

# SYMPOSIUM B

## Molecular and Biomolecular Electronics

April 17 – 18, 2001

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Proceedings to be published online  
(see *ONLINE PUBLICATIONS* at [www.mrs.org](http://www.mrs.org))  
as Volume 679E  
of the Materials Research Society  
Symposium Proceedings Series.

\* Invited paper

SESSION B1:  
Chair: William M. Tolles  
Tuesday Morning, April 17, 2001  
City (Argent)

**8:30 AM INTRODUCTORY COMMENTS.** Chad Mirkin

**8:45 AM \*B1.1**

**MOLECULES AND ELECTRONICS - A NEW WAY TO COMPUTE.** Christie R.K. Marrian, William L. Warren, Defense Advance Research Projects Agency (DARPA), Arlington, VA.

To create discovery beyond silicon, DARPA has started a program in Molecular Electronics (Moletronics) that proposes that both computational functionality and input/output architecture can be designed in molecular systems. These systems will have high device density (scalable to  $10^{11}$  device/cm<sup>2</sup>) and be amenable to greatly simplified manufacturing fabrication using hierarchical self-assembly, a bottom-up manufacturing approach. It is also anticipated that architecture, a top-down approach, will play an immense role in steering discovery as well. The talk will discuss three over-riding themes of Moletronics: molecular devices, hierarchical assembly, and architecture, and the interconnection between these themes. The first task is the development and optimization of molecular devices such as switches, nanotubes, multistate molecules and molecules exhibiting highly non-linear characteristics. The molecular devices need to be robust and congruous with the associated architecture; specific examples of molecular devices will be presented. The second task to be discussed is hierarchical self-assembly, i.e., bridging the nano- to the micro-worlds. This can be described as the interconnection of individual molecules into nano-modules and the interconnection between nano-modules to form computationally functional circuits with input/output (i/o). The third task is the development of circuit and systems architectures. Various architectures to be discussed will encompass programmability of the molecular circuit, general scalability issues (power dissipation, access time, etc.) as well as defect tolerance.

**9:15 AM \*B1.2**

**THE DESIGN AND MEASUREMENT OF MOLECULAR ELECTRONIC SWITCHES AND MEMORIES.** Mark Reed; Departments of Electrical Engineering and Applied Physics, Yale University, New Haven, CT.

Molecular-scale devices have recently become possible with the utilization of advanced microfabrication and self-assembly techniques. We have demonstrated a number of simple molecular devices and circuits, such as ; a negative resistance device that exhibits peak-to-valley ratios exceeding 1000:1; and a molecular memory cell with refresh times exceeding 10 minutes. The designs of molecular switches, memories, and their circuit applications will be discussed.

**10:15 AM \*B1.3**

**ELECTRICAL CHARACTERIZATION OF MOLECULAR DEVICES INTEGRATED WITH METAL NANOWIRES.** Theresa S. Mayer, Department of Electrical Engineering, Penn State University, University Park, PA; Thomas E. Mallouk and Christine D. Keating, Department of Chemistry, Penn State University, University Park, PA.

In this talk, we will discuss the electrical properties of self-assembled molecular monolayers that have been integrated within individual nanowires or at the intersection of crossing nanowires. The metal nanowires that we use are synthesized by electrodeposition of Au into a polycarbonate mesoporous membrane, which is dissolved to produce a colloidal suspension of 70-nm diameter nanowires. Molecular layers such as alkanes and phenyls are integrated onto the metal nanowires using thiol-based self-assembly. Following molecular assembly, we transfer individual nanowires and crossing nanowires from suspension onto insulating substrates where they are aligned between large area probe pads using an electric-field assisted alignment technique. The nanowires are contacted at the probe pads and the I-V characteristics are measured as a function of temperature to determine the transport properties of metal nanowires and molecular layers.

**10:45 AM B1.4**

**CHARGE TRANSFER AT MACROMOLECULAR SEMICONDUCTOR INTERFACES.** Carrie Daniels-Hafer, Meehae Jang, Frank E. Jones, Shannon W. Boettcher, Mark C. Lonergan, University of Oregon, Dept. of Chemistry and The Materials Science Institute, Eugene, OR.

Inorganic semiconductor — conjugated polymer interfaces lie at the intersection between traditional semiconductor devices and molecular electronics. As such, they provide a platform for studying issues of charge transfer and charge equilibration relevant to both areas. We present a detailed analysis of the charge transport characteristics of

the InP — polypyrrole interface demonstrating the importance of nanostructure and the failings of classic transport theories. Apparently anomalous current-voltage and capacitance-voltage data can be consistently interpreted by invoking heterogeneity models. The analysis highlights the conditions under which majority carrier transmission coefficients, a form of charge transfer rate constant, can be accurately extracted at semiconductor interfaces. Multiple orders-of-magnitude errors are possible if apparently slight deviations from classic transport theories are ignored. The dependence of the transmission coefficient and barrier height at the InP — polypyrrole interface on the doping type (n vs. p) of the InP, the doping level of the oxidatively doped polypyrrole, and the orientation of the InP are reported. The relation of these results to the molecular level engineering of semiconductor interfaces is discussed.

**11:00 AM \*B1.5**

**MOLECULES AS ELECTRONIC SWITCHES.** R. Stanley Williams, Hewlett-Packard Laboratories, Quantum Science Research, Palo Alto, CA.

