on monolayers demonstrate the chemical stability of the films over millions of cycles in an inert atmosphere.

Modified AC voltammetry was used to probe the redox kinetics of the semiconductor film junction in order to measure the rate for film oxidation and reduction under an applied potential. Monolayers formed from solution phase assembly reactions were further characterized using scanning probe microscopy.

OF+EL-WeP7 Characterization of OLED Degradation by Emission Microscope, ***N. Miura***, *Y. Luo*, *K. Takagi*, ITES Co. Ltd., Japan

The purpose of this study is to investigate how an emission microscope has been applied to evaluation for the degradation mechanism of organic light-emitting devices (OLED). One of the most effective ways to characterize OLED degradation is to study a physical and chemical phenomenon that occurs with an exact point of interest. The problem, however, is one of isolating the exact point of degradation. Thickness of a luminescent layer is around 0.1 microns. Consequently, a less-than-0.1-micron foreign matter can become a cause of an electrical short failure. On the other hand, a size of a pixel is the approximately one hundred microns. Therefore pinpoint detection of a failure location is extremely difficult. In order to solve this problem, an emission microscope used for a failure analysis of Si-based LSIs has been applied to detect a degradation point in plane luminescent devices. An emission microscope is a tool to detect a faint light emitting at a failure point with PMT or CCD camera and to find out a point of interest by adding an optical image and a detected one. This study describes a method for applying emission microscope in the failure analysis of OLED and demonstrates the effectiveness of this method. It is confirmed that an observation under sub-threshold bias condition is effective to find out a failure point. Although no electro-luminescence is observed under this condition with an optical microscope, an emission microscope can get detect a photon emission at a failure location. Some case studies are described to demonstrate the effectiveness of this method. Cross sectional TEM observations of defects located with this technique are also included.

OF+EL-WeP8 Polyatomic Ion Deposition of Thiophenic Thin Films, ***Y. Choi***, *E.R. Fuoco*, *L. Hanley*, University of Illinois at Chicago

Oligo- and polythiophenes are utilized as conducting polymers in many applications. Polyatomic ion deposition at ion impact energies below 200 eV is an effective method for the growth of thin organic films on polymer, metal, and semiconductor surfaces.[1] We demonstrate here the growth of thiophenic thin films on aluminum and silicon substrates by mass-selected <200 eV $C_4H_4S^+$ ion beams. Thiophenic films are also grown by non-mass selected ion beams containing <200 eV $C_4H_4S^+$ and fragment ions. Our non-mass selected ion deposition method permits rapid film growth over wide substrate areas and it is described here for the first time. X-ray photoelectron spectroscopy and atomic force microscopy are used to compare the film chemistry and morphology for the two methods. Oxidation of the films during aging in air is observed.

[1] L. Hanley and S.B. Sinnott, Surf. Sci. 500 (2002) 500.

OF+EL-WeP9 Mg-Phthalocyanine Thin Films with High Sensitivity for Chlorine Gas, ***T. Miyata***, *S. Kawaguchi*, *T. Minami*, Kanazawa Institute of Technology, Japan

There has been considerable interest in the study of organic substances such as phthalocyanines in thin film form for use as the active layer in gas sensor devices. In particular, the electronic properties of metal phthalocyanine (MPc) thin films are known to be affected by the presence of a foreign gas. Recently, we have demonstrated newly developed high-sensitivity chlorine (Cl_2) gas sensors using Cu-phthalocyanine (CuPc) thin films. However, these CuPc thin film gas sensors still have several unsolved problems such as low sensitivity at operating temperatures above 150°C and the necessity of a heat treatment process for repeated operation. In this paper, we introduce newly developed chlorine gas sensors that can be operated at high temperatures using Mg-phthalocyanine (MgPc) thin films. The Mg-phthalocyanine thin films (thickness from 30 to 180 nm) were evaporated onto substrates; Au thin films were deposited as electrodes. The substrate temperature was varied from RT to 180°C. Gas sensitivity is defined as ratio $(I-I_0)/I_0$. Here, I_0 and I are the currents through the sensors before and after gas introduction, respectively. The sensor resistance decreased when exposed to chlorine gas; MgPc thin film gas sensors exhibited high sensitivity at the operating temperatures as high as 230°C. The characteristics of MgPc thin film sensors were strongly dependent on the preparation conditions of the MgPc thin films. For example, sensitivity increased as the substrate temperature of the MgPc thin films was increased from RT to 180°C: maximum sensitivity at a thin film deposition temperature of 180°C. At an operating temperature of 200°C, the sensitivity of the optimized MgPc thin film gas sensor linearly increased with the Cl_2 gas concentration in the range of 0.35 to 35 ppm.

