SYMPOSIUM Q
“Smart” Surfaces and Interfaces
March 29 - 30, 2005

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* Invited paper
At 8:00 AM, the session titled "Responsive Polymer Brushes Through Main Chain Self-Assembly" kicked off. Stephen L. Craig, from Duke University, Durham, North Carolina, discussed the role of polymer brushes on surfaces and the properties they confer. Polymeric brushes modulate an array of properties such as colloidal stabilization and ordering, adhesion, wettability, and friction.

Another interesting talk was presented at 8:30 AM by Tamer Farhan, Omar Azzaroni, and Wilhelm T. S. Huck from the Department of Chemistry, University of Cambridge, Cambridge, United Kingdom. They explored Charged Polymer Brushes: Really Soft Matter, focusing on the stiffness of stimuli-responsive materials.

At 9:00 AM, a talk on "Self-Recognising Fluid Monolayers of DNA-Based Surfactants: Properties and Applications" was given by Yesselin N. Paunov from the Chemistry Department, University of Hull, Hull, North Humberside, United Kingdom. This presentation highlighted the design and use of novel surfactants prepared by covalent attachment of a hydrophobic aromatic group to the (3'- or 5') end of short DNA oligonucleotides. These surfactants were shown to adsorb in air-water and oil-water interfaces, which is of great interest toward the fabrication of new materials.

A talk by Chun Xu, Pietro Taylor, and Paul D. J. Fletcher from the Department of Chemistry, University of Hull, Hull, North Humberside, United Kingdom, discussed the directed three-dimensional self-assembly of microstructures and nanostructures through the selective hybridization of DNA. This process is reversible by heating, with a characteristic aggregate dissociation process observed with optical microscopy.

At 9:30 AM, "Selective, Controllable, and Reversible Aggregation of Polystyrene Latex Microspheres via DNA Hybridization" was presented by Phillip Henry Rogers from the Chemistry Department, Columbia University, New York, New York. This talk explored the use of DNA-functionalized small liposomes for microcontact printing, which allowed for the efficient attachment of DNA strands to solid surfaces and hybridization with complementary fluoroscintently-tagged oligonucleotides.

Finally, at 10:00 AM, Colin Nuckolls from the Chemistry Department, Columbia University, New York, New York, and Nanoscience Center, Columbia University, New York, New York, discussed "New Monolayers: Molecular Recognition, Catalysis, and Electronics." This presentation explored the use of DNA-functionalized small liposomes for the selective hybridization of DNA. This LED-based technique allows for the rapid preparation of DNA-assays and genetic biochips.
short length scales. One strategy that is explored here is the use of hydrogen bonding and pi stacking to work synergistically. There are three significant benefits from studies to date, the dipole moments of the subunits provide a stack that has a macroscopic dipole moment. Second, because the association in the stacking direction is stronger than in typical pi stacks, it is possible to create isolated molecules that can be visualized with scanning probe microscopy. Third, it is possible to create the shortest of pi stacks, dimers, on metallic surfaces that are held together through noncovalent forces. Another area of exploration is in developing devices that can generate and detect electronic signals. The surface of high k dielectrics. We have found new chemistry to afford linear acenes that have their short ends functionalized with endgroups that react with surface oxides. Incorporating this assembly motif into electronic devices allows field effect transistors to be constructed that are one molecule high with approximately a 100 molecules separating the source and drain electrodes.

10:30 AM Q1.7
Modifying Interfacial Interactions, Thomas P. Russell1, Duyeol Ryu1, Eric Drocenmuller2 and Craig J. Hawker3; 1Polymer Science and Engineering, University of Massachusetts, Amherst, Massachusetts; 2IBM Almaden Research Center, San Jose, California; 3Materials Research Laboratory, University of California, Santa Barbara, California.

The chemical dissimilarity of the constituent blocks in a copolymer will, in general, lead to the preferential segregation of one of the blocks to an interface. Since the blocks of the copolymer are covalently linked, the microphase separated morphology will orient parallel to the interface. In thin films, this produces an orientation of the microdomains of the block copolymer parallel to the film surface. While external fields can be used to overcome these interactions, manipulation of the interfacial interactions can be used to the same end. For any surface, specific chemistries can be developed to alter the chemical nature of a surface, designing a generalized approach has been a major impediment. Here, using a crosslinked thin film of a random copolymer where the chemical composition of the copolymer can be varied, an approach has been developed where interfacial interactions can be controlled on a virtually any surface. Using this approach surfaces of many materials, including passivated silicon, silicon oxide, aluminum, gold and an aromatic polyimide, have been controlled. Asymmetric diblock copolymers of polystyrene and polymethylmethacrylate having a cylindrical microdomain morphology are used to demonstrate the effectiveness of this approach.

11:00 AM Q1.8
Towards Tunable Interaction between Conjugated Molecules and Metal Surfaces in Self-Assembled-Monolayers: A Theoretical View. Georg Heinze1, Egbert Zojez1,2 and Jean-Luc Bredas3; 1School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia; 2Institute of Solid State Physics, Graz University of Technology, Graz, Austria.

Highly ordered self-assembled monolayers (SAMs) of molecules on (noble) metal surfaces are currently the focus of intense, multidisciplinary research. Potential applications of such SAMs include molecular electronics, chemical sensors, the tuning of macroscopic surface properties like wetting or corrosion stability, the improvement of electrode interfaces in organic light-emitting devices and photovoltaics, and many more. In order to endow these self-assembled systems with functionality suitable for use in either macroscopic or nanoscale (opto-)electronic devices, the use of σ-conjugated systems has been proposed. The goal of our work is to gain a basic understanding of the interfacial processes occurring in conjugated-SAM/metal systems and how they can subsequently be fine-tuned to work as building blocks in molecular electronics and/or macroscopic electronic devices. In our present theoretical study, we focus on a simple model system consisting of σ-conjugated molecularly self-assembled on a metal substrate: substituted benzen-thiols on Au(111). DFT band structure methods are employed in order to give a full theoretical characterization of the 2D-periodic infinite system, including adsorption energies, geometries, band alignment, charge transfer, interface dipoles, core-level shifts, grazing-incidence infrared absorption spectra, and STM images. Particular emphasis is put onto the effect of donor and acceptor substitutions on the alignment of the frontier molecular orbitals with the Fermi energy of the substrate, the resulting charge transfer, and changes in the metal work function. Furthermore, we investigate the influence of the substrate electronic environment on the conjugation within the metal substrate (represented by gold quantum-wells and gold nano-clusters, respectively) on the degree and nature of electronic coupling between the SAM and the supporting metal substrate.

11:15 AM Q1.9
Phospholipid Morphologies on Photochemically Patterned Silane Monolayers. Micheal C. Howland1, Annapoorna R. Sapuri-Butti1, Sanhita S. Dixit2, Andrew P. Dattelbaum2, Andrew P. Shreve3 and Atul N. Parikh4; 1Applied Science, University of California, Davis, Davis, California; 2Biocience Division, Los Alamos National Laboratory, Los Alamos, New Mexico.

We have studied the spreading of phospholipid vesicles on photochemically patterned n-octadecylsiloxane monolayers using epifluorescence and imaging ellipsometry measurements. Self-assembled monolayers of n-octadecylsiloxanes were patterned using short-wavelength ultraviolet radiation to produce periodic arrays of patterned hydrophilic domains separated from hydrophobic surroundings. Exposing these patterned surfaces to a solution of small unilamellar vesicles of phospholipids and their mixtures resulted in a complex lipid layer morphology epitaxially reflecting the underlying pattern of hydrophilicity. The hydrophilic square regions of the photopatterned OTS monolayer reflected lipid bilayer formation and the hydrophobic OTS residues supported lipid monolayers. We further observed the existence of a boundary region composed of a non-fluid lipid phase and a lipid-free moist at the interface between the lipid monolayer and bilayer morphologies spontaneously coraling the fluid bilayers. The outer-edge of the boundary region was found accessible for subsequent adsorption by proteins (e.g., streptavidin and BSA), but the inner edge closer to the bilayer remained resistant to adsorption by protein or vesicles. Mechanistic implications of our results in terms of the effects of substrate topographical character are discussed. Furthermore, our results provide a basis for the construction of complex biomembrane models, which exhibit fluidity barriers and differentiate membrane properties based on correspondence between lipid leaflets. We also envisage use of this construct where two-dimensional wetted fluid, low-defect lipid layers serve as sacrificial resists for the deposition of protein and other material patterns.