Molecular electronics offers the possibility of constructing circuits with much higher device densities and lower power consumption than standard Si CMOS. I will outline some of the arguments that have been used in the past to define the limits to the operation of electronic devices, and classify them as kinetic or thermodynamic issues, and in the latter case if the transition is reversible or nonreversible. Then, I will present a model system to show how these limits apply (or don't apply) to molecules. Finally, I will present some preliminary electronic measurements collected on thin films of molecules to see if and how fundamental limits may apply to actual molecular switches at this stage of their development.

**11:30 AM B1.6**

**ANALYSIS OF THE USE OF MOLECULAR RESONANT TUNNELING DIODES FOR LOCAL REFRESH OF DYNAMIC RANDOM ACCESS MEMORY CELLS.** Jonas Berg, Stefan Bengtsson, Per Lundgren, Chalmers University of Technology, Department of Microelectronics, Göteborg, SWEDEN.

Device simulations have been made to analyze the use of molecular resonant tunneling diodes for local refresh of DRAM memory cells. Local refresh can be provided by a latch of a pair resonant tunneling diodes connected to the storage capacitor of the cell. Such a solution would significantly reduce the standby power consumption of the DRAM cell. We have compared the requirements on the resonant tunneling diodes for proper refresh operation with the electrical properties of published molecules with resonant IV-curves. The simulations show that no molecules with resonant electrical properties published so far in the literature have properties making them useful for this particular application. This is true also for low temperature operation. The issues of maximum tolerable series resistance and of maximum tolerable fluctuations in the number of attached molecules have also been addressed. Our results show that the focus for development of molecules with resonant electrical properties should be to find molecules with resonance for lower applied voltages and lower current levels than the molecules published so far. If the synthesis of new molecules with attractive properties is successful the merging of silicon technology and molecular electronics, for instance for new generations of DRAM cells, is a realistic future path of microelectronics.

**11:45 AM B1.7**

**RESONANT TUNNELING DIODES BASED ON MOLECULAR WIRES INCORPORATING SATURATED SPACERS: A QUANTUM-CHEMICAL STUDY.** Yasser Karzazi<sup>a</sup>, Jérôme Cornil<sup>a</sup>, and Jean-Luc Brédas<sup>a,b</sup>, <sup>a</sup>Service de Chimie des Matériaux Nouveaux, Université de Mons-Hainaut, BELGIUM; <sup>b</sup>Department of Chemistry, The University of Arizona.

The search for novel alternatives allowing increased miniaturization of electronic circuits has opened the way to the emerging field of molecular electronics. This research area has been recently stimulated by the demonstration that single molecules or a small number of self-assembled molecules can perform the basic functions of traditional electronic components, such as wires and diodes. In particular, it was shown that molecular wires inserted into nanopores can be used as active elements for the fabrication of resonant tunneling diodes (RTDs), whose I/V characteristics reveal a Negative Differential Resistance (NDR) behavior (i.e., an initial raise of the current followed by a sharp decrease when the voltage is progressively increased); interestingly, such a peak profile can be exploited for the design of switching devices and more complex memory and logic circuits. In this contribution, we provide a detailed description at the quantum-chemical level of the mechanisms leading to the NDR behavior observed experimentally for a polyphenylene-based molecular wire incorporating saturated spacers [1]. To do so, we have characterized the evolution of the one-electron structure of this

molecular wire and some of its derivatives under the influence of a static electric field aligned along the molecular axis, which simulates the driving voltage applied between the two electrodes in the RTD devices. We also illustrate the way the main parameters controlling the NDR behavior can be modulated through molecular engineering of the wires.

[1] M.A. Reed, IEEE Proc. 87, 652 (1999).

#### SESSION B2:

Chair: Edwin A. Chandross  
Tuesday Afternoon, April 17, 2001  
City (Argent)

#### 1:30 PM \*B2.1

PHYSICAL AND ARCHITECTURAL LIMITS FOR MOLECULAR-SCALE DEVICES IN COMPUTERS. Rick Lytel, Sun Microsystems, Palo Alto, CA.

This talk describes the fundamental physical limitations placed on molecular-scale devices that can be integrated into computers. It also describes some potential interconnect networks and architectures consistent with the physical limits, and incorporates requirements that modern computer systems are necessarily designed for high availability.

#### 2:00 PM \*B2.2

MONODISPERSE NANOCRYSTALS AS MOLECULAR-SCALE ELECTRONIC BUILDING BLOCKS. C.B. Murray, Shouheng Sun, C.T. Black, Glenn Held, IBM T.J. Watson Research Center, Yorktown Heights, NY; Wolfgang Gaschler, BASF, Ludwigshafen, GERMANY.

We explore the potential of monodisperse magnetic and semiconductor nanocrystals (NCs) as molecular-scale electronic building blocks for future magneto-electronic and optoelectronic applications. General synthetic routes to produce monodisperse NCs are discussed with examples drawn from Co, FePt and PbSe systems. The NC composition, size and shape are controlled and the NC size is tunable from 2-16 nm diameter with a standard deviation less than 5 percent standard deviation in these systems. These NC samples exhibit a distinct set of physical properties by virtue of the precisely controlled size, shape and composition and thus constitute a discrete set of molecular scale building blocks. High quality samples allow studies of the size dependent evolution of magnetic, electronic and optical properties with NC size. These monodisperse NCs assemble on solid substrates to form 2D and 3D epitaxial superlattices (colloidal crystals). The magnetic NC assemblies are explored as models for high-density density recording media and granular giant magnetoresistive (GMR) effects. The PbSe NCs exhibit tunable absorption and emission properties in technologically important infra-red optical bands. Optical and structural characterization of the PbSe NCs and NC superlattices will also be presented.