OF+EL-WeP10 The Surface Stress under Ion Irradiation on Si and SAM-coated Si, ***A.N. Itakura***, *M. Kitajima*, Institute for Materials Science, Japan, *R. Berger*, IBM Deutschland Speichersysteme GmbH, Germany

Evaluation of stress in the Si stencil mask is very important for ion projection patterning or ion lithography technology, because the stresses would cause a deformation of the projected patterns. Ar ion irradiation makes a compressive stress on Si(001) surfaces.[1] Stencil masks often become folded during the ion projection patternings, which should be owing to this ion induced compressive stress. In this paper, we have studied the stress evolution of Si membranes under ion irradiation. Bare Si and alkanethiol-coated-Si were examined during ion irradiation from ion energies of 5 to 50eV. The stresses were in-situ real-time monitored by using a microcantilever sensor technique combined with ion irradiation system in UHV. Self-assembled monolayers (SAM) such as alkanethiol, $HS-(CH_2)_{n-1}-CH_3$ for n=4,6,8,12, on gold induced compressive stresses.[2] In contrast to the compressive stress during SAM growth, a strong tensile surface stress of about -0.7 N/m was found when the sensor is exposed to Ar ions. This value is 3-4 times larger than the compressive stress. The constant value of the tensile stress for an Ar-ion dose higher than 4×10^{14} ions/cm^2 indicates that a stable monolayer forms during Ar-ion irradiation. Stable protective monolayers featuring tensile stress can play a key role in micro-machining and as protective overlayers for silicon mask lithography.

[1] T.Narushima, A.N.Itakura and M.Kitajima, Appl.Phys.Lett.79, 605-607 (2001),

[2] A.N.Itakura, R.Berger, T.Narushima and M.Kitajima, Appl.Phys.Lett.(2002), in printing.

OF+EL-WeP11 Controlled Growth of Ultrathin Molecular Films, ***E.J. Kintzel, Jr.***, Florida State University, *D.-M. Smilgies*, Cornell High Energy Synchrotron Source, Cornell University, *J.G. Skofronick*, *S.A. Safron*, *D.H. Van Winkle*, Florida State University

Controlled growth of the aromatic p-phenylene oligomer molecules adsorbed onto KBr(001), KCl(001), NaCl(001), and NaF(001), has been investigated by x-ray diffraction (XRD) and atomic force microscopy (AFM). XRD analysis provides evidence that the substrate temperature during deposition, substrate lattice constant, and molecular length affects the molecular orientations within these ultrathin films. AFM images contribute independent evidence for a surface microstructure evolution that is consistent with the XRD results. Oriented films can therefore be grown with the desired molecular orientations by careful selection of an appropriate combination of the above deposition parameters.

OF+EL-WeP12 Current Sensing AFM Study on Electric Property of Organic Monolayer Formed on Hydrogen Terminated Si(111) via Si-C Bond, *K. Uosaki*, ***J.-W. Zhao***, Hokkaido University, Japan

Current Sensing AFM was used to measure the conductivity of alkyl monolayer of various chain length formed on hydrogen terminated Si(111) via Si-C Bond. Conductance was dependent on chain length, bias and force. The current increased exponentially with the bias. Based on the chain length dependence of the Log(current) - bias relation, the conduction mechanism is discussed. The force dependence of the conductance at a given bias was well explained by the bending of the monolayer and the chain length dependence of the mechanical property of the monolayer will be discussed.

OF+EL-WeP13 Surface Structure and Surface Properties of Organosilane Monolayers Selectively Assembled on the Si-wafer Substrate, ***A. Takahara***, *T. Koga*, *M. Morita*, *H. Otsuka*, Kyushu University, Japan

Three-component micropatterned organosilane monolayers were successfully fabricated on Si-wafer substrate by stepwise vacuum ultraviolet-ray (VUV) photolithography technique with a rotation of line-type photomask. The introduction of different organosilanes was confirmed by X-ray photoelectron spectroscopy (XPS). Atomic force microscopic and lateral force microscopic observations revealed that the line-widths of micropatterned surface corresponded to those of photomask. Micropatterning of the surface functional groups influenced the magnitudes of surface free energy.