11:30 AM Q1.10

Dendrimers are three-dimensional, globular, highly-branched macromolecules made up of a central core surrounded by repetitive units all enclosed by a terminal group shell. They can be synthesized with highly controllable sizes (they are monodisperse) determined by the core size, extent of branching, and nature of the branching groups, in the range from a few to several tens of nm in diameter. Dendrimers also assemble into monolayers on technologically interesting substrates using simple cleaning, dipping, and rinsing procedures. In this condensed monolayer phase dendrimers can act as surfactants mediating the growth of ultra-flat films, and create novel nanomechanical, adhesive, frictional, and tribological behavior. We have recently reported on the dramatically enhanced quality (superior flatness and adhesion) of metal films deposited on dendrimer monolayers. Different tribological responses are also observed in dendrimer-mediated metal thin films. The physical intermixing between the dendrimer and metal wafer is proposed to explain the distinct physical, mechanical, and chemical properties of the resulting dendrimer-based nanocomposites. To better understand substrate/dendrimer monolayer/adlayer interactions, we designed an experiment to better understand the intermixing between metals (in this case Au) and dendrimer monolayers as a function of deposited metal film thicknesses.
switched in a reversible fashion will be reviewed: 1) poly(n-isopropylacrylamide) monolayers for the adsorption and release of proteins and interactions of repulsive hydration forces, 2) lectin-spirogyran monolayers for the optical switching of electrical double layer forces, and 3) monolayers in which host-guest interactions can be mediated via electrochemistry for the localized capture and release of specific functional groups.

2:00 PM *Q2.2 Super-hydrophobic Surfaces: From Natural to Artificial, Lei Jiong, Center for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing, China.

The wettability of solid surfaces is a very important property, and is governed by both the chemical composition and geometrical micro- and nanostructure of the surface. Currently, super-hydrophobic surfaces with water CA higher than 150° are arousing much interest because they will bring great convenience in daily life as well as in many industrial processes. Various phenomena, such as snow sticking, contamination resistance, and current conduction, are expected to be inhibited on such a surface. Conventionally, super-hydrophobic surfaces have been produced mainly in two ways. One is to create a rough structure on a hydrophobic surface, and the other is to modify a smooth surface by materials with low surface free energy. While the water CA has commonly been used as a criterion for the evaluation of hydrophobicity of a solid surface, this alone is insufficient to assess the sliding properties of water droplets on the surface. A fully super-hydrophobic surface should exhibit both high CA and low sliding angle. Our recent studies on lotus and rice leaves reveal that a super-hydrophobic surface with both a large CA and small sliding angle needs the cooperation of micro- and nanostructures, and the arrangement of the microstructures on this surface can influence the way a water droplet tends to move. These results from the natural world provide a guide for constructing artificial super-hydrophobic surfaces and controlling their wettability.

Accordingly, super-hydrophobic surfaces of aligned carbon nanotube films, aligned polymer nanofibers and differently patterned aligned carbon nanotube films have been fabricated. The large-scale fabrications of nanofiber surfaces and hierarchically structured surfaces have been developed by modification of the traditional method, the adoption of one-step coatings and electrophoretic nanocoatings, respectively. The super-hydrophobic surface is also realized in all pH range, which extends its applications not only to pure water, but to acid and base solution as well. By combining the two factors of super-hydrophobic and super-oleophilic, the water-oil separation mesh has been built successfully. Considering the arrangement of the micro- and nanostructures, the surface structures of the waterstrider’s legs were studied in detail, indicating the relationships between super-hydrophobicity and orientation of the micro- and nano-scale composite structures, which will guide us to fabricate micro-fluidic devices artificially in the near future. In further, the cooperation between surface micro- and nanostructures and surface modification of poly (N-isopropylacrylamide) gave reversible switching between superhydrophilicity and superhydrophobicity in a narrow temperature range of about 10°C. The transition can be enhanced by depositing the polymer onto patterned silicon substrates. Additionally, UV light stimulated switcher of super hydrophobic and superhydrophilic transition by aligned ZnO film are successfully obtained.

2:30 PM *Q2.3 Manipulating Liquids using Nanostructured Surfaces, Ashley Taylor, Bell Labs, Lucent Technologies, Murray Hill, New Jersey.

Surfaces with appropriately engineered nano-scale topography can provide a powerful mechanism to modify liquid-solid interfacial behavior. A number of reported surface properties such as advancing and receding contact angles, contact line mobility, and viscous drag can be dynamically modified using this approach. This potentially opens new ways of manipulating liquids at both micro and macro scales. This talk will concentrate on two important phenomena recently demonstrated, electrically tunable nanostructured superhydrophobic surfaces. The dependence of the superhydrophobic - wetting transition on the liquid surface tension, surface coatings, and geometry of the nanostructured layer will be discussed. Possible ways to achieve reversibility of the wetting transition will be addressed. Several emerging applications of these surfaces including microfluidics, chemical microreactors, and skin drag reduction will be discussed as well.

3:00 PM *Q2.4 Dynamically Reconfigurable Surfaces For Microfluidic Applications, Richard B. Fair, ECE, Duke University, Durham, North Carolina.

Microfluidic systems based upon manipulation of discrete microdroplets within open structures are a promising alternative to conventional continuous flow systems. A number of methods for manipulating microdroplets based on direct electrical control of transport surfaces have been proposed, including dielectrophoresis, electrowetting, and charge-control manipulation at the solution/insulator interface of dielectric droplets by applying voltage to a control electrode. The MIST is the MOSFET equivalent for microfluidics, and it has been shown to be a versatile component for dispensing, transport, splitting, merging and mixing of aqueous droplets. We have shown that it is possible to transport biological liquids by electrowetting, including protein solutions of concentration up to 10 mg/ml. A silicone oil transport medium surrounds the droplet and forms an interface between the droplet and the hydrophobic transport surface. We find that the oil interface prevents non-specific protein adsorption on the hydrophobic transport surface. However, as the applied electrowetting voltage is increased, the oil is squeezed out from beneath the droplet. This effect has been verified using dynamic capacitance measurements. As a result, proteins in a droplet solution can be selectively stamped onto a receiving surface. This effect has been demonstrated in an oil-based electrowetting system for stamping proteins on MALDI plates. Besides sensitive deposition of proteins, we have also shown that it is possible to collect adsorbed inorganic particles from an impacted hydrophobic surface by a scanning droplet method. The sample collection is performed by impacting airborne particles directly onto the surface of the chip. After the collection phase, the surface of the chip is washed with a micro-droplet of solvent that is clad with a thin film of silicone oil. The droplet is digitally directed across the impaction surface in a v-shaped oil collection geometry. Because of the very small droplet volume used for extraction of the sample from a wide collection area, the resulting solution is relatively concentrated and the collected analytes can be detected after a very short sampling time (1 min) due to such pre-concentration.

3:30 PM *Q2.5 Strategies for Assembly of Live Cells into BioComposite Coatings and Membranes, Orin D. Velley, Shalini Gupta, Lindsey B. Jenkins, Rossitza G. Koleva and Peter K. Kilpatrick, Dept. of Chemical and Biochemical Engineering, North Carolina State University, Raleigh, North Carolina.

The self-assembly of colloidal micro- and nanoparticles is a powerful tool for making new materials with advanced functionality. We have developed a range of techniques for nanoparticle assembly into materials with well defined 2D and 3D structure. Live cells can be used as "particles" in similar types of assembly, yielding new classes of "smart" biomaterials with potentially rich areas of application. A powerful and versatile method for manipulation and assembly of cells is dielectrophoresis, interactions at high electric fields. We demonstrate how on-chip dielectrophoresis can be used to co-assemble yeast cells and synthetic micro- and nanoparticles. Depending on the frequency of the field and relative position of the cells and particles, one or two distinct arrays can be obtained. These arrays can be bound into permanent bio-composites by using molecular recognition. Lectin molecules are used to bind selectively to polysaccharides on the yeast cell surfaces to obtain cell-nanoparticle chains and membranes, which can function in a wide range of applications.

4:00 PM *Q2.6 Biological Detection based upon Nanoaggregation, Philip Joseph Costanzo1, Kevin Liang2, Timothy Patten3 and Rosemary Smith1, 1Chemistry, University of California at Davis, Davis, California; 2Electrical Engineering, University of California at Davis, Davis, California; 3Electrical and Computer Engineering, University of Maine, Orono, Maine.

Novel micro- and nano-scale aggregates were prepared from inorganic building blocks using biological crosslinkers: Difunctional, asymmetric poly(ethylene glycol) (PEG) linkers were synthesized and utilized to prepare water-soluble, biologically active nanoparticles. Suspensions of these particles were prepared and upon addition of the appropriate analyte, aggregation was observed. Aggregation was induced by small molecules, proteins, and antibodies, which demonstrated the versatility of the system. The kinetic growth
I'm Pharm. Res. 19, 1289 liposome systems that release their β-gal/X-gal, and a of DOPE liposomes with tunable reaction upon local heating is used to thick p-GaN doped with Mg. The activation presence. The guided wave may also be attenuated sensing with thermocapillary manipulation. Liquid droplets soluble molecules to the cytoplasm of KB cells upon endosomal functionality.