#### 2:30 PM B2.3

A SILICON STRUCTURE FOR ELECTRICAL CHARACTERISATION OF NANOSCALE ELEMENTS. P.J.A. Sazio, University of Cambridge, Cavendish Laboratory, Cambridge, UNITED KINGDOM; J. Berg, Chalmers University of Technology, Department of Microelectronics ED, Gothenburg, SWEDEN; C.J.B. Ford, University of Cambridge, Cavendish Laboratory, Cambridge, UNITED KINGDOM; P. Lundgren, Chalmers University of Technology, Department of Microelectronics ED, Gothenburg, SWEDEN; N.C. Greenham, D.S. Ginger, University of Cambridge, Cavendish Laboratory, Cambridge, UNITED KINGDOM; S. Bengtsson, Chalmers University of Technology, Department of Microelectronics ED, Gothenburg, SWEDEN; A.G. Davies, University of Cambridge, Cavendish Laboratory, Cambridge, UNITED KINGDOM.

The problem of mass manufacturing electrode structures suitable for contacting nanoscale elements lies primarily in the difficulty of fabricating a nanometre-scale gap between two electrodes in a well controlled, highly parallel manner. In ULSI circuit production, the gate and substrate in MOSFETs are routinely fabricated with a precise vertical spacing of 3 nm between them. In this work, we have reconfigured the ubiquitous MOS device structure to operate as electrodes to molecular-scale components. The silicon dioxide layer that provides vertical separation and electrical insulation between two regions of silicon (the crystalline substrate and the poly-crystalline gate) gives a leakage current of 1 nA per square micron at 1 V for an oxide thickness of 2 nm [1]. This will enable objects the size of single molecules that are held across this layer to be detected electrically if they provide currents on the nanoampere scale, assuming a parasitic area for leakage between gate and substrate of order one square micron. The issues of providing strong physical and chemical contact between various molecules and a silicon substrate have been addressed in a number of studies [2]. The MOS nanocontacting device will give

information regarding the net electrical response of the silicon-nanoscale element-silicon structure, where factors such as doping levels, surface treatment and temperature dependence are likely to play important roles. In the future this kind of device has the potential to provide a bolt-on technology for the fabrication of ULSI circuits in which conventional CMOS devices are directly hybridised with functional nanoscale elements. [1] M. Hirose, M. Koh, W. Mizubayashi, H. Murakami, K. Shibahara and S. Miyazaki, Semicond. Sci. Technol. 15 485 (2000) [2] G.P. Lopinski, D.M. Wayner and R.A. Wolkow, Nature 406 48 (2000)

#### 2:45 PM B2.4

ELECTRONIC PROPERTIES OF BISMUTH NANOWIRES.

S.B. Cronin<sup>a</sup>, Yu-ming Lin<sup>b</sup>, O. Rabin<sup>c</sup>, M.R. Black<sup>b</sup>, M.S. Dresselhaus<sup>a,b</sup>, J.Y. Ying<sup>d</sup>, <sup>a</sup>Department of Physics, <sup>b</sup>Department of Electrical Engineering and Computer Science, <sup>c</sup>Department of Chemistry, and <sup>d</sup>Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA.

We have synthesized Bi nanowire arrays by a template-assisted pressure injection method. The nanowire arrays are embedded in an anodic alumina template. Since Bi has very small electron effective masses and a high carrier mobility, it is desirable to observed quantum confinement effects in Bi nanowires. By varying the template fabrication conditions, nanowires with diameters ranging from 10 to 200 nm and length  $\sim 50 \mu\text{m}$  can be produced. The nanowires are found to be highly crystalline and exhibit a preferred crystal orientation dependent on the wire diameter along the wire axis. Alloying Bi with Sb causes significant change in the band structure of the material. Bi-Sb, Te doped Bi and pure Bi nanowires are prepared and characterized. Various transport measurements are performed on these nanowires for different Bi-Sb ratios, Te doping concentrations and wire diameters. Magnetoresistance measurements show boundary scattering effects indicating a long carrier mean free path, and a 1D to 3D localization effect below 4K. Theoretical modeling for these cylindrical nanowires is developed to explain the experimental results. It is found that Bi-Sb nanowires provide a highly flexible 1D system in which the band structure, and therefore various electronic properties, can be engineered by carefully tailoring the wire diameter and Sb and Te concentrations.

We gratefully acknowledge the support of MURI subcontract 0205-G-7A114-01, NSF grant CTS-9257223 and DMR-98-04734, and the US Navy contract N00167-92-K0052.

#### 3:30 PM B2.5

ELECTRON TRANSPORT IN LOW-DIMENSIONAL METAL NANOPARTICLE ARRAYS CHEMICALLY-ASSEMBLED ON BIOPOLYMER SCAFFOLDS. Laura Clarke, Christopher A. Berven, Martin N. Wybourne, Department of Physics and Astronomy, Dartmouth College, Hanover, NH; Jana Mooster, James E. Hutchison, Department of Chemistry and Materials Science Institute, University of Oregon, Eugene, OR.

As microelectronic device feature sizes decrease towards molecular scales, this size evolution is facing serious technical, fundamental and economic challenges. A number of revolutionary departures from the conventional semiconductor device paradigm are currently being investigated to address these issues. In particular, nanostructures, in which inherent single electron tunneling and charging effects can be exploited for device applications are receiving much attention. Although patterned nanostructures at the limits of electron-beam lithography (ca. 15 nm) are too large to achieve clear single electron effects at room temperature, assemblies of metal or semiconductor nanoparticles that have well-defined dimensions are small enough that single electron effects can be exploited at room temperature. In order to utilize nanoparticle building blocks, or even to explore their electrical properties, we and others have developed methods to assemble arrays and make electrical contact to them. Although considerable progress has been made toward rational assembly of nanoparticle arrays, few measurements of the lateral transport through spatially defined nanoparticles arrays have been reported. Our method for nanofabrication involves the assembly of functionalized metal nanoparticles onto rigid biomolecular scaffolds cast upon an insulating substrate and bridged between narrowly spaced electrodes. This simple, wet chemical approach yields one- and two-dimensional arrays of gold nanoparticles that exhibit more stable electrical behavior (Coulomb blockade) compared with non-patterned samples. Current-voltage measurements and AFM imaging suggest that electron transport is dominated by one-dimensional nanoparticle chains. Further, the electrical response shows clear, robust single electron charging effects that are insensitive to defects within the chemical assembly. Given the simple assembly method used, the transport properties and defect tolerance are unexpected. The structural parameters that lead to the unique properties of these arrays, including defect tolerance, will be discussed.

**3:45 PM \*B2.6**

MOLECULAR WIRES: CHARGE INJECTION, CHARGE TRANSPORT AND MOTION MECHANISMS IN MOLECULAR INTERCONNECT JUNCTIONS. Y.A. Berlin, A.L. Burin, V. Mujica, A. Nitzan, Y. Xue and M.A. Ratner, Northwestern University, Evanston, IL.

The passive molecular interconnect, or molecular wire, provides charge transport between macroscopic electrodes, but is itself a nanoscale entity for discrete molecular energy levels. Charge can transport through such molecular junctions either coherently (Landauer tunneling) or incoherently (injection and thermalized hopping). We will discuss both limits of such processes, focusing on charge injection, electrostatic optimization, the Poisson determination of the applied field, and the nonlinear/cold characteristics to be expected in the molecular wires of different structures, including pi-systems, DNA and coherent structures such as nanotubes.

**4:15 PM \*B2.7**

HIGHLY REGULAR ANODIC ALUMINA TEMPLATES FOR POSSIBLE NANOELECTRONICS APPLICATIONS. Martin Moskovits, Diyaa Almalawi, Anita Osika, Ken Bosnick, Alexej Michailowski, Dept. of Chemistry, University of Toronto, CANADA.

Anodic alumina can be electrochemically produced with a highly regular pore structure, pore diameters ranging from ~4 to ~400 nm and pore lengths exceeding one hundred micrometers. Judicious use of electrochemical deposition, CVD or other deposition strategies can produce metal semiconductor or insulator nanowires or nanotubes inside the pores of these anodic alumina templates. By sequentially applying these strategies one can fabricate "insulated" nanowires, nanocapacitor arrays, and other structures with potential application in nanoelectronics. Some of these will be described.

SESSION B3: POSTER SESSION  
Tuesday Evening, April 17, 2001  
8:00 PM  
Metropolitan Ballroom (Argent)

**B3.1**

SYNTHESIS AND LB FILM-FORMING PROPERTIES OF AN AMPHIPHILIC DYE IN WHICH THE HYDROPHOBIC TAIL IS FULLY CONJUGATED. Geoffrey J. Ashwell, Andrew Green, Mukhtar A. Amiri, Richard Hamilton, Cranfield University, The Nanomaterials Group, Centre for Photonics and Optical Engineering, Cranfield, UNITED KINGDOM.

Conventional Langmuir-Blodgett materials have for many years been derivatised containing hydrophobic alkyl chains. These serve to aid the alignment at the air-water interface but, within the deposited film, incorporate insulating layers between the active units. Their removal would be expected to produce an increased second-order susceptibility and improved molecular rectification and photovoltaic properties. To this end we have synthesised a series of unconventional hemicyanine derivatives in which the hydrophobic group is conjugated. Preliminary LB studies confirm that these materials align at the air-water interface and may be transferred to solid substrates. The second-harmonic intensity of one of these materials, 1-butyl-2-[2-(4-dibutylaminophenyl)-vinyl]-6-hepta-1,3,5-trienyl-pyridinium iodide, is 230 pm/V at 1064 nm. An analysis of the surface plasmon resonance data indicates a film thickness of 1.2 nm and real and imaginary components of the dielectric permittivity of 3.1 and 0.7 respectively at 532 nm. The chromophore is tilted by 36° from the substrate normal. Further work is ongoing to improve the molecular alignment of these and analogous materials with the reality of a truly legless LB film-forming molecule now within sight.

**B3.2**

ULTRATHIN FILMS OF ORIENTED BACTERIORHODOPSIN: NANOSTRUCTURED FILMS FOR INVESTIGATING THE PRIMARY PHOTOEVENT IN VISION PROCESSES. Rigoberto C. Advincula and Mi-kyoung Park Department of Chemistry, University of Alabama at Birmingham Birmingham, AL.