Organic Films and Devices
Room: C-102 - Session OF+EL+SC-WeA

Molecular and Organic Films and Devices
Moderator: N. Koch, Princeton University

2:00pm **OF+EL+SC-WeA1 Recent Developments in Organic Optoelectronics**, ***S.R. Forrest***, Princeton University **INVITED**

The interest in organic materials for optoelectronic device applications has undergone explosive growth in the last several years. This growth has been propelled by advances in organic thin films for displays, and for low cost electronic circuits. With a few successful product introductions employing active electronic organic devices, it is possible that the "age of organic optoelectronics" has finally arrived. This talk discusses some of the recent progress in organic device technology, with an eye to the future which may include making active electronic devices with a single molecule. In particular, we discuss extremely high external emission efficiency organic light emitting devices used for displays and lighting applications. Also, similar progress in high bandwidth, high efficiency of organic photodiodes, and efficient thin film photovoltaic cells are discussed. For example, multilayer organic nanostructure photodetectors are found to have very high frequency response with detection sensitivity in the visible spectral range. Finally, we present some new ideas on organic device fabrication enabling patterning of structures on the nanometer scale in both the vertical and horizontal directions.

3:00pm **OF+EL+SC-WeA4 Electron Transport in Platinum Complex Molecules: An Approach to Molecular Electronics**, *T.L. Schull, J.G. Kushmerick,* ***R. Shashidhar***, Naval Research Laboratory

Molecules that are highly conducting and which can be attached to metal on both sides via a functional chemical group form the basic elements of a molecular electronic device. Electron transport across different types of organic molecules are being actively investigated using different types of measuring test beds. In this paper, we present results of our electron conduction studies across a family of organo metallic molecules using a new cross-wire test bed developed recently.[1] We show that trans-platinum-bis-acetylides show good electron transport across their molecular length that are even better than the properties of the corresponding π-conjugated oligo(phenyleneethynylene) studied by several groups. The dependence of the metal ligands on the electron transport properties of materials is discussed. We have also used a simple extended Huckel Theory coupled with a Green Function approach to calculate the current voltage characteristics of these molecules. These theoretical calculations are compared with experiments.

1. J.G. Kushmerick, D.B. Holt, J.C. Yang, J. Naciri, M.H. Moore and R. Shashidhar, to be published.

3:20pm **OF+EL+SC-WeA5 Organic Light-Emitting Diodes and Solar Cells with Electrically Doped Transport Layers**, ***K. Leo***, TU Dresden, Germany **INVITED**

In classical semiconductor technology, controlled n- and p-type doping has always been a standard technique. In contrast, organic materials for devices such as organic light-emitting diodes (OLED) are usually prepared in a nominally undoped form. We discuss results of a comprehensive study of controlled electrical doping of various thin-film molecular organic materials. The layers are prepared by co-evaporation of matrix materials with acceptor molecules and characterized by several electrical techniques. UPS and XPS measurements directly show the Fermi level shift and the reduction of space charge layer width due to increasing doping.[1] We further show that these electrical doping concepts can be successfully applied in devices. The concept of molecular doping is applicable for amorphous wide-gap hole transporting materials and allows for realizing devices with the lowest operating voltages reported so far for small-molecule devices.[2] The concept of controlled doping has also enabled us to prepare a semitransparent inverted OLED with outstanding performance. It features an inverted layer sequence with ITO efficiently injecting electrons into a highly n-doped layer, despite a very large energy barrier of around 1.8eV. The devices reaches display brightness of 100Cd/m2 at 3.4V, which is far below any other literature result. We will also present first results on doped phosphorescent OLEDs which show that the concept of electrical doping can be extended to high-efficiency emitters. Finally, we will discuss the application of doped transport layers in solar cells. (Work done in collaboration with M. Pfeiffer, J. Blochwitz-Nimoth, X. Zhou, J. Huang, D. Qin, B. Maennig, D. Gebeyehu, A. Werner, J. Drechsel.)

[1] J. Blochwitz et al., Organic Electronics, 2 , 97 (2001)

[2] J. Huang et al., Appl.Phys. Lett. 80, 139 (2002).

4:00pm **OF+EL+SC-WeA7 Understanding Charge Transport Across Metal-Molecule-Metal Junctions**, ***J.G. Kushmerick***, *R. Shashidhar*, Naval Research Laboratory

Charge transport across a metal-molecule-metal junction is regulated by three factors 1) the structure of the molecule 2) the nature of the metal-molecule contacts and 3) the choice of metal electrode. We use an experimentally simple crossed-wire tunnel junction to interrogate how each of these three factors influences the current-voltage characteristics of a molecular junction. Results on symmetric and asymmetric junctions demonstrate that a specific molecular core can act either as a molecular wire or a molecular rectifier depending on its coupling to the metal electrodes. We will also show that the experimentally measured conductance of a molecular wire can be directly related to how well it's π-conjugated backbone mimics an ideal one-dimensional metal.

4:20pm **OF+EL+SC-WeA8 Zero-bias Anomaly in Molecular Monolayer Tunneling**, ***D.R. Stewart***, *D.A.A. Ohlberg, P.A. Beck, R.S. Williams*, Hewlett-Packard Laboratories

Electron tunneling is the dominant transport mechanism in nearly all proposed molecular electronic devices. Standard tunneling theory is normally used to predict device behavior, yet few experimental investigations of molecular tunneling exist due to the difficulty in constructing high quality molecular monolayer films. We describe detailed electronic transport characterization of several planar electrode / Langmuir-Blodgett (LB) molecular monolayer / electrode systems that show a large zero-bias anomaly and an anomalous exponential temperature dependence. Single-species LB monolayers of C_{22}, C_{20}, C_{18}, C_{16} and C_{14} carboxylic acid alkanes were sandwiched between upper and lower platinum electrodes, with active device areas of 7-200μm^2. Current and differential conductance were measured as a function of voltage ±1V and temperature 2-300K. Below 40K, device characteristics were constant. Surprisingly, from 40-300K device currents were exponential in temperature. A very wide ±150mV dip in conductance was also present and temperature activated. Both results contradict standard tunnel theory, indicating that the electronic transport is not yet understood even in this simplest symmetric alkane monolayer system.

4:40pm **OF+EL+SC-WeA9 Lateral Confinement of Interfacial Electrons by a Surface Dipole Lattice**, ***X.-Y. Zhu***, *G. Dutton*, University of Minnesota

Interface formation between molecules and a solid substrate often involves charge redistribution, the extent of which can influence a wide range of physical and chemical phenomena. In high mobility field effect transistors (FETs) based on organic single crystals, charge transport is believed to occur in one to two layers of molecules at the organic-dielectric interface. Such an interface may involve charge redistribution and dipole formation. The presence of surface dipoles may significantly alter lateral charge transport in the thin organic layer. When the interface is disordered, these surface dipoles are scattering centers for band transport. On the other hand, if the interface is ordered, there is essentially a two-dimensional lattice of dipoles. Such a surface dipole lattice should give rise to an electrostatic potential which provides periodic confinement of valence and conduction band electrons. We demonstrate this effect for image electrons on C60 thin film covered Cu(111) using angle resolved two-photon photoemission spectroscopy. Metal-to-molecule electron transfer within the first layer creates a (4x4) superlattice of surface dipoles. Such a surface dipole lattice provides lateral confinement of image electron wavefunction, effectively eliminating parallel dispersion for the n=1 image state on one monolayer C60 covered Cu(111). This is in contrast to the significant dispersion observed at higher coverages. The electrostatic potential from the surface dipole lattice is screened by additional layers of C60 molecules, thus, restoring the expected free electron behavior (parallel to the surface) for image states. Quantum mechanical simulation reproduces experimental findings and reveals the extent of wavefunction localization by the surface dipole lattice.

5:00pm **OF+EL+SC-WeA10 Measurement of the Site Specific PDOS of Organic Electronic Materials via Soft X-ray Emission Spectroscopy[1]**, ***J.E. Downes***, *C. McGuinness, P. Sheridan, K.E. Smith,* Boston University, *J.A. Schlueter, U. Geiser,* Argonne National Laboratory, *G. Gard*, Portland State University

Recent advances in the technique of soft x-ray emission spectroscopy (XES) have produced a method to directly measure the bulk elementally and, in certain cases chemically, specific partial density of states of materials. While the detailed measurement of the valence band electronic structure of solids has traditionally been the realm of photoemission spectroscopies several problems have been encountered with the application of these techniques to organic materials. The principal issue is photon induced damage to the compound that modifies the electronic structure as it is being measured. Another is the fact that photoemission measurements probe the surface electronic structure of a material, which may or may not be representative of the bulk. We will show that the use of XES can avoid both of these problems and allows the detailed valence band electronic structure of recently developed organic electronic compounds to be measured. An overview of the technique of XES and its advantages for studying these organic compounds will be followed by specific results from several organic electronic compounds of current interest in the fields of molecular organic semiconductors, (TDATA, Alq_3, TPD, Cu-Pc etc.), and ET based conducting organic charge transfer salts, (β-$(ET)_2SF_5CH_2CF_2SO_3$).