For in-situ droplet detection and analysis. Given that portability is a of magnitude. This capability clearly shows that the reactivity of the fields requires the development and integration of innovative methods.

Due to inefficient drug release once the carrier has accumulated at the bean, the light in the waveguide is attenuated, providing a basic indicator of sample presence. The guided wave may also be attenuated by absorption due to analytes in solution. We show that the attenuation signal correlates well with an increase in the concentration of FAD/C blue dye in 400 nm droplets. This same attenuation property is used to measure the rate of an enzyme-catalyzed reaction induced on the chip surface. Two droplets, one phosphate buffer solution containing the enzyme β-gal, and a second dimethylsulfoxide droplet, containing X-gal, were merged by thermocapillary actuation over the optical beam path. The enzyme catalyzed the conversion of X-gal into a blue precipitate leading to signal attenuation from which the reaction rate could be estimated. The microheaters used for droplet transportation can also increase the temperature of spatially confined droplets. The measured increase in the rate of the β-gal/X-gal reaction upon local heating is used to extract information about the thermal dependence of the reaction rate. The integration process is described here is expected to work equally well with open-format microfluidic devices based on electrowetting on dielectric layers and dielectrophoretic systems.

4:45 PM Q2.9
Abstract Withdrawn

SESSION Q3: Poster Session
Tuesday Evening, March 29, 2005
8:00 PM
Salons 8-15 (Marriott)

Q3.1 Physical and Electrical Characteristics of p-GaN after Cl2/Ar Dry Etching. Hsueh Kuang-Po1, Huang Shou-Chian1, Sheu Jinn-Kong2 and Hsin Yue-Ming1; 1Department of Electrical Engineering, National Central University, Chung-Li, Taiwan; 2Institute of Electro-Optical Science and Engineering, National Ching Kung University, Taiwan, Taiwan.

Although GaN based devices have been developed comprehensively for wireless and optical communications, GaN based HBTs are still under development due to the difficulties of obtaining high-quality GaN base and good ohmic contacts. The major reason is that the roughness and the contamination resulted from the dry etching process of p-GaN surface will increase Schottky barrier height (SBH) at the metal/semiconductor interface. However, the dry etching process is required for GaN based npn or pnp HBTs, it is the key research to obtain the good ohmic contact on p-GaN after dry etching. This paper presents both the etched surface root mean square (RMS) roughness and the depth display monitor (the Bearing analysis) of the doped p-GaN after Cl2/Ar reactive ions etching (RIE) as well as the study of Ni(20nm)/Au(20nm) metallization. All GaN materials were grown by MOCVD on sapphire substrates. A 0.5 μm undoped GaN layer with thickness of 2 μm was grown first, followed by the growth of a 1 μm thick p-GaN doped with Mg. The activation annealing was carried out at 750°C for 20 min in the furnace. Dry etching effect of 500 nm p-GaN using RIE has been investigated by etching the SBHs are 0.50 eV, 0.52 eV and 0.60 eV for RF power of 50 W, 100 W and 200 W, respectively. From experimental results, the surface roughness RMS is not directly related to the I-V characteristics of Ni/Au contacts, but Bearing ratio is. We concluded that the I-V characteristics (and thus Schottky barrier height) is more consistent with the Bearing analysis of existing nanorods than that with surface roughness in the Cl2/Ar etch.

Q3.2 Versatile Helical Polymer Films: Chiroptical Switching and Memory with Re-Writable (RW) and Write-Once Read-Many-Times (WORM) Modes. Akihiro Ohira1, Michiya Fujiki1, Masanobu Naito1, Shinobu Sakurada1, Takahiro Hagihara1, Fujiki1, Masanobu Naito1, Kento Oeishi1, Takahiro Hagihara1 and Mamoru Kunitake2; 1Graduate School of Materials Science, Nara Institute of Science and Technology, Ikoma, Nara, Japan; 2Applied Chemistry and Biochemistry, Kumamoto University, Kumamoto, Kunitake, Japan.

Recent development of various microfluidic devices based on modulation of the liquid surface tension through electric or thermal fields requires the development and integration of innovative methods for in-situ droplet detection and analysis. Given that portability is a major design constraint, microfluidic sensors should be directly incorporated into the chip to minimize size requirements without compromising measurement sensitivity. Ideally, the sensing mechanisms should be based on non-intrusive techniques, which don’t alter the liquid sample properties. Sensing integration can also provide additional benefits such as reduction in fabrication and packaging costs. We present here an integrated system capable of microfluidic actuation, detection and analysis that combines evanescent wave sensing with thermocapillary manipulation. Liquid droplets transported across the beam path of a planar thin film waveguide cause attenuation of the propagating waveguide mode. In this study, the attenuated signal is used to monitor droplet location, dye concentration in solution and reaction kinetics for enzymatic hydrolysis of the sugar X-galactoside (β-gal). The chip is a multi-layer structure composed of microheaters, an insulating layer, a planar optical waveguide and a chemically patterned patterned optical waveguide to electrically control sample pathway. The observed Bearing ratio of the nanorods on etched surface decreased significantly with decreasing the RF power and reached almost 0% at RIE power of 50 W. As a function of RF power, calculations show that the SBHs are 0.50 eV, 0.52 eV and 0.60 eV for RF power of 50 W, 100 W, and 200 W, respectively. From experimental results, the surface roughness RMS is not directly related to the I-V characteristics of Ni/Au contacts, but Bearing ratio is. We concluded that the I-V characteristics (and thus Schottky barrier height) is more consistent with the Bearing analysis of existing nanorods than that with surface roughness in the Cl2/Ar etch.
Solid-state chiroptical switching and memorizing property of molecules was created for molecular based devices such as optical switch and data storage applications. By carefully designing chiral molecules and chiral polymers, several chiral switching and memorizing systems have been achieved in solution. Among the polymers, several cationic helical polymers exhibit excellent chiroptical amplification and chiroptical inversion due to high cooperativities. However, a more versatile solid film system exhibiting chiroptical inversion "1 and 1" or on-off "0 and 1" switching and/or chiroptical inversion-multiple-times (WORM) and re-writable (RW) modes based on molecular and/or polymeric materials still remains rare. Here we demonstrate an easy, versatile approach for chiroptical inversion switching and chiroptical memory with RW and WORM modes in solid films by using certain polysilanes that can undergo helix-helix transition at -20 degree Celsius in isooctane by controlling both their molecular weight and thermal modulation. In the case of low molecular weight fraction (Mw: 1.3x10^4, Mw/Mn = 1.25), another memory state can be obtained from dark state by the chiroptical inversion switching based on reversible change of circular dichroism (CD) signal in heating and slow-cooling cycle. The transition temperature was 47 degree Celsius estimated from the temperature dependence of Kuhn's dissymmetry ratio (solid = DetoD/OD). The transition in the solid state was also observed in differential scanning calorimetry (DSC) thermogram. A chiroptical memory state, furthermore, occurred during rapid quenching from above the transition temperature. This memory effect is resettable by heating to above transition temperature. These results reveal that a chiroptical memory switch and chiroptical memory with RW modes are feasible by controlling the cooling conditions in a solid film and the molecular weight of the polymers. At the middle molecular weight fraction (Mw, 6.9 x 10^4, Mw/Mn = 1.25), another memory state can be achieved by controlling the molecular weight only. In this case, management of cooling condition is not required. The transition is only observed during heating, and the state above transition temperature remains unchanged during the cooling phase. This irreversible change in the CD signal indicates the non-erasable memory as the WORM mode. Concerning the high molecular weight fraction (Mw: 3.9 x 10^5, Mw/Mn = 1.02), no transition in the CD signal is no longer observed. These different behaviors as to molecular weight might be ascribed to entanglement of polymer chains in the solid films.

Q3.3 Nucleation of Pd Nanoparticles on a Smart Molecular Surface of Fibrous Hydrogen-Bonded Molecular Assemblages. Daisuke Ishii1, Masaru Nakagawa1, Tomomasa Iyoda2, Taichi Nagashima2, Shinichi Kawasaki2 and Mitsuaki Yanada2; 1Chemical Resources Laboratory, Tokyo Institute of Technology, Yokohama, Japan; 2Osaka Gas Co., Ltd., Osaka, Japan.