We have developed a protocol for investigating Bacteriorhodopsin (BR) biomimetic systems as ultrathin films. BR is one of the most well studied proteins important for investigating the primary photo-event in vision processes. The use of macromolecular assembly approaches to solid support substrates, e.g. SiO<sub>x</sub>, gold- or ITO-coated glass (electrode) provided an "engineering dimension" to correlate photocurrent generation, photoelectric response, pH change, chromophore behavior, etc. with protein orientation approximating that of membrane and physiological conditions. Membrane and protein morphology was correlated to these measurements using nanoscale tools, e.g., atomic force microscopy (AFM), self-assembled monolayers

(SAM), quartz crystal microbalance (QCM), etc. on solid-substrate systems. This can lead to optobioelectronic devices (perhaps biosensors) using patterning in a transducer array configuration, e.g. using current, light, pH change, etc. for stimulation and amplification. We report our initial results on highly ordered and oriented BR protein arrays of controlled thickness, layer order, and orientation. This was done primarily using the alternate polyelectrolyte deposition (APD) approach on functionalized substrate surfaces.

**B3.3**

A MICROFABRICATED DEVICE FOR CHARACTERIZATION OF BIOLOGICAL SPECIES. H. Chang, A. Ikram, M. Young, R. Bashir, School of Electrical and Computer Engineering, Purdue University, W. Lafayette, IN; F. Kosari, G. Vasmatzis, Mayo Clinic, Rochester, MN.

The movement of charged species in an electrical field has been commonly used for separation and characterization of biological species. This paper will present preliminary work on a micro-fabricated device which can be used to acquire useful information regarding biological species based on the above principle. We have micro-fabricated silicon devices with pore sizes ranging from 10µm x 10µm to 2µm x 2µm. These devices are used to perform studies on the drift of charged polystyrene beads (1-5µm diameter) under a certain electric field. The passage of beads through the pore result in a decrease of the current, we can thus observe some pulses in the I-T (current to time) plots. The width of the pulse varies inversely with the applied voltage. An effective electrophoretic mobility of the beads or other biological species can thus be extracted. The device can be used to count bacterial cells and can provide useful information regarding them. Using electron beam lithography, we are extending the work to produce nano-scale pores for the characterization of proteins and DNA.

**B3.4**

SOLE TUNNELING ACROSS MOLECULARLY MODIFIED MERCURY/SILICONE JUNCTIONS. Yoram Selzer, Adi Solomon, David Cahen, Weizmann Institute of Science, Dept of Materials and Interfaces, Rehovot, ISRAEL.

Hole tunneling experiments involving Hg/p-Si junctions incorporating alkanethiolate monolayers are described. Formation of the junctions {Hg-SC<sub>n</sub>-SiO<sub>2</sub>-Si} is accomplished by bringing small mercury drop electrodes covered with alkanethiolate monolayers in contact with oxide covered (1 nm thick) p-Si surfaces. Tunneling currents in the junctions were measured for voltage biases extending to ±1.5 V. The dual effect of monolayer thickness on tunneling currents as well as on band bending is discussed. The presumably pin hole free structure of alkanethiolate monolayers on Hg, and the non-reactive behavior of Hg towards Si, make the experimental setup extremely powerful. In fact it enables to measure hole conduction through simple molecules in a highly defined system for the first time. A set of experiments was also performed with Junctions in which both the Hg and Si surfaces were modified (the latter by Octadecyltrichlorosilane, OTS), Comparison between the two sets of experiments enables to estimate the barrier to interchain hopping of holes.

SESSION B4:  
Chair: Sarah H. Tolbert  
Wednesday Morning, April 18, 2001  
City (Argent)

**8:30 AM \*B4.1**

OPTOELECTRONIC APPLICATIONS OF THE INTIMATE COUPLING OF PROTEINS AND DNA WITH SILICON-BASED MATERIALS. Daniel E. Morse, Jennifer Cha, Jan Sumerel, University of California at Santa Barbara, Materials Research Laboratory, Santa Barbara, CA; John Gaul, Dow Corning Corp., Midland, MI.

The precision of nanoscale architectural control of structures fabricated by biosilicification is a reflection, in some instances, of the intimate coupling between biopolymers and silicon-based components. We are exploring the nature of these interactions and their applicability to electronic and optoelectronic device fabrication with proteins and nucleic acids. We have developed a convenient synthetic route to produce a universal linker for the conjugation of genetically engineered proteins to the surfaces of silicon wafers. Using this linker to attach silicatein (the structure-directing protein catalyst of siloxane polymerization that we previously isolated, cloned and characterized from the biosilica of a sponge) enables us to write nanostructural features of silica and other siloxanes on silicon surfaces. In other work, we are exploring the intimate coupling between DNA and siloxanes. Potential applications include integrated optoelectronic sensors, in which detection of the analyte is reported directly as the electronic or optical output from a microaddressable domain on a semiconductor surface.

**9:00 AM B4.2**

COULOMB BLOCKADE IN A SINGLE-MOLECULE DNA TRANSISTOR. Mingshaw W. Wu, L.L. Sohn, Princeton Univ, Dept of Physics, Princeton, NJ.

Electron transfer and transport in double-stranded DNA has long been a topic of much interest and debate. The possibility that DNA may be useful in electronic devices is tantalizing, because of the flexibility in customizing the molecules in terms of both sequence and topology. The ability of DNA to conduct may find applications in molecular-scale and single-molecule electronics. In this regard, we have fabricated a single-molecule DNA "transistor" using bacteriophage- $\lambda$  DNA. Our transistor consists of a pair of metallic electrodes with a single  $\lambda$ -phage DNA molecule. We have performed gated-DC transport measurements at low temperatures (77K and 4.2K). As we will show, this molecular transistor exhibits single-electron effects such as coulomb blockade and staircase, similar to those observed in quantum dot and carbon nanotube devices.

**9:15 AM B4.3**

BIOMOLECULAR RECOGNITION AND CONTROL OF NANO MAGNETIC AND SEMICONDUCTOR MATERIALS. Angela M. Belcher, Christine Flynn, Chuanbin Mao, Sandra Whaley, Erin Gooch, University of Texas at Austin, Department of Chemistry and Biochemistry, Austin, TX.

Biological systems have a unique ability to control crystal structure, phase, orientation and nanostructural regularity of inorganic materials. We are currently investigating the principles of natural biological molecular recognition in materials and developing new methods to pattern useful non-biological electronic and magnetic materials on new length scales. A peptide combinatorial approach has been employed to identify proteins that select for and specifically bind to inorganic structures such as semiconductor wafers and semiconductor and magnetic nanoparticles (Nature 405, 665-668, 2000). This approach utilizes the inherent self-organizing, highly selective properties of biologically derived molecules. We are currently investigating peptide recognition and interaction with III-V and II-VI semiconductor materials, magnetic materials and calcium carbonates and phosphates. We have selected peptides that can specifically bind to and discriminate zinc-blende III-V semiconductor surfaces. These peptides show crystal face specificity and are being used to organize nanoparticles heterostructures. We have also selected peptides that can nucleate and control particle diameter and aspect ratio of II-VI semiconductor nanoparticles. These peptides are being used to grow nanoparticles and nanowires of specific crystallographic structure and orientation. Using these molecular interactions and specific nanoparticles we are organizing organic/inorganic materials into supramolecular architectures.

**10:00 AM \*B4.4**

MOLECULAR ELECTRONICS FOR COMPUTING AND MEMORY. Jim Heath UCLA, Dept of Chemistry, Los Angeles, CA.

Progress toward a molecular electronic circuitry for computing and memory applications will be discussed. Advances in bio-molecular devices based on physiologically active voltage gated ion channels will also be presented.

**10:30 AM B4.5**

EXCITON AND CHARGE CARRIER DYNAMICS IN ORIENTED CONJUGATED POLYMER-MESOPOROUS SILICA COMPOSITE. Junjun Wu, T.Q. Nguyen, V. Doan, B.J. Schwartz, S.H. Tolbert, UCLA, Dept of Chemistry and Biochemistry, P. Tran, G. Grüner, UCLA, Dept of Physics, Los Angeles, CA.

Oriented polymer/silica composites have been synthesized by incorporating the conjugated semiconducting polymer MEH-PPV into the pores of an aligned, hexagonally ordered mesoporous silica. Polymer chains which are oriented in the aligned nanoporous silica show strong polarization anisotropy in their photoluminescence ( $I_{VV}/I_{VH} = 4.4$ ,  $I_{HH}/I_{HV} = 0.68$  for vertically oriented pores). Polarized femtosecond spectroscopies show that excitations migrate unidirectionally from aggregated, randomly oriented polymer segments outside the pores to isolated, aligned polymer chains within the pores. Energy migration along the conjugated polymer backbone occurs more slowly than Forster energy transfer between polymer chains. Resonant microwave cavity methods are used to probe the charge transport properties in these composite. These results provide insights for optimizing nanostructured materials based on single molecular wires for use in optoelectronic devices.

**10:45 AM \*B4.6**

MEASURING AND CONTROLLING MOLECULAR-SCALE PROPERTIES FOR MOLECULAR ELECTRONICS. P.S. Weiss and D.L. Allara, Department of Chemistry, The Pennsylvania State

University, University Park, PA; and J.M. Tour, Department of Chemistry, Rice University, Houston, TX.

We isolate single molecules and bundles of molecules in two-dimensional matrices for study with scanning probe microscopy. We measure and control the conductance of these molecules. We relate our scanning tunneling microscopy measurements to measurements in test structures that can be fashioned into molecular electronic logic and memory. From these measurements we seek to determine and to optimize the mechanisms of switching. One focus of our work has been on functionalized oligo(1,4-phenyleneethynylene)s, as members of this family of molecules have been proposed as both molecular wires and molecular switches. We measure the dependence of the switching on the bias conditions and on the number of molecules in the bundle. We use the persistence time in a conductance state given these conditions and the molecules' environment to elucidate the switching mechanism.

**11:15 AM \*B4.7**

SYNTHESIS AND FUNCTIONALIZATION OF NANOTUBES FOR MOLECULAR SENSORS. Hongjie Dai, Stanford University, Department of Chemistry, Stanford, CA.

I will present our latest work in controlled synthesis of carbon nanotubes leading to nano-electronic devices for chemical sensor applications. It will be shown that non-covalent functionalization of the sidewalls of nanotubes represent a viable route to sensitive and selective miniature sensors for detection of molecules in the gas phase and in liquids. Immobilization of biological molecules on the functionalized nanotube sidewalls are carried out aimed at nanotube biosensors.

**SESSION B5:**

Chair: Aristos Christou  
Wednesday Afternoon, April 18, 2001  
City (Argent)

**1:30 PM \*B5.1**

NEAR INFRARED PHOTO-INDUCED HYBRIDIZATION OF DNA IN AQUEOUS SOLUTIONS AND TECHNIQUES TO ATTACH DNA PROBES TO GaAs AND GaN SURFACES. Shayan Modarres, Honxia Feng, Mahnaz Chaychian, Mohamad Al-Sheikhly, Joseph Silverman, Department of Materials and Nuclear Engineering, University of Maryland, MD; William Bentley, Department of Chemical Engineering, University of Maryland, MD.

We are investigating the hybridization reaction in a single-stranded DNA by means of near infrared irradiation. Our purpose is to apply this principle to the development of a gel-semiconductor DNA module for information storage. The research is intended to develop procedures to replace or enhance enzyme-based hybridization reactions in sequencing applications and in the polymerase chain reaction (PCR). In achieving this goal, our approach would lead to a paradigm shift from enzymatic aqueous reactions to photo-induced surface hybridization reactions, and the use of photo-induced hybridization of surface-attached DNA probes to link them by hydrogen bonding with DNA target molecules in a gel. The objective of our work is to develop a high-density DNA module with data storage and retrieval capability. Such a system is envisioned as a mono-layer of single-strand DNA oligonucleotides (probes) attached to the surface of a semiconductor wafer in a combinatorial light-addressable array. This strategy to move from enzyme-based reactions in aqueous solutions to reactions in a solid state would require to permit memory storage and retrieval in an addressable hybrid architecture. This will be accomplished using photo-excitation of hybridization reactions to produce double-stranded DNA suitable for information storage on a semiconductor-based module.

**2:00 PM \*B5.2**

SURFACE MOLECULAR ENGINEERING FOR BIOMATERIALS APPLICATIONS. Buddy Ratner, Univ of Washington, Seattle, WA.

Surfaces that are engineered for biorecognition require precise molecular control of structure and topography. There are also some novel surface synthesis concepts that can be used to impart elements of biospecificity to surfaces. This talk will overview (1) a templating approach, (2) a randomized receptor approach and (3) a molecular assembly strategy for placing trigger molecular sites on surfaces. (1) Tailored protein-binding cavities have been created by an imprinting approach based on RF-plasma deposition of organic thin films. A polysaccharide-like surface with imprinted "nanocavities" complementary to the shape and chemistry of protein molecules allows only the template protein to fill the cavity, and to bind strongly. The bound protein in its "pit" is prevented from exchange with dissolved protein because of strong non-covalent interactions and steric hindrance. The recognition specificity is demonstrated by the fact that

lysozyme imprints have a 26 fold increase in adsorption of lysozyme (MW 14,600) versus ribonuclease A (MW 13,700). (Shi, H; Tsai, W-B; Ferrari, S; Ratner, BD Nature 398, 593-597, 1999) (2) Receptor sites are an array of chemical groups immobilized in a specific geometry. In this experiment, amino acid terminated n-alkane thiols that were self assembled on gold were shown to make cell-recognizable receptor sites. The head groups were arginine (R), glycine (G) and aspartic acid (D), and an RDG peptide. The mixed R-G-D surfaces showed cell attachment as good or better than the RGD peptide. (3) To develop novel recognition surfaces, we require the ability to precisely spatially distribute recognition groups on a surface. In this project, designed porphyrin molecules were synthesized and have been shown to assemble on surfaces. These molecules permit us to deliver recognition signals (peptides) with control of surface geometry (Boeckl,MS; Bramblett, AL; Sasaki, TK; Hauch, K; Ratner, BD; Rogers, JW Jr: Self-Assembly of Tetraphenylporphyrin Monolayers on Gold Substrates, Langmuir, 16 (13); 5644-5653, 2000).

### 2:30 PM **B5.3**

**PROTON-GATED MOLECULAR DEVICES BASED ON ROD-SHAPED METAL COMPLEXES IMMOBILIZED ON SOLID SURFACE.** Masa-aki Haga, Youichi Shiozawa, Miyao Inoue, Takahito Kawai, Chuo Univ, Dept of Applied Chemistry, Tokyo, JAPAN.

Proton translocation coupled to redox reaction is often seen in a biological membrane, and plays an important role for the energy transduction. Thus, the combination of proton transfer and electron transfer is attractive in designing biomimic molecular electronics based on the proton movements. We have prepared Ru/Os complexes containing tridentate bis(benzimidazolyl)pyridine (L) derivatives, which show proton-coupled electron transfer reaction. Once metal center is oxidized, the remarkable decrease of pKa value on the metal complex induces the release of proton from the complex sphere. We have succeeded the preparation of novel rod-like  $M(L)_2$  ( $M = Ru$  or  $Os$ ) complexes with thiol (L-S) or phosphoric acid (L- $PO_3H_2$ ) anchoring group. These complexes were successfully self-assembled on the solid surface such as Au or ITO. Furthermore,  $M(L-PO_3H_2)_2$  complex exhibits the selective layer-by-layer growing with the combination of Zr ion coordination. The self-assembled monolayer of rod-like Ru/Os polynuclear complex capping with  $LH_2$  ligands exhibits the orbital energy can be controlled by solution pH, and therefore an electron rectifying behavior has been observed by the change of bulk proton concentration. Not only the control of metal-metal interaction and distance for the electron transfer but also molecular orientation of the rod-like metal complex on the surface are important to realize the molecular proton-gated devices.