[1] Work supported in part by the DOE under DEFG0298ER45680; the SXE spectrometer was funded by the U.S. ARO under DAAH04950014. The experiments were performed at the NSLS which is supported by the U.S. DOE, Divisions of Materials and Chemical Sciences.

Thursday Morning, November 7, 2002

Surface Science
Room: C-112 - Session SS+EL+OF-ThM

Reactions and Patterning of Organics on Silicon
Moderator: S.F. Bent, Stanford University

8:20am **SS+EL+OF-ThM1 Fixation of Alkyl Groups on Si(111) Surface through C-Si Single Covalent Bond formed by Reaction of Grignard Reagent and H:Si(111)**, ***T. Yamada***, *T. Inoue, K. Yamada, N. Takano, T. Osaka,* Waseda University, Japan, *H. Harada, K. Nishiyama, I. Taniguchi*, Kumamoto University, Japan

Alkyl adsorbates that are directly bonded to the outermost atoms of silicon wafer surfaces have prospective properties for application in nanometer-scale fabrication and surface functionalization.[1] Several methods have been proposed to deposit alkyl groups on hydrogen-terminated H:Si(111).[2] The conversion of the H-Si bonds in H:Si(111) into C-Si bonds caused by chemical processes is an important issue in preparing the organic adlayers. In this work, high-resolution electron energy loss spectroscopy (HREELS) was utilized to prove the formation of single covalent bonds between Si(111) surface atoms and alkyl groups by the chemical reaction of a Grignard reagent and hydrogen-terminated H:Si(111)(1x1).[2] The reaction was performed by heating a piece of H:Si(111) in 1M tetrahydrofuran (at 65°C) or diethylether solution (at 30°C) of desired alkylmagnesium halide for 18 hours under Ar atmosphere. By this reaction condition, somewhat 20% of the product surface were still covered with residual hydrogen. The bending vibration mode of the residual hydrogen (630 cm^{-1}) obscured the alkyl signals in the range of 600 - 700 cm^{-1}. By using deuterium-terminated D:Si(111), the vibration at 680 cm^{-1}, assigned to the C-Si bond, was isolated within the spectrum of CH_3-. The CH_3 groups were thermally stable at temperatures below 600 K. Similar features were observed for C_2H_5-, phenyl- and so on. The C-Si bonds are essential for enhancing the stability and lowering the mobility of alkyl moieties. Such properties of alkyl moieties of will lead to a new prospective science and technology in nanometer-scale fabrication.

[1] T. Yamada, N. Takano, K. Yamada, S. Yoshitomi, T. Inoue, and T. Osaka, Jpn. J. Appl. Phys. 40 (2001) 4845.

[2] R. Boukherroub, S. Morin, F. Bensebaa and D. D. M. Wayner, Langmuir 15 (1999) 3831.

8:40am **SS+EL+OF-ThM2 Chemomechanical Production of Sub-Micron Edge Width, Functionalized, ~20 Micron Features on Silicon**, ***M.R. Linford***, *Y.-Y. Lua, T.L. Niederhauser, B.A. Wacaser*, Brigham Young University, *I.A. Mowat,* Charles Evans & Associates, *A.T. Woolley, R.C. Davis*, Brigham Young University, *H.A. Fishman*, Stanford University Medical School

We have recently reported that monolayers on silicon can be formed, and silicon substrates concomitantly patterned, when native oxide-terminated silicon is scribed with a diamond-tipped instrument in the presence of 1-alkenes,[1,2] 1-alkynes,[1,2] alkyl halides (chlorides, bromides, and iodides),[2,3] and alcohols.[3,4] Monolayers were prepared in the open laboratory with reagents that had not been degassed.[1-4] However, while this method is particularly facile, the features produced using a diamond scribe are coarse and irregular.[1] The high degree of edge and surface roughness in these features will no doubt limit the utility of our earlier work in some circumstances. Here we describe a substantial improvement in our earlier method by showing the production of sharp, well-defined, functionalized features on silicon that are invisible to the naked eye and very shallow. In contrast to the earlier procedure that used oxide-terminated silicon and a diamond-tipped scribe,[1-4] this new method consists of 1) cleaning and drying a silicon shard, 2) immersing the silicon in a fluoride ion etch to remove its native oxide and produce hydrogen-terminated silicon, 3) wetting the dry, H-terminated silicon surface with a reactive liquid, and 4) scribing the surface with a small tungsten carbide ball. Both Si(100) and Si(111) were successfully patterned and functionalized with this new method.

[1] Niederhauser, T. L.; Jiang, G.; Lua, Y.-Y.; Dorff, M. J.; Woolley, A. T.; Asplund, M. C.; Berges, D. A.; Linford, M. R. Langmuir 2001, 19, 5889-5900.

[2] Lua, Y.-Y.; Niederhauser, T. L.; Matheson, R.; Bristol, C.; Mowat, I. A.; Asplund, M. C.; Linford, M. R. In Press Langmuir 2002.

[3] Niederhauser, T. L.; Lua, Y.-Y.; Sun, Y.; Jiang, G.; Strossman, G. S.; Pianetta, P.; Linford, M. R. Chem.Mater. 2002, 14, 27-29.

[4] Niederhauser, T. L.; Lua, Y.-Y.; Jiang, G.; Davis, S. D.; Matheson, R.; Hess, D. A.; Mowat, I. A.; Linford, M. R. In press Angewandte Chemie 2002.

9:00am **SS+EL+OF-ThM3 Formation of Nanoscale Organic and Inorganic Features on Semiconductor Surfaces**, ***J.M. Buriak***, Purdue University **INVITED**

Integration of molecular devices and nanoscale materials with semiconductors, including silicon and germanium, is an area of intense interest, due to the potential for interfacing nanomaterials with the macroworld. We have developed a number of wet chemical routes which allow for covalent attachment of both organic functionalities, including molecular wires, and inorganic nanoparticles. For instance, a cathodic electrografting reaction between alkynes and hydride-terminated silicon surfaces results in alkynyl moieties bound directly through Si-C bonds, with no intervening oxide layer. The surfaces are air and water stable, and can withstand boiling pH 12 solutions. In order to pattern these alkynyl groups on the silicon surface in nanoscale regions, conducting probe lithography has been utilized to write the organic monolayers, with feature sizes as small as 30 nm. For inorganic structure patterning, electroless deposition has been combined with microcontact printing, dip pen nanolithography (DPN), and UV-mediated hydrometallation to produce nano- and micron-scale features. These approaches and others will be described.

9:40am **SS+EL+OF-ThM5 Structures, Dynamics, and Chemical Reactivity of Si (001) at Finite Temperatures: A First Principles Study**, *D. Pillay, Y. Wang,* ***G.S. Hwang***, The University of Texas at Austin

Imparting organic functions onto a well-defined functionality of semiconductor surfaces with atomic-scale precision provides an enormous opportunity to develop new molecular devices including chemical and biological sensors and molecular electronic devices. For semiconductor systems, the rates and pathways of chemical reactions are strongly influenced by local electronic structures determined by surface reconstructions and defects. Due to such complex structural effects, chemical dynamics on semiconductor surfaces has not been fully understood. To gain molecular-level control, therefore, first we must develop a detailed understanding of structures, dynamics, and chemical reactivity of clean, defective, or modified (with various adsorbates) surfaces at finite temperatures, along with the structures and bonding of organic compounds onto the surfaces. In this talk we will present first principles quantum mechanics [Density Functional Theory with plane-wave basis sets and pseudopotentials] simulations for structures, dynamics, and chemical reactivity (towards organic species) of (001)-faced Si and Ge surfaces at finite temperatures. This includes the dynamics of buckled dimers on clean and defective surfaces and their effects on adsorption dynamics of various organic molecules.

10:00am **SS+EL+OF-ThM6 Superexchange Interactions in STM-Organic-Semiconductor Systems**, ***L.C. Teague***, *J.J. Boland*, University of North Carolina at Chapel Hill

The incorporation of organic layers and individual molecules into existing semiconductor technologies requires a thorough understanding of surface/molecule reactions. Although numerous studies have focused on the reaction of individual molecules with the Si(100) surface, the specific reaction mechanisms remain poorly understood. The similarity of the Si(100)-2 x 1 surface chemistry with that of C=C systems opens up the possibility of a wide range of organic chemistry reactions. Here, a combination of Scanning Tunneling Microscopy (STM) and Density Functional Theory (DFT) calculations are used to study and interpret the reaction of 1,3-cyclohexadiene (1,3-CHD) with the bare Si(100)-2 x 1 surface. Because STM probes the local density of states (LDOS), the local bonding geometry of 1,3-CHD can be inferred from the location of the π bond in the adsorbed molecule. Other groups have reported similar observations.[1,2] However, DFT calculations indicate the π^* orbital is located several eV above the Fermi Energy and should be energetically inaccessible under typical bias conditions. Here, we show that these images can be understood by considering the interaction between the STM tip and the molecule-surface system. The superexchange mixing of the tip dangling bond state with the filled π state on the molecule produces a new state within the tunneling window. This state is responsible for the observed image contrast and suggests superexchange effects of this type may be important in understanding the charge transfer that occurs through these molecular systems.

[1] Hamaguchi, K.; Machida, S.; Nagao, M.; Yasui, F.; Mukai, K.; Yamashita, Y.; Yoshinobu, J.; Kato, H. S.; Okuyama, H.; Kawai, M.; Sato, T.; Iwatsuki, M. J. Phys. Chem. B 2001, 105, 3718.

[2] Hovis, J. S.; Liu, H.; Hamers, R. J. J. Phys. Chem. B, 1998, 102, 6873.

10:20am **SS+EL+OF-ThM7 Modifying the Semiconductor Interface with Organonitriles**, ***M.A. Filler***, *C. Mui, C.B. Musgrave, S.F. Bent*, Stanford University

Organic functionalization of group-IV semiconductor surfaces has recently garnered considerable attention and applications in the areas of molecular electronics, biological recognition, and reagentless micropatterning have been proposed. If these and other concepts are to become technologically feasible, however, the creation of an ordered and selectively grown layer as well as the ability to successively attach additional organic monolayers will be necessary. Organonitrile compounds were studied as potential candidates for first and subsequent layer surface reactions on Si(100)-2x1 and Ge(100)-2x1. Bonding is investigated experimentally with infrared spectroscopy and theoretically with density functional theory. We find that acetonitrile does not react on the Ge(100)-2x1 surface at room temperature and explain this result with kinetic and thermodynamic arguments. A [4+2] cycloaddition product through the conjugated π system and a [2+2] C=C cycloaddition product through the alkene are found to be the dominant surface adducts for the multifunctional molecule 2-propenenitrile. While the non-conjugated molecules 3-butenenitrile and 4-pentenenitrile are not expected to form a [4+2] cycloaddition product, both show vibrational modes characteristic of this adduct and we propose the possibility of a surface catalyzed reaction. Pathways directly involving only the nitrile functional group are thermodynamically unfavorable at room temperature on Ge(100)-2x1 and the conversion of the remaining nitrile functionality as well as its use in additional surface reactions will also be presented.

10:40am **SS+EL+OF-ThM8 Adsorption and Reaction of Allyl- and Ethyl-amine on Germanium and Silicon Surfaces**, *P. Prayongpan*, ***C.M. Greenlief***, University of Missouri-Columbia

The adsorption and reaction of allyl- and ethyl-amine with the Ge(100) and Si(100) surfaces is examined. These processes are followed by a variety of surface sensitive techniques including ultraviolet photoelectron spectroscopy and temperature programmed desorption. Possible adsorption structures are also examined by theoretical methods. Density functional theory calculations are used to help interpret the photoelectron spectroscopy data. The calculated molecular orbital energies (within Koopmans' approximation) are used to help identify adsorbed molecular species, as well as, reaction intermediates. The interaction of these nitrogen-containing molecules with surface dimmer bonds and ordering of the resulting surface layers will be discussed.

11:00am **SS+EL+OF-ThM9 Adsorption Chemistry of Cyanogen Bromide and Iodide on Silicon (100)**, ***N.F. Materer***, *P. Rajasekar, E.B. Kadossov*, Oklahoma State University

The adsorption of cyanogen iodide (ICN) and bromide (BrCN)on a silicon (100) surface is studied by X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS) and thermal desorption spectroscopy (TPD). After submonolayer exposures, XPS indicates that the CN triple bond of both ICN and BrCN emains intact upon adsorption at 100K. The UPS spectrum of these molecules contains two peaks assigned to the pi electrons in the CN triple bond. The splitting of these levels, due to the interaction between the pi electrons on the cyanogen and the halide, show that some portion of the initially adsorbed cyanogens halide also remains intact upon low temperatures adsorption. In contrast, the UPS spectrum of ICN and BrCN adsorbed at room temperature on Si(100) contains only one peak due to the pi electrons in the carbon nitrogen triple bond. The lack of splitting in the room temperature UPS spectrum is a result of XC (X=Br, I) bond dissociation. Thus, the XC bonds breaks while the CN bond remains intact during room temperature adsorption on Si(100). Upon annealing the Si(100) surface to higher temperatures, the UPS spectra indicates that the C-N triple bond remains intact until approximately 700 K. Simultaneous changes in the C 1s photoelectron peak are consistent with the idea that C-N bond cleavage in the cyanogen halides is correlated with silicon carbide formation.

11:20am **SS+EL+OF-ThM10 Theoretical Adsorption Studies of ICN on the Si(100) Surface**, ***E.B. Kadossov***, *P. Rajasekar, N.F. Materer*, Oklahoma State University

Ab initio quantum calculations have been used to study the adsorption and surface reactions of ICN on the Si(100) surface represented by Si_2H_{12} single-dimer cluster. At low temperatures, experiments show that some faction of the initially exposed ICN is molecularly absorbed to the surface. Calculations of the molecularly absorbed species support the formation of end-on configuration with the N forming a dative bond with the lone pair on the Si(100) surface. Upon annealing, experiments reveal that the remaining molecular adsorbed ICN species dissociate to produce I and CN species on the surface. Calculations show that this process can take place directly or through a stable side-on adsorption intermediate. The transition barrier to form the side-on intermediate species is slightly lower than for the direct reaction (12.82 vs. 17.26 kJ/mol). After dissociation, the CN is bound to the silicon surface through either the C or the N ends. The C bound species possesses the lowest energy and is consistent with experimental XPS results. In addition, these two possible structures are separated by an activation barrier of 107.39 kJ/mol, easily overcome by the excess adsorption energy. An alternate pathway for the ICN side-on species is to isomerize into an INC structure through a 212.26 kJ/mol activation barrier. However, the activation barrier between this new species and the dissociated state is 5.53 kJ/mol. This transition barrier is even lower than the 84.05 kJ/mol barrier between side-on ICN surface species and the dissociated state.

11:40am **SS+EL+OF-ThM11 Infrared Study of Adsorption of C_6H_6 onto Si(100)(2x1)**, *M. Shinohara, H. Watanabe, Y. Kimura, H. Ishii*, ***M. Niwano***, Tohoku University, Japan

The interaction of benzene with the (100) and (111) surfaces of silicon has proven to be an interesting model system for molecular adsorption on semiconductor surfaces. The adsorption of benzene on the Si(100)(2x1) surface has been expensively studied in recent years both experimentally and theoretically. Previous elaborate theoretical calculations predicted that adsorption of benzene onto the Si(100)(2x1) surface leads to two different adsorption structures: One corresponds to benzene adsorbed on top of a dimer row between two adjacent Si dimers. This structure has four C atoms of benzene bonded to four Si atoms from two adjacent dimers. The other corresponds to the benzene molecule that sticks on top of the dimer row and has two of its C atoms bonded to two Si atoms of a single surface dimer. However, there still is a controversy regarding which structure is more favored. In this study, we have investigated the adsorption of benzene C_2H_6 on the Si(100)(2x1) surface using infrared absorption spectroscopy (IRAS) in the multiple internal reflection geometry (MIR) and the so-called hybrid density-functional theory (DFT) to determine the most preferred adsorption structure of benzene on Si(100)(2x1) at room temperature. IRAS-MIR provides us with valuable information about the hydrogen bonding configurations on semiconductor surfaces. We analyzed IRAS spectra in the C-H stretching vibration region to determine the detailed adsorption structure of benzene. The central result is that benzene adsorbs in different manners depending on the surface coverage of benzene: at low coverage the molecule adsorb on the surface to favor the formation of benzene adsorbed on two adjacent dimers. On the other hand, at high coverage the molecule adsorb on the Si surface to generate benzene adsorbed on a single dimer. We also discuss the reason why the adsorption structure depends on surface coverage.

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