Pyridinecarboxylic acids bearing both hydrogen acceptor and donor groups form fibrous molecular assemblages having a submicron diameter in aqueous solutions.1 We have recently reported that the fibrous molecular assemblages are available for a template-directed synthesis of hollow nickel-phosphorus (Ni-P) microfibers through electroless plating. The hollow Ni-P microfibers could be obtained by immersing the template fibers in an acidic aqueous solution containing palladium chloride (PdCl2) as a catalyst precursor and in a Ni-P electroless plating bath containing phosphinate ions as a reducing agent.2 After removal of the organic template with aqueous alkaline solution, the hollow microfibers were composed of amorphous Ni-P nanoparticles having a diameter of about 30 nm, which formed a uniform 50 nm Ni-P layer without deposition defect. In general, Ni-P electrodeposition on organic substrate surfaces involves a surface-etching process using a strong acid before the PdCl2 treatment. The fibrous molecular assemblages required no etching process to form the Ni-P layer on the surfaces. We wondered why the deposition proceeded on the organic molecular surface of the fibrous template. In this report, we describe the nucleation of Pd nanoparticles as plating catalysts on the organic molecular surface of the template fiber. The Pd nucleation and the subsequent formation of Pd nanoparticles were studied by X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM) and atomic force microscopy (AFM). The amphoteric compound of 6-(2-propyl-4-(4-pyridylazo)phenoxy)hexanoic acid was used as a pyridinecarboxylic acid. To comprehend the formation mechanisms of Pd and Ni-P nanoparticles in the electroless plating, we prepared four kinds of fibrous molecular assemblages in respective steps after template formation, PdCl2-treatment, reductant-treatment and plating-treatment of Ni-P nanoparticles. The subsequent formation of Ni-P nanoparticles was studied by X-ray photoelectron spectroscopy (XPS). The PdCl2 solution was adsorbed as PdCl4 through coordination bonds with the pyridyl groups. The reduction phosphinate ions included in the plating bath reduced the surface-adsorbed PdCl4 species to Pd nanoparticles having a diameter of about 10 nm. The effect of the Pd deposition was due to dense adsorption of the PdCl4 species on the surface pyridyl groups existing periodically at a molecular level.1 Aoki, K.; Nakagawa, M.; Iyomura, K. J. Am. Chem. Soc. 2000, 122, 10997. [2] Ishii, D.; Aoki, K.; Nakagawa, M.; Seki, T. Trans. Mater. Res. Soc. Jpn. 2002, 27, 517. [3] Nakagawa, M.; Ishii, D.; Aoki, K.; Seki, T.; Iyoda, T. Adv. Mater. in press.

Q3.4 Hydrophilic Effect of Indium Tin Oxide (ITO) and Leadframe by Using Electroless Processing. Won-Yool Choi1, Jung-Hoe Cho2, Bang-Kwon Kang2 and Saes-Hoon Kim1; 1Kangnung National University, Kangnung, South Korea; 2Changjo Engineering Co., Ltd., Hwaseong, South Korea.

We report on a novel method for the surface modification of indium tin oxide (ITO) in LCD glass and metal leadframe (alloy 42) by direct exposure to a dielectric barrier discharge (DBD) at atmospheric pressure and room temperature. To make the oxide and metal surfaces hydrophilic, the atmospheric pressure DBD was used. Argon (Ar) and oxygen (O2) were used as the ignition gas and cleaning gas, respectively. The addition of O2 gas to Ar decreased the contact angle of water and increased the surface cleaning rate due to the increase of oxygen radicals in the plasma. The ITO contact angle of 64° before the plasma treatment was decreased to 7° in the processing condition with oxygen flow rate of 50 secm, treatment speed of 100 mm/sec, and input power of 300 W. And the leadframe contact angle of 82° before the plasma treatment decreased to 6° by the same process. The morphologies of the ITO and leadframe surfaces were analyzed with atomic force microscopy (AFM). The chemical characteristics of the surfaces after the plasma treatment were investigated using X-ray photoelectron spectroscopy (XPS), and new carboxyl group bond at binding energy E1=288.5 eV was produced. The carboxyl group bond (O-C=O) offered a better wettability and adhesion. These hydrophilic effects will be very useful in the manufacturing process of LCD glass and electroplating process.

Q3.5 Stable Charge Storage in Granular Thin Films. Fengting Xu1, Seen M. Thaler2, Alejandro Butera2, James L. Weston1 and John A. Barnard1; 1Materials Science & Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania; 2Centro Atómico Bariloche, Rio Negro, Argentina; 3Center for Materials for Information Technology (MINT), The University of Alabama, Tuscaloosa, Alabama.

Unique opportunities exist for utilizing thin film electrets (dielectrics which exhibit quasi-permanent charge or alignment of dipoles) and nanoscale charge patterning for electrostatically directed assembly of complex functional nanostructures from discrete charged/polarized nanoparticles and macromolecules. Realization of such nanostructures depends on developing a thorough understanding of the basic mechanisms and dynamics of charge storage and dissipation combined with high resolution quantitative characterization of electrostatic interactions in these systems. Highly stable local charge storage by SPM methods has been observed for the first time in Fe-SiO2 (and Co-SiO2) granular thin films (5 nm metal granules embedded in SiO2) with times as much as the orders of magnitude longer than previously reported for heterogeneous films. Charge dissipation is well described as occurring in two regimes, a comparatively fast regime at short times (decays times of thousands of seconds) and a much slower regime at longer times (decays times of tens of minutes). Positive charge occurs more readily in these systems but positive charges are significantly more stable. Granular thin films thus appear to have great potential as a new class of stable, tunable electrets suitable for charge patterning and electrostatically directed assembly of nanostructures.

Q3.6 Wettability Changes Depending on Wavelengths of UV-Light in an Organosilane Monolayer Bearing a 4-(2-Naphthylmethylsulfonyl)phenyl Moiety. Motohiro Tagaya, Masaru Nakagawa and Tomokazu Iyoda; Chemical Resources Laboratory, Tokyo Institute of Technology, Yokohama, Japan.

It is essential in surface science to comprehend interfacial phenomena such as wettability, adhesion, friction and so forth at a molecular level. From this viewpoint, photoactive self-assembled monolayers and/or adsorbed monolayers are interesting materials. Our coworkers have demonstrated that the photoreactive monolayers are applicable to liquid crystal photoalignment,[1] light-driven liquid manipulation,[2] mesoporous silicon array,[3] particle manipulation[4] and selective materialization.[5] To achieve photoactive polymer drafting, we previously synthesized a new type of UV-sensitive silane coupling reagent of 2-(4-benzylsulfonyl)phenyl ethyl-1-trichloro-1-dimethylsilane (BPSI).6 By exposure to 254 nm UV-light, the BPSI monolayer was transferred to a monolayer having chemically active benzenesulfonic acid due to photoconversion of the benzyl group. However, the BPSI monolayer had a problem that the photogenerated sulfonic acid group was decomposed by UV-light. To avoid this chemical reaction,

Q3.7 Interface Engineering for Improved Growth and Microstructural Control of Dense/Porous Multilayer Devices. Aram Amusias, Richard Verhees, Jolanta Ewa Klemberg-Sapieha, Patrick Denjaurias and Ludvik Martinj.

We investigate the growth of dense/porous SiN_{1.3} multilayers by dual-mode radiative microlithography/microplasic-enhanced chemical vapor deposition using in situ real-time spectroscopic ellipsometry (RTSE) and post-deposition atomic force microscopy. Dense SiN_{1.3} films grown under medium-energy (0.1 to 0.4 keV) ion bombardment on flat (100) Si substrates are very smooth and exhibit a roughness of R = 0.5 μm at an average n = 1.6 and R = 2 nm. When SiN_{1.3} layers undergo high ion-energy bombardment conditions on porous films, RTSE analysis reveals a rapid, but incomplete filling of surface porosity, at a rate depending on the incident precursor flux, before the total film thickness starts to increase. Films grown under these conditions exhibit a lower roughness (R < 3 nm) and a higher precision at the initial stages of film growth. We also demonstrate that the use of a different substrate, under identical conditions, can be used to enhance the growth rate of the porous films, SiN_{1.3} layers grown under high ion-energy bombardment conditions on porous films, RTSE analysis reveals a rapid, but incomplete filling of surface porosity, at a rate depending on the incident precursor flux, before the total film thickness starts to increase. Films grown under these conditions exhibit a lower roughness (R < 3 nm) and a higher precision at the initial stages of film growth. This work was supported by the Japan Society for the Promotion of Science under Grant 21246090.

Q3.8 Porous Germanium. Chang Sung, Sae Young, Le Jiang, Jaeren Carstensen and Helmut Foell.

Porous semiconductors are of growing interest for a range of reasons. First, porous materials are attractive due to their superior electrical and optical properties. Second, porous materials can be used in a variety of applications, including catalysis, sensors, and energy storage. In this study, we investigated the growth of porous Ge by using a low-temperature process. The results are presented and discussed in detail. The growth process was studied by using optical and electrical techniques. The growth rate was found to be approximately 1 μm per hour. The porosity of the samples was measured by using confocal microscopy. The average porosity of the samples was found to be approximately 50%. The optical properties of the porous Ge were studied by using photoluminescence spectroscopy. The photoluminescence spectra show a broad peak in the visible region, with an onset at approximately 400 nm. The electrical properties of the porous Ge were studied by using Hall effect measurements. The Hall effect measurements show that the resistivity of the samples is significantly lower than that of the bulk Ge. The study was supported by the National Science Foundation under Grant 1225523.

Q3.9 Modeling of Break-Junction Experiments. Lorenzo Romero, Eigit Zojer, Jean-Luc Bredas; School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia; Institute of Solid State Physics, Graz University of Technology, Graz, Austria.

We present theoretical studies investigating the conductance properties of a single molecule under systematic variation of the geometric arrangement of the electrodes. These calculations are performed on the corresponding system without the effects of thermal fluctuations. This study is based on the experimental observations of the electronic transport through molecules. We focus on systems consisting of diisothiocanate conjugated molecules sandwiched between two infinitely extended metallic electrodes. The results are compared for different degrees of surface coverage. All calculations are performed with the SHELXA and TRANSIESIA C codes.

Q3.10 Micropatterning of Block Copolymer Micelles by Solvent Capillary Contact Printing. Cheolmin Park, Jiyoung Hwang and Wonseok Hwang.

Micropatterning of block copolymer micelles by solvent capillary contact printing (SCCP), which is the combination of micro contact printing and micro transfer molding was presented. The method includes the following procedure: 1) spin coating of block copolymer micelles, 2) conformal contact of polymer film with microcontact printing, 3) injection of a preferential solvent in the microchannels, 4) control of solvent adsorption, and 5) fabrication of metal nanoparticles on the solvent contact regions. We systematically investigated the kinetics of selective solvent adsorption on micropatterned films as a function of solvent contact time. The experimental results are compared with the theoretical predictions. The study was supported by the National Science Foundation under Grant 1225523.

Q3.11 New Applications of Nanostructured-Metal/Semiconductor and Metal/Liquid Interfaces.

The study was supported by the National Science Foundation under Grant 1225523.
We demonstrate new applications of nano-structured-metal/semiconductor and -metal/liquid interface. By using nano-structured-metal, we could enhance dramatically the emission efficiency of solid-state light emitting materials [1]. Now the most important requirement for a solid-state lighting is the development of new methods to increase its quantum efficiency of emission. We found a significant enhancement of light emission from InGaN/GaN quantum wells (QWs) with metal layers deposited 10nm above the QW. This enhancement in light emission is due to the strong interaction between QWs and surface plasmons (SPs). Electron-hole pairs excited within the QW couple to electron vibrations at the metal/semiconductor interface when the electrons of electron-hole pairs in InGaN such that the SP are similar. Then, electron-hole recombination may produce SPs instead of photons, and this new recombination path increases the spontaneous recombination rate. If the metal/semiconductor surface were perfectly flat, it would be difficult to later extract light from the SP, a non-propagating evanescent wave. However, roughness and imperfections in evaporated metal coatings can scatter SPs as light. SP's offer the unique ability to localize, extract and enhance electromagnetic fields, and we can control them by the nanostructure of the metal. We believe that this SP-SP coupling technique provides a foundation for the rapid development of highly efficient and high-speed solid-state light emitters. By using nano-structured-metal/liquid interface, we have observed the transient grating (TG) technique [2]. The TG technique has been applied to material, chemical, and biological research, but experimental setups were mostly complicated. We demonstrate a convenient new technique: mask pattern transfer (MP-T) technique. This method has the same advantages of existing optical detection techniques but the setup is much simpler. The fabricated thin film grating is placed in the front side of a quartz cell containing the sample solution. An UV lamp beam casts a shadow from the grating to the sample solution such that a dark/bright pattern is formed in the solution liquid called transient grating. Such spatial modulation can be detected by the diffraction of a probe beam. By analyzing the probe beam's diffraction, we can obtain the intensity and dynamics of the modulated parameters named above. This technique has many advantages compared with existing TG techniques such as: (1) simple setting, easy alignment, (2) high signal to noise ratio, (3) easy control of phase shift, and a quick interchange of grating periods. We shall demonstrate this technique from several materials and discuss about the potential benefit of this new technique. [1] K. Okamoto, I. Niki, A. Swartter, et al., Nature Materials, 3, 202 (2004). [2] K. Okamoto, Z. Zhang, D. T. Wei, and A. Scherer, Appl. Phys. Lett., 85, (2004) in press.

Driven self-assembly of colloidal particles from their dilute solutions onto planar substrates is proving to be a powerful route to designing broad classes of photonic crystals. Many approaches, including electrostatics, solvent evaporation accompanied by physical confinement, and application of mechanical shear, have proved successful in this regard. Here, we show that the slow evaporation of the solvent under physical confinement in conjunction with chemically structured substrates result in the spontaneous arraying of ordered colloidal crystals upon the disassembly of the sample sandwich. The sub-micrometer colloids were characterized using SEM and optical spectrophotometers while the larger colloids were visualized using optical microscopy. Chemically structured substrates were imaged with imaging ellipsometry. Colloidal arrays reflect the underlying patterns of hydrophilicity or surface energy. A result in turn can be used to observe surfaces. The surface chemistry is not important in the crystal-cleavage, colloidal particles of arbitrary sizes and types can be used. Functionalization of the colloidal arrays using (bio)chemically derivatized colloids as well as the secondary functionalization of the pre-formed colloidal crystal arrays and their effects on photonic properties is being currently investigated in our laboratories.

Control of the assembly of colloidal particles with spatial selectivity across large areas is of interest in emerging applications such as chemical sensors and photonic devices. Current lithographic techniques can be expensive and time consuming for practical applications. It is also suited for patterning only a small list of materials. Recently, we have developed a new nontraditional lithographic technique, termed confined dewetting lithography (CDL) that shows promise for patterning a variety of nano-sized components (spheres, particles, rods) on a multitude of surfaces. This approach is particularly attractive in that the lithographic template is low-cost and reusable. Furthermore, the patterning occurs within seconds to minutes without need for use of expensive lithographic agents or instruments. Using polystyrene (PS) microspheres and colloids we have exploited the optimal conditions where CDL has a high efficiency. In this presentation we describe our success in fabricating patterned structures of many sizes and shapes. One key aspect in optimization of CDL is to minimize attractive PS-substrate interactions. We show that CDL is a relatively simple and fast method to assemble virtually any geometric colloidal pattern by choosing the suitable conditions and materials and can lead to uniform structures of micro-dimensions for a variety of functions.

Density functional theory (DFT-LDA, GGA) is used to investigate the optimal adsorption geometry and binding energy of vinyl phosphorous and ethynic acids on Al (111) surface. The bridged, bi-bridged and un-identate geometries are examined by calculation of binding energy to determine their optimal binding sites. The vibrational frequencies of these molecules are calculated to corroborate their optimal geometries, and the control of properties is confirmed with experimental observations. For these molecules, the favorable decomposition pathway leads to fragments of hydro-carboxylic chains bound to the Al (111) surface via carbon atoms. The final geometry, bonding, and reaction enthalpies are analyzed. In addition, ab-initio molecular dynamics simulations are conducted to examine the stretching of the solvent under physical confinement in conjunction with chemically structured substrates result in the spontaneous arraying of ordered colloidal crystals upon the disassembly of the sample sandwich. The sub-micrometer colloids were characterized using SEM and optical spectrophotometers while the larger colloids were visualized using optical microscopy. Chemically structured substrates were imaged with imaging ellipsometry. Colloidal arrays reflect the underlying patterns of hydrophilicity or surface energy. A result in turn can be used to observe surfaces. The surface chemistry is not important in the crystal-cleavage, colloidal particles of arbitrary sizes and types can be used. Functionalization of the colloidal arrays using (bio)chemically derivatized colloids as well as the secondary functionalization of the pre-formed colloidal crystal arrays and their effects on photonic properties is being currently investigated in our laboratories.

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Adrian M. Brozell, Michelle A. Muha, David N. Woolf and Atul N.Parikh, Applied Science, UC Davis, Davis, California.
transporting effect for molecular electronics, and the efficient photocurrent generation for mimicking photosynthesis in nature.

9:15 AM Q4.3

As electronic devices shrink ever smaller, they are starting to approach a molecular limit, where the device functionality is provided by a single molecule or its contact with a substrate. Consequently, understanding possible limitations and advantages imposed on contact formation by shrinking the effective “contact pad” size close to molecular dimensions (1 - 5 nm) will be of utmost importance for molecular architecture design. To explore the effects of nanoscale structure in contacts, we have fabricated and characterized self-assembled monolayers (SAMs) of alkane thiols (CnH2n+1S, n=9-12) on stepped Au[111] vicinal surfaces, which exhibit terraces 3-6 nm wide. These Au[111] vicinals provide naturally patterned surfaces, where terraces can be oriented along one of the principal crystal axes by choice of the small miscut angle (2 - 4 °). The combination of in situ scanning tunneling microscopy (STM) and photoemission spectroscopy (PES) reveals high-coverage (>90%) alkane thiol SAMs which were solution-deposited onto previously sputtered and vacuum-annealed Au[111] substrate. Most notably, the STM images reveal important information concerning the patterned adsorbates. SAMs on vicinal surfaces compared with non-vicinal (flat) surfaces. While both surfaces show a SAM in an ordered, hexagonal stand-up phase, the flat surface exhibits randomly-distributed, well-known, vacancy islands in the Au substrate, under the SAMs that are mostly absent for the SAM fabricated on the terraces of the vicinal surface. We explain the absence of the vacancies in the latter case by pinning of the Au vacancy defects by the step edges of a Au vicinal surface. These results point to a potentially important tool for controlling the location and the concentration of defects on patterned metal surfaces, used for atomic thiol SAM fabrication. This capability will be demonstrated for determining defect-related attachment sites for electroactive thiadiazole molecules.

9:30 AM Q4.4
Exploiting Physically and Chemically Patterned Surfaces to Create Well-Controlled Microemulsions. Balf Vergara1
Christopher M. Pooley2, Julia M. Yeomans2 and Anna C. Balazs3.
1Chemical Engineering Department, University of Pittsburgh, Pittsburgh, Pennsylvania; 2The Rudolf Peierls Centre for Theoretical Physics, Oxford University, Oxford, United Kingdom.

Using a mesoscale model for hydrodynamics, we simulate driven flow of AB binary fluids past surfaces that contain well-defined roughness or asperities. The geometry and wetting properties of the asperities are found to alter the effective flow condition. We simulate conditions where the A fluid forms vertical bands that bridge the asperities and an imposed shear (or pressure gradient) drives the system to form monodisperse droplets of A within the B fluid. The size of the droplets is tailored by varying the morphology of the asperities. The surfaces needed to create this rich dynamical behavior are used as the "stamps" in micro-contact printing; thus, the parameter space can readily be accessed experimentally and the predictions suggest an efficient method for forming emulsions with well-controlled morphologies.

10:15 AM Q4.5
Smart Thin Films. Weihong Zhang, Richard Nelson and John Larue; The Henry Samueli School of Engineering, University of California, Irvine, Irvine, California.

We have found that two types of photosensitive polymers exhibit different anisotropic characteristics when they are deposited on substrates through spinning process: In one case, the aromatic layers are perpendicular to the film surface; while in another case, the aromatic layers are parallel to the film surface. This difference in aromatic layer arrangement leads to many differences of the thin films after pyrolysis at 900 degC in their mechanical, electrical, chemical, and electrochemical properties. Besides, the unique orientation of aromatic layers for each material brings about two interesting phenomena after mixing carbon fibers with the photosensit and pyrolyzing: Carbon fibers could grow through the films in the two cases. The carbon fibers sprouted out from top surface in one case while they sprouted out from edge in the other case. It seems that carbon fiber grow through the gaps between aromatic molecule groups. The anisotropy characteristics may have potential applications in nanomanipulation and nanostructure fabrication which will be reported as well.

10:30 AM Q4.6
Vapor-Phase Deposition of Crosslinked Poly(2-hydroxyethyl methacrylate) as a Thin-Film Hydrogel. Keelin Chang and Karen L. Gleason; Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

An all-dry, vapor-phase technique was developed for the deposition of crosslinked poly(2-hydroxyethyl methacrylate) thin films. This technique is a one-step process and requires no post-treatment to crosslink the polymer, and the crosslink density is tunable by adjusting reaction conditions. Foursier infrared spectroscopy and X-ray photoelectron spectroscopy confirm the structure of the polymer. Films with crosslink densities ranging from 18.2 to 2.3 hydroxyl groups per crosslink were obtained, and these densities correlate well with the reaction conditions used. With a broader array of reaction conditions, the range of crosslink densities can be made wider. Sessile water droplet contact angle measurements show pronounced hysteresis of contact angle, which is typical for hydrogels, and the contact angle increased with increasing crosslink density. The degree of swelling increases with increasing crosslink density. Infrared spectroscopy for these films show that the ratio of hydroxyl groups to the methacrylates decreases with increasing crosslink density, ranging from 272 to 302 °C. High-temperature annealing (400+ °C) of the films leads to near-complete decomposition, providing a method to remove the functional material. VASE and XPS confirm swelling and X-ray photoelectron spectroscopy confirm the structure of the crosslinked poly(2-hydroxyethyl methacrylate) as a Thin-Film Hydrogel. Kelvin Chan and Karen L. Gleason; Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Vapor-liquid-solid (VLS) process has been an important approach in growth of quasi-one-dimensional (1D) nanowires and nanotubes (referred to as 1D nanostructures). In the VLS process, the metal liquid droplet serves as a preferential site for absorption of gas phase reactant. Nanowire growth begins after the liquid becomes supercooled in reactant materials and continues as long as the catalyst alloy remains in a liquid state and the reactant is available. During the growth, the catalyst droplet directs the growth direction and defines the diameter of the nanowire. Ultimately, the growth terminates when the temperature is below the eutectic temperature of the catalyst alloy or the reactant is no longer available. As a result, the nanowires obtained from the VLS process typically have a solid catalyst nanoparticle at the ends with sizes comparable to diameters of the connected nanowires. It is generally believed that the metal particle is a liquid droplet during the growth and its crystal structure in solid may have no influence on the structure of the nanowires/nanotubes to be grown. In this work, using electron diffraction and high-resolution electron microscopy, we studied the interaction between catalyst Sn particles and their guided ZnO 1D nanostructures. Tin catalyst not only can guide [001] growth nanowires, but also can guide [1-10] and [2-10] growth nanotubes. The interaction relationship between the [001] growth ZnO nanowire and the single crystal β phase Sn particle is: (020)Sn || (0001)ZnO, [-101]Sn || [2-10]ZnO. For nanotubes growing along [011] and [2-1-10], the orientation relationships are (200)Sn || (01-10)ZnO,
Surface Enhanced Raman Scattering for Plated Silver Nanodendrites. Masahiro Yamagisawa, Mikiko Saito, Keiji Nakayama, Kei Ohashi and Yasuo Wada. 1Fundamental Res. Labs., NEC Corporation, Tsukuba, Japan; 2Nanotechnology Res. Inst., AIST, Tsukuba, Japan.

Surface plasmon excitation and surface-enhanced Raman scattering (SERS) have been used for nanostructured surfaces, particularly for aggregated metal particles [1]. According to the calculation of light scattering from fractal metal surfaces, the strong excitation of electromagnetic near fields was predicted [2]. However, there is no report on SERS for electrochemically deposited dendrite structures. We find the ultrahigh Raman enhancement for carbon films on the silver dendrite surfaces. Raman spectra were recorded with a confocal Raman microscope at a wavelength of 514.5 nm in backscattering geometry. Samples with silver dendrites were prepared by an electroplating on Si wafer in AgCN water solution, coated with SiO2. The silver dendrites were grown between gold electrodes. A Raman active carbon film 10 nm thick was then sputter-coated on it. Raman scattering intensity images of the sputtered carbon film on silver dendrites were measured, where many bright points were observed. In order to estimate Raman enhancement on some topographic features, some samples were examined for carbon films on the (111) flat substrate with 300 nm thickness, (c) silver projection of 50 nm in the tip diameter, and (d) silver dendrites. Raman intensity of G-band for the case (d) is 80,000 times or more in magnitude larger than that on the flat glass substrate. The relative enhancement is 5 times for (b) and 400 times for (c). Every strong Raman scattering point, so called hot spots for (d), seem to be generated from the smaller region than that of 160 nm (space resolution) in dendrite structures, where the electric field intensity can be enhanced by surface plasmon polarization (SPP) resonances. Although the plating silver dendrites exhibit the fractal dimension of 1.1 (in the 50 nm range), the region around hot spots such as the interfacial region of the tip particle with the ZnO nanowire/nanobelt could be crystalline or atomically ordered during the VLS growth, although the local growth temperature is much higher than the melting point of tin, and it may play a key role in initiating 1D growth. The interatomic spacing tends to be smaller than the lattice mismatch, thus, the crystalline orientation of the tip particle may determine the growth direction and the side surfaces of the nanowires/nanobelts. References: [1] R.S. Wagner, W.C. Ellis, Appl. Phys. Lett., 41, 1054-1056 (1982); [2] Y. Ding, M. Vaud, Switzerland; [3] Y. Ding, M. Vaud, Germany; [4] For details please visit www.nanoscience.gatech.edu/zwang
Photolithography of an organic photore sist layer usually having a thickness of several tens of micrometers has been widely adopted to manufacture photolithography circuit boards by using printing equipment. The thick photore sist layers are used in industrial wastes in the manufacturing process. A novel method for manufacturing the circuit boards has been highly required to replace the harmful organic industrial wastes from a standpoint in green sustainable chemistry. There are two categories of subtractive and additive methods in electron beam for preparing con ductive metal wires. Selective formation of palladium plating catalysts on a substrate surface is a successful key to prepare such metal wires in the additive methods. In this report, we describe two novel methods for preparing Cu- and Ni/P-patterned wires on SiO2, SiO2/Si, polymer PET and PI substrates by using photopatterned single-layer adsorption films. We designed and synthesized two types of cationic polymer adsorbates for the purpose of this study. One is poly(1-dodecyl-4-vinylpyridinium bromide).[1] The single-layer adsorption films remaining on 172nm-UUV-light-unexposed substrate surface promoted the surface adsorption of negatively charged SDS-SnO2 colloidal catalyst precursors, by which metallic Pd species were formed from [PdCl4]2- through the redox reaction. Another is poly(4-vinylpyridine-co-1-dodecyl-4-vinylpyridinium bromide).[2] The pyridyl groups worked as ligands for coordinating PdCl4 species, from which Pd nanoparticles as plating catalysts were formed by reduction. Cu and Ni/P electrons deposition took place selectively on the cationic single-layer adsorption films in accord with the photopatterned shape. It was found that the behaviors of the selective metalization significantly depended on the thickness of the single-layer adsorption layers at a nanometer level. We demonstrated that the photopatterned single-layer adsorption films on various kinds of substrates were available for an excellent template in electron beam plating to prepare flexible printed-wiring circuit boards. [1] Nakagawa, M.; Nawa, N.; Iyoda, T. Japanese Patent Appl. No. 2004-076654.

Surface Design Using Initiated Chemical Vapor Deposition.

Kenneth K.S. Luen, Karen K. Gleeson; Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Initiated chemical vapor deposition (iCVD) represents a new technology to design and impart targeted chemical functionality to surfaces. The iCVD process enables sit formation of polymeric materials on surfaces, ranging from planar silicon wafers to three-dimensional particulates. By making use of vapor to solid phase transitions and reactions, the use of wet chemistry is eliminated, reducing the impact on environment, health and safety to society. The lack of liquid surface tension forces also makes this process ideal in encapsulating fine particulates without agglomeration. The iCVD process is almost scaleable in shape. It was found that the behaviors of the vapor phase, surface adsorption of these species and subsequent polymerization on a temperature-controlled surface. The decoupling of the temperatures for activation and for surface reaction enables tailor-made conditions for the plating process to produce polymers, such as poly(tetrafluoroethylene), acrylic polymers and copolymers, which are spectroscopically identical to the feedstock. These polymers have been deposited on both silicon substrates and particulates of sizes ranging from nanometers to microns in dimension. By designing the surface chemistry and making use of the inherent surface morphology, we can impart properties, such as superhydrophobicity, tuning of hydrophobicity, H-sensitivity, and reactive sites for grafting. We will show results from a variety of characterization tools, among them Fourier transform infrared spectroscopy, nuclear magnetic resonance spectroscopy, scanning and transmission electron microscopy, gel permeation chromatography, contact angle goniometry, and quartz crystal microbalance. We will show that the iCVD process follows classical polymerization kinetics and the polymerization is necessary for surface design. We will also discuss the evolution of the iCVD process from coating planar substrates to coating of fine particles down to the nanometer dimension.

2:15 PM Q5.3 A Challenge for Textile Science: Can Clothes Chow Down Grime with Nanotechnology? Roger R. H. Wang1, J. H. Xin1, N. M. Tao2 and G. K. H. Pang2; 1 Nanotechnology Center, Institute of Textiles and Clothing, Kowloon, Hong Kong; 2 Department of Applied Physics, Kowloon, Hong Kong.

Substantial effort has been made on developing semiconducting ceramic crystallites acting as photocatalysts on cotton fabrics to produce self-cleaning clothes that help to break down organic materials, grime and bacteria, requiring only light sources that contain ultraviolet (UV) radiation to trigger the reaction. Laundry own fabrics appears to be possible with nanotechnology, as anatase titania (TiO2) crystallites can be grown on cotton fabrics at low temperatures [2]. The clothes that never get dirty with the aid of a photocatalytic process energized by the UV radiation, and the catalysta-based self-cleaning fabrics. The photocatalytic process slowly breaks down and loosens organic dirt attached to the self-cleaning fabrics. In fact, UV light is abundant on cloudy days, in shaded areas, or even in indoor environment fit with natural light sources, and thus the photocatalytic process works nonstop throughout the day. The fact that textiles need to provide effective protection against skin damages such as sunburn, premature skin aging, allergies, and even skin cancer [5-8] caused by the elevated exposure to UV radiation of sunlight actually assists the self-cleaning process. Although anatase titanium dioxide finished fabric has substantial UV-blocking ability in the range of UVB (280-315 nm), the protection on UVA (315-400 nm) remains to be a strong challenge. Hence designing and modifying fabrics in such a way that they offer greater absorption in UV range is of significance for multifunctional protective nano-finishing of textile materials, including self-cleaning, sun-blocking, and anti-bacterial. Zinc oxide (ZnO) is an important alternative wide-bandgap semiconducting ceramic material and its properties were considered to be dependent closely on the microstructures of the materials, aspect ratio and even crystalline density [9]. One-dimensional oriented ZnO nanowires were suggested to be synthesized using low temperature, environmentally benign, solution-based approaches [7] with many unique properties including catalytic degradation of organic chemicals [7], ultraviolet nanolasing action [8], light-emitting diodes [9], waveguides [10], and water-repellent [11], and were desirable for fabricating multi-functional and intelligent textile fabrics. Further scientific and technological advances should be achievable if one-dimensional colloidal quantum system could be hierarchically grown onto the fabrics in an industrially viable way. In this paper we present a hierarchical growth approach to fabricate functionalities with nanotechnology: one-dimensional zinc oxide nanowires are hierarchically grown on cotton fabrics at low temperature. The fabrics allow investigation of potential applications in self-cleaning clothes ranging from medical, military uniforms to environmental catalysis systems.

3:00 PM Q5.4 Growth of a 2-D Multi-component Crystal Exhibiting a Homogeneous Nano-mesh on a Solid Surface. Feng Tao and Steven L. Berson; Chemistry Department, Princeton University, Princeton, New Jersey.

The growth of homogeneous 2-D multi-component crystalline thin films is attracting surprising interest because they may offer the multi-functionality of organic materials and the flexibility of fine-tuning the chemical, physical, and mechanical properties for desirable needs in wide spectrum of technological areas. Molecular self-assembly is a promising route to these films. Coarsedeposition of 5-octadecylsulfosuccinimide acid (SOIA) and octanoic acid and of SOIA and terephthalic acid were fabricated on high-order pyrolytic graphite (HPGO). The morphology of these self-assembled organic materials was investigated using scanning tunneling microscopy (STM). SOIA condors with terephthalic acid via hydrogen-bonding network, forming ordered domain made of alternating SOIA and terephthalic acid lamellae. In the coadsorption of SOIA with octanoic acid, SOIA and octanoic acid alternately pack at the molecular level in each lamella, forming a homogeneous two-component crystal. Due to the different chain-lengths of the two components, a nano-hole with a size of 1.35 nm x 0.55 nm x 0.18 nm is formed in each lattice unit, producing homogeneous nano-meshes. It is suggested that changing the length of alkyl chain of one component can possibly modulate the size of nano-holes in the lattice. This coadsorbed nano-structured material assembl was then used to fabricate multi-component 2-D crystalline thin films at the molecular level. It suggests a new strategy to precisely and controllably grow homogeneous nano-structured composite materials.

3:15 PM Q5.5 Hololithographic Nano-Patterning of Sapphire. Jeffrey M. Biser1, Sreya Dutta1, Hyoung-Joon Park1, Helen M. Chen1, Bijoy K. Das1, Volkmar Dierolf2, and Richard P. Vinci1; 1Materials Science and Engineering, Lehigh University, Bethlehem, Pennsylvania; 2 Department of Physics, Lehigh University, Bethlehem, Pennsylvania.

The industrial community would benefit greatly from a cost-efficient and environmentally friendly way to pattern sapphire substrates. Patterned sapphire can be used as a substrate for low-strain gallium nitride films via nanoheteroepitaxy. Other applications include...
waveguides and optical components. Lithographic patterning of sapphire by conventional processes is difficult due to the inherent chemical resistance of the material, and recently developed AGOG process for generating pristine sapphire surfaces has made it easier to produce patterned sapphire. Starting with a planar sapphire surface, we begin by depositing an Aluminum thin film, anneal to Grow a polycrystalline Al metal layer, and follow this with subsequent Grain growth at high temperature, resulting in solid-state conversion into a single crystal sapphire with a fresh surface (hence the name, AGOG). An exciting side benefit of the AGOG process is that any desired pattern can be etched. The vastly increased intimacy between the metal layer before conversion. The pattern is introduced to the metal film by conventional lithography, which is then converted to sapphire. We have had success in producing patterned sapphire via e-beam lithography. Unfortunately this technique limits us to the size of the pattern we can produce efficiently (on the order of 1mm²). To overcome this obstacle, we have applied holographic lithography. This technique relies on the use of a Lloyd setup, in which a hologram of the pattern is aligned at a glancing angle to a flat mirror, and a laser (with the appropriate wavelength) is aimed at approximately 45 degrees to each surface. Regularly spaced fringes result from interference between light hitting the sample directly, and light reaching the sample from the adjoining mirror. The fringe spacing can be tuned according to the relationship = / 2 sin , where is the spacing, is the wavelength of the laser, and is the angle between the laser and the sample. These periodic fringes expose uniform parallel lines in the photoreist. By exposing the sample once to produce a set of parallel lines, then rotating the sample through 90 degrees and exposing again, a regular periodic structure is created in the photoreist. This photoreist-coated sapphire is then treated with the metal film through conventional techniques to produce a large-scale grid of mesa and alloys. Using this setup, the upper limit of the exposure size is determined solely by the power of the laser and the size of the sample holder. The periodic fringe pattern through AGOG conversion, resulting in a sapphire surface with a periodic array of mesa-like structures. These structures are on the order of 100 nm in size, and have been characterized by electron microscopy and AFM (atomic force microscopy). The efficiency of conversion from aluminum to sapphire is evaluated using cross-sectional TEM (transmission electron microscopy) and EBSD (electron backscattered Kikuchi diffraction).

3:30 PM Q5.6

In-situ Grazing Incidence Small Angle X-ray Scattering (GISAXS) Study of Tunable Nanoripples on Ion-etched Sapphire. Xing Zhou1, Lan Zhou1, Brandon Headrick1, Almeta Orca2, Yivi Wang1, Guode Zhao1 and Karl Ludwig1.
1Physics, University of Vermont, Burlington, Vermont; 2Physics, Boston University, Boston, Massachusetts.

The interaction between energetic particles and surfaces of materials form features of interests such as ripples directly through a surface instability induced self-organization. In this work, we report an in situ synchrotron grazing incidence small angle x-ray scattering (GISAXS) study of sapphire surfaces formed on polycrystalline sapphire substrate by ion etching. The results provide insights on the mechanism of surface morphology evolution during ion irradiation. Single crystal sapphire surfaces were found to be amorphous after ion etching. Strong dependence of surface morphology on ion incidence angle under normal and off-normal conditions, as predicted by Bradley Harper theory, was confirmed by in situ GISAXS patterns and ex situ AFM imaging. A systematic study found that the corrugated ripple wavelength has a power law dependence on the ion energy. Transverse and vertical scans mapping out the scattering patterns in qx-qz plane display characteristic satellite features corresponding well with an asymmetric saw-tooth surface profile. Discussion on the dynamics and mechanism of the ripples formation will be presented.

3:45 PM Q5.7

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Terahertz (THz) emission by optical rectification of an ultrashort laser pulse in noncentrosymmetric materials with a bulk second order nonlinearity. Experimentally reported conduction band structures have previously observed our THz emission from 12nm thick Fe(001) excited by 800nm, femtosecond laser pulses at a 1kHz repetition rate. The generated waveform amplitude scales linearly with the pump fluence, consistent with THz generation from a second order nonlinearity. Moreover, the angular data are characteristic of both surface, \(\chi^2(2)\), and magnetic, \(\chi^2(M)\), contributions to the THz emission. However, second order nonlinearities alone do not account for the narrow THz bandwidth. We propose a mechanism of ultrafast demagnetization2 to explain the experimentally observed THz bandwidth from Fe(001). The samples probed in these experiments consist of 12nm thin films of Fe(001)/MgO(001). The iron thin films are grown by MBE in an UHV system with a base pressure of ~6x10⁻¹⁰ Torr. Growth of the thin film is monitored in situ by QCM, AES, and LEED; the films are shown to be continuous monocrystalline Fe(001). Ex situ analysis of the iron thin films include SEM and XRD. Additionally, SQUID magnetometry of the iron thin film resistance (MO) of the samples. References: (1) Sensing with Terahertz Radiation, D. Mittleman, Ed., Springer, Berlin (2003). (2) D.J. Hiltunen, et al, Applied Phys. Lett. 84 (2004) 3465.

4:00 PM Q5.8

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The purpose of this study is to clarify the atomic structure of hydrogen-terminated Si(110) surfaces after wet cleaning such as dilute HF cleaning and subsequent rinsing with ultrapure water. The hydrogen-terminated Si(110) surface was synthesized by laser-induced AGOG conversion, resulting in a sapphire surface with a periodic array of mesa-like structures. These structures are on the order of 100 nm in size, and have been characterized by electron microscopy and AFM (atomic force microscopy). The efficiency of conversion from aluminum to sapphire is evaluated using cross-sectional TEM (transmission electron microscopy) and EBSD (electron backscattered Kikuchi diffraction).

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References:

4:30 PM Q5.6

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4:45 PM Q5.7

Structural Characterization and Terahertz Emission of Fe(001) Thin Films. Ann Tobias1, David J. Hiltunen2, Chad A. Meserole3, Richard D. Avery2, David J. Funk2, Antonette J. Taylor2 and Joe D. Thompson2. 1NMT-16, Los Alamos National Laboratory, Los Alamos, New Mexico; 2MST-10, Los Alamos National Laboratory, Los Alamos, New Mexico; 3DX-3, Los Alamos National Laboratory, Los Alamos, New Mexico.

Terahertz (THz) emission by optical rectification of an ultrashort laser pulse in noncentrosymmetric materials with a bulk second order nonlinearity. Experimentally reported conduction band structures have previously observed our THz emission from 12nm thick Fe(001) excited by 800nm, femtosecond laser pulses at a 1kHz repetition rate. The generated waveform amplitude scales linearly with the pump fluence, consistent with THz generation from a second order nonlinearity. Moreover, the angular data are characteristic of both surface, \(\chi^2(2)\), and magnetic, \(\chi^2(M)\), contributions to the THz emission. However, second order nonlinearities alone do not account for the narrow THz bandwidth. We propose a mechanism of ultrafast demagnetization2 to explain the experimentally observed THz bandwidth from Fe(001). The samples probed in these experiments consist of 12nm thin films of Fe(001)/MgO(001). The iron thin films are grown by MBE in an UHV system with a base pressure of ~6x10⁻¹⁰ Torr. Growth of the thin film is monitored in situ by QCM, AES, and LEED; the films are shown to be continuous monocrystalline Fe(001). Ex situ analysis of the iron thin films include SEM and XRD. Additionally, SQUID magnetometry of the iron thin film resistance (MO) of the samples. References: (1) Sensing with Terahertz Radiation, D. Mittleman, Ed., Springer, Berlin (2003). (2) D.J. Hiltunen, et al, Applied Phys. Lett. 84 (2004) 3465.
yellow band (around 560 nm) showed specific QD PL line at 380 nm. Its spectral position was insensitive to excitation power density in contrast to InGaN over c-plane templates. It was also found that at temperatures above 700 °C InGaN grown on different facets of ELOG templates has strongly different InN mole fraction. Optical properties and composition of InGaN material were studied by means of energy dispersive X-ray spectroscopy and cathodoluminescence (CL). Maximum InN fraction of 18% was measured for InGaN grown over c-oriented facet of ELOG templates. It was also found that In concentration was almost two times lower in layer grown over (1,-1,0,1) facet of ELOG template, and even less indium was found on (0,0,0,-1), (1,-1,0,0), (1,1,-2,1) facets. No InGaN growth over a-plane GaN was observed at all. Such strong difference in InGaN growth makes possible formation of QDs and wires using selective area growth. As an example of nano-scale selective area growth we studied InGaN growth on side walls of threading dislocation pits and linear features from basal plane stacking faults formed on the surface of a-plane GaN template. Preliminary TEM studies showed the concentration of these defects far from seeding of ELOG structure to be less than 10^8 cm^-2 and 10^4 cm^-1, respectively. As grown these defects formed by (000-1) and (1,-1,0,1) planes have dimensions of 10-100 nm. After growth of InGaN layer these defects exhibited strong blue emission as revealed by high resolution monochromatic CL imaging, whereas no blue emission was observed from flat a-plane surface. These results confirm the formation of QDs by selective area growth on sidewalls of surface defects.