### 3:15 PM **\*B5.4**

**COMPUTATIONS WITH CHEMICAL KINETICS DETERMINATION OF COMPLEX REACTION MECHANISMS.** John Ross, Department of Chemistry, Stanford University, Stanford, CA.

Logic functions, and sequential as well as parallel computations, can be implemented by means of macroscopic chemical kinetics. Computational functions can be found in well-known biochemical reaction systems. These studies lead to the possibility of determining reaction pathways, and reaction mechanisms, by designed experiments and appropriate theories of interpretation, rather than guessing such mechanisms.

### 3:45 PM **B5.5**

**SUPRAMOLECULAR ULTRATHIN FILM STRATEGIES FOR DNA ASSEMBLIES: SUBSTRATES FOR OPTOBIOELECTRONICS, GENE THERAPY AND MICROARRAYS.** Rigoberto Advincula, Bhatia Gautam, Seth Stepleton, Mi-Kyoung Park, Xiaowu Fan, Wally Blanton and Yingfan Wang, Department of Chemistry, University of Alabama at Birmingham, Birmingham, AL.

We describe our strategies and results in the preparation of supramolecularly ordered ultrathin films of cDNA assemblies. This involves the use of the layer-by-layer alternate solution adsorption technique and amphiphilic block copolymer modified surfaces. The properties of DNA is intimately associated with their polyelectrolyte behavior in solution. Deposition at surfaces is governed by the conformation, orientation, charge density of these biomolecules in relation to the physisorption phenomena in oppositely charged surfaces. Controlling the "texture" of surfaces is important in modifying the adsorption phenomena. A number of surface sensitive spectroscopic and microscopic techniques are used to probe the adsorption and multilayer assembly. This includes surface plasmon resonance spectroscopy (SPS), AFM, QCM and ellipsometry. By combining with the alternate assembly of azobenzene and phthalocyanine dyes, we have been able to prepare optobioelectronic substrates where the phenomena of irradiation and electrochemistry can be used to probe the ordering and response of these films. This is important for future biosensor applications. Strategies on patterning in surfaces are currently being pursued.

### 4:00 PM **B5.6**

**NON-CENTROSYMMETRIC LANGMUIR-BLODGETT FILMS: FROM SECOND-HARMONIC GENERATION TO MOLECULAR RECTIFICATION.** Geoffrey J. Ashwell, Cranfield University, The Nanomaterials Group, Centre for Photonics and Optical Engineering, Cranfield, UNITED KINGDOM.

Interest in Langmuir-Blodgett films for both second-harmonic generation and molecular rectification stems from the fact that the LB technique permits control of the alignment at the molecular level. A non-centrosymmetric arrangement is necessary and may be realised by alkylating opposite ends of the hydrophilic donor-( $\pi$ -bridge)-acceptor chromophore. The LB film surface is then invariably hydrophobic and, thus, overcomes the problem of conventional amphiphilic dyes which pack alternately head-to-head and tail-to-tail. Furthermore, the concentration of the active components within such films has been increased by using wide-bodied chromophores and an interdigitating arrangement of the alkyl tails, either at a single interface ("molecular zip") or both top and bottom ("molecular Lego"). Another development at Cranfield has involved conjugated molecules where an extended  $\pi$ -electron bridge has replaced the hydrophobic tail of conventional amphiphilic dyes. The films show greatly improved nonlinear optical susceptibilities because all inert regions have been eliminated. Various non-centrosymmetric structures will be reported with the alignment, in each case, being indicated by a quadratic increase of the second-harmonic intensity with the number of layers. One such dye has shown molecular rectification when sandwiched between symmetrical gold electrodes, this being the first example of asymmetric I-V characteristics for a gold/(LB film)/gold device of an SHG-active material. The nonlinear electrical and optical properties will be discussed.

### 4:15 PM **\*B5.7**

**TOWARDS THE PROGRAMMABLE SELF ASSEMBLY OF DNA MOLECULES ON SURFACES.** Bryce P. Nelson, Hye Jin Lee, Ming Li, Liman Wang, Lloyd M. Smith and Robert M. Corn, Department of Chemistry, University of Wisconsin, Madison WI.

The manipulation of complex DNA solutions with genetic engineering tools has been proposed recently as a chemical methodology for solving instances of computationally intractable (NP-complete) combinatorial problems. We have recently demonstrated that a scalable model of DNA computing can be realized by using DNA attached to gold surfaces. In these experiments, the DNA must be attached to the surface in a high density fashion, yet each DNA strand must remain accessible to hybridization from solution and to enzymatic reactions. Initially, planar surfaces coated with well-defined self-assembled monolayers are used to control the attachment chemistry and DNA surface coverage. In this talk we describe some of the various pieces of the DNA computing project, including: (i) DNA word design, (ii) DNA surface attachment chemistry and array fabrication, (iii) manipulation of the surface-bound DNA by enzymatic reactions, and (iv) novel methods such as surface plasmon resonance (SPR) imaging for the label free detection of DNA and RNA molecules on gold surfaces. Preliminary results on the detection and application of RNA on surfaces and the self assembly of DNA multilayer structures will also be discussed.