Thursday Evening Poster Sessions, November 16, 2006

Surface Science
Room 3rd Floor Lobby - Session SS-ThP

Surface Science Poster Session

SS-ThP1 The Study of the Silicon Oxide Growth Modes with Ambient-Pressure X-Ray Photoelectron Spectroscopy, *B.S. Mun*, Lawrence Berkeley National Laboratory; *Y. Enta,* Hirosaki University, Japan; *M. Rossi,* Lawrence Berkeley National Laboratory; *K. Lee, S.-K. Kim,* Seoul National University, Korea; *P.N. Ross,* Lawrence Berkeley National Laboratory; *C.S. Fadley,* Lawrence Berkeley National Lab. & UC Davis; *Z. Hussain,* Lawrence Berkeley National Laboratory

The growth rates of silicon oxide and the nature of the chemical bonding at the oxide interface have been investigated at ambient pressures of oxygen and water up to 1 torr in real time. The growth rates of silicon oxidation at various substrate temperatures and gases pressures of oxygen and water have been monitored. In the case of oxygen (a dry oxidation process), the growth rate of oxide is very rapid up to the thickness of one monolayer and this is followed by a second fast regime up to ca. 2 nm oxide thickness, after which the reaction rate slows considerably. In the case of water (a wet oxidation process), the growth rates of oxide become significantly slower compared to the dry process. Qualitative theoretical modeling is presented to explain the difference between dry and wet oxidation processes.

SS-ThP2 Cathodoluminescence Degradation of SiO@sub 2@:Ce,Tb Powder Phosphors Prepared by a Sol-Gel Process, *O.M. Ntwaeaborwa*, *H.C. Swart, R.E. Kroon,* University of the Free State, South Africa; *P.H. Holloway,* University of Florida

Auger electron spectroscopy (AES), cathodoluminescence (CL) spectroscopy and X-ray photoelectron spectroscopy (XPS) were used to study degradation of the CL intensity of SiO@sub 2@:Ce,Tb powder phosphors prepared by a sol-gel process. The AES and CL data were collected simultaneously when the powders were irradiated for 10 hours with a beam of electrons of energy 2 keV and a current density of 54 mA/cm@super 2@ in an ultra high vacuum chamber containing either 1x10@super -8@ or 1x10@super -7@ Torr O@sub 2@. A decrease of CL intensity during electron beam bombardment occurred simultaneously with desorption of oxygen from the surface, i.e. there is a correlation between the degradation of CL intensity and desorption of oxygen. The AES and XPS data suggest that a non-luminescent oxygen-deficient layer of SiO@sub x@ (x<2)was formed on the surface and resulted in the decrease of CL intensity. The formation of the SiO@sub x@ layer is consistent with an electron stimulated surface chemical reaction (ESSCR) model. Mechanisms by which oxygen desorption leads to a reduction of the CL intensity are discussed.

SS-ThP3 Development of an Efficient Charge Transfer Potential for the Molecular Dynamics Study of Metal-Metal Oxide Interfaces, *B.D. Devine,* University of Florida; *A. McGaughey,* Carnegie-Mellon University; *S.R. Phillpot, S.B. Sinnott,* University of Florida

The metal-metal oxide interface poses several challenges to theoretical modeling. A molecular dynamics approach requires an expression for potential energy that captures both ionic bonding in the oxide and metallic bonding in the base metal. Changes in the electron density of atoms at the interface must also be approximated with a classical expression of charge. Electronic structure theory approaches are limited to simulations of systems with comparable lattice parameters or with a high degree of lattice strain. This work presents the development of an electrostatics potential based on the work of Streitz and Mintmire@footnote 1@ whereby the partial charge on each atom is allowed to vary with atomic positions. The charge on each atom is treated as a dynamic variable, which allows for efficient parallelization and scaling with system size. The efficiency of the parallel code allows for the simulation of systems of sufficient size to compensate for lattice mismatch through a dislocation network. @FootnoteText@This work is supported by the National Science Foundation (grant no. DMR-0426870). @footnote 1@ Streitz, F., Mintmire, J, Phys Rev. B 1994, 50, 996. @FootnoteText@ 1. Streitz, F., Mintmire, J, Phys Rev. B 1994, 50, 996

SS-ThP5 Surface Conduction Measurement on SrTiO@sub 3@ (110) by a UHV-Compatible Microprober, *H. Bando,* Y. Aiura, AIST, Japan; *I. Konishi,* Ibaraki University, Japan; *A. Urata,* International Servo Data Corp., Japan; *Y. Nishihara,* Ibaraki University, Japan

SrTiO@sub 3@ (110) surface shows metallic character after annealing in UHV at relatively low temperature, @<=@ 1073 K, until the surface is exposed to O@sub 2@ at room temperature. The surface metallic electronic states had been confirmed by our previous work by photoelectron spectroscopy, scanning tunneling microscopy/spectroscopy, and in situ surface conduction measurement. The (110) surface has an anisotropic structure, with Ti-O chains parallel to [001]. An Ultra-High Vacuum compatible microprober was employed to assess how the structural anisotropy affects the electronic surface conduction on the SrTiO@sub 3@ (110). The result was understood in terms of the arrangement of the Ti-3d orbitals.

SS-ThP6 Comparison of the Sputter Rates of Fe@sub 2@O@sub 3@, Cr@sub 2@O@sub 3@, CeO@sub 2@, ZnO, and TiO@sub 2@, Films to the Sputter Rate of SiO@sub 2@, *M.H. Engelhard,* D.R. Baer, T. Droubay, A.S. Lea, P. Nachimuthu, Pacific Northwest National Laboratory

Because of the increasing technological importance of oxide films for a variety of applications, there is a growing interest in knowing the sputter rates for oxides relative to the sputter rate for SiO@sub 2@, a common sputter rate reference material. To support our research programs, we have made a series of measurements of the sputter rates for oxide films that have been grown by oxygen plasma assisted molecular beam epitaxy (OPA-MBE) or pulsed laser deposition (PLD). The film thicknesses and densities of these films were measured using x-ray reflectivity (XRR). These samples were mounted in a Phi Quantum 2000 where x-ray photoelectron spectroscopy (XPS) was used to monitor composition during sputtering using a 2 keV Ar@super +@ ion beam 45° from surface normal. We find that the sputter rates of Fe@sub 2@O@sub 3@, Cr@sub 2@O@sub 3@, and CeO@sub 2@, are all significantly slower than what is observed for SiO@sub 2@. In addition to the observed sputter rates, the XPS measurements allow observation of ion beam induced reduction of the oxides. Sputter rate measurements of both anatase and rutile forms of TiO@sub 2@, and ZnO will also be reported.

SS-ThP7 The Interaction of H2O with MgO(100) as Studied with Ambient Pressure Photoemission Spectroscopy, *D.E. Starr, G. Ketteler,* Lawrence Berkeley National Laboratory; *S. Yamamoto,* Stanford Synchrotron Radiation Laboratory; *T. Kendelewicz, G.E. Brown Jr.,* Stanford University; *A. Nilsson,* Stanford Synchrotron Radiation Laboratory; *M. Salmeron, H. Bluhm,* Lawrence Berkeley National Laboratory

Water-oxide interactions play an important role in chemical, environmental and biological systems. Even though these systems have been extensively studied, the nature of the water-oxide interface remains poorly understood. Due to its simplicity and environmental relevance, the MgO(100) surface has become a prototype for studying such interactions. However, basic issues such as molecular versus dissociative adsorption at the H2O/MgO(100) interface have not been resolved. We have utilized Ambient Pressure Photoemission Spectroscopy at beamline 11.0.2 of the Advanced Light Source to address such questions. This unique experimental set-up is capable of performing photoemission experiments in the Torr pressure range allowing measurements of the H2O/MgO(100) interface under equilibrium conditions. We will present experimental results relating to the degree of dissociation and uptake of H2O on a MgO(100) thin film grown on Ag(100) at equilibrium conditions and compare these results to the current understanding of this important prototypical system.

SS-ThP8 Adsorption of Atmospheric Gases on Iron Oxide Surface, *J. Baltrusaitis, V.H. Grassian,* University of Iowa

Iron oxides are a reactive component of air, water and soil. The adsorption of several atmospheric gases including SO@sub 2@, HNO@sub 3@ and CO@sub 2@ as a function of relative humidity has been examined on iron oxide particle surfaces. Results from several techniques including a newly designed XPS reactor/analysis system will be presented. These studies show that adsorbed water plays an important role in the surface chemistry of iron oxide particles with these molecules.

SS-ThP9 Thermal- and Electron-Induced Reactions on the Ru(10-10) Surface: Relevance to Extreme Ulltraviolet Lithography, *T.E. Madey,* B.V. Yakshinskiy, R. Wasiliewski, Rutgers University

Our goal is to provide insights into surface processes that affect the reflectivity of Ru-coated mirrors used in extreme ultraviolet (EUV) lithography applications. Thin capping layers of Ru are found to reduce

contamination and oxidation of Mo/Si multilayer reflecting optics surfaces, and extend the useful lifetime of EUV multilayer mirrors. However, reflectivities of even the Ru-coated mirrors degrade in time during exposure to vacuum background gases and EUV radiation. Several techniques, including temperature programmed desorption (TPD), x-ray photoelectron spectroscopy (XPS), low energy ion scattering (LEIS) and electron stimulated desorption (ESD), are used to characterize thermally-induced and electron impact-induced surface reactions of gases found typically in vacuum chambers of EUV lithography systems. We present data concerning the interaction of water and acetone vapors with clean, O-covered and C-covered Ru(10-10) surfaces. A 100eV electron beam is used to mimic excitations initiated by 13.5 nm wavelength radiation employed in EUV applications. The data show non-wetting behavior of water on the air-exposed or the carbon-covered surfaces; however, water becomes more strongly bonded to an oxygen-dosed substrate. We report on the electron-induced dissociation and desorption of water adsorbed on these surfaces at low temperature. The clean Ru surface is shown to be easily covered by carbon as a result of the thermally-induced dissociation of acetone, but this reaction demonstrates different behaviour on the preoxidized Ru. Electron-stimulated desorption of O from Ru proceeds at electron energies > 25eV. Our results may provide insights into contamination and mitigation processes that affect EUV mirror lifetimes.@footnote 1@ @FootnoteText@ @footnote 1@ T. E. Madey, B. V. Yakshinskiy, N. S. Faradzhev, N. V. Edwards, Appl. Surf. Sci. (2006), in press.

SS-ThP10 Surface Studies of Size-Selected Molybdenum Oxide Clusters, *M.J. Patterson, J.M. Lightstone, M.G. White,* StonyBrook University/Brookhaven National Laboratory

A cluster deposition apparatus has recently been constructed and employs a magnetron sputtering source for generating gas-phase cation clusters of pure metals and metallic compounds. Of particular interest are clusters of the transition metal oxides such as Mo@sub x@O@sub y@@super +@. Bulk molybdates are one of the most widely used selective oxidation catalysts for processes such as the conversion of methanol to formaldehyde,@super 1@ and smaller molybdenum oxide clusters, x=1-3;y=1-9, have shown activity towards CO oxidation and dehydrogenation of cyclopropane@super2@. The work reported here examines the gas-phase production of an array of molybdenum oxides clusters as a first step towards investigations of model catalysts prepared by size-selected deposition. Preliminary Scanning Transmission Electron Microscope (STEM) imaging of the Mo@sub 46@O@sub 132@@super +@ cluster deposited on amorphous carbon, shows the propensity for aggregation of these clusters as the coverage increases. Current efforts involve the use of size-selected deposition to study the size-dependent structure and reactivity of supported Mo oxide nanoclusters using thermal desorption, x-ray photoemission and STEM particle imaging. @FootnoteText@ @footnote 1@ Gai-Boyes, P.L.; Catal. Rev. Sci. Eng, 1992, 34, 1-54.@footnote 2@ Fialko,E.F.; Kikhtenko, A.V.; Goncharov, V.B., et.al.; J. Phys. Chem, 1997, 101, 8607.

SS-ThP11 Noncontact Atomic Force Microscopic Studies on Atomic Scale Structures of TiO@sub 2@ Single Crystal Surfaces Prepared by Wet Chemical Process, *Y. Namai, S. Miyazoe, O. Matsuoka,* Mitsui Chemicals, Inc., Japan

We succeeded in observing the atomic scale structures of rutile-type TiO@sub 2@ surfaces prepared by the wet chemical method of chemical etching in an acid solution (H@sub 2@SO@sub 4@+H@sub 2@O@sub 2@) and surface annealing at 873 K in air. We tried to perform noncontact AFM observations at 450 K, which is above a desorption temperature of molecularly adsorbed water on the TiO@sub 2@(110) surface, and could obtain the atomic scale structure of the TiO@sub 2@(110) surface prepared by the wet chemical method. The surface structure was consistent with the (1 x 1) bulk-terminated model of TiO@sub 2@(110) surface. In the noncontact AFM measurements at room temperature, however, the atomic scale structure of the TiO@sub 2@(110) surface was not observed. The TiO@sub 2@(110) surface may be covered with molecularly adsorbed water after the surface was prepared by the wet chemical method. We consider that the wet chemical method is an important method in preparing atomic scale structures of TiO@sub 2@ surfaces under atomospheric conditions.

SS-ThP12 Photoemission Analysis with Synchrotron Radiation for Nitridation of SiO@sub 2@ Thin Film on Si(001) by Irradiation of N@super +@ Ion Beams, *Y. Teraoka,* Japan Atomic Energy Agency, Japan*; S. Hachiue, K. Yokota, M. Tagawa,* Kobe University, Japan

Energetic atomic and molecular beams are useful for modification of ultra-thin layers in ULSI devices. The silicon dioxide overlayers on Si(001) substrates were fabricated by a rapid thermal oxidation (RTO) method. The thickness was ranging from 1.6 nm to 2.8 nm, which was estimated by ellipsometry. Nitrogen gas was discharged in a PIG-type cold-cathode plasma ion source. The ions generated in the ion source were extracted and accelerated up to a translational kinetic energy of 3 keV and focused by a pair of Einzel lens. The atomic nitrogen ions were separated from other ionic species by using a Wien filter (E x B separator). The mass-selected atomic nitrogen ion beams were decelerated and irradiated at the ultra-thin silicon dioxide overlayers on Si(001) substrates by 6.3x10@super 15@ to 2.0x10@super 16@ particles/cm@super 2@ at room temperature. Chemical bonding states of Si, O, and N atoms in the nitrogen-impinged region were analyzed via photoemission spectroscopy using high brilliance and energy-resolution synchrotron radiation of 688 eV after transferring the samples from the ion beam apparatus to the photoemission apparatus. Photoemission spectra of N-1s core level could be observed in addition to Si-2p and O-1s peaks owing to the high brilliance synchrotron radiation. It was found that the silicon dioxide overlayer and the interface were effectively nitrided even by the dose of 10@super 15@ particles/cm@super 2@ order as well as the Si(001) substrate. N-1s photoemission spectra were asymmetric and deconvoluted into four components. Consequently, they were assigned to (a) N(-Si)@sub 3@, (b) N(-SiO@sub 3@)@sub 3@, (c) SiN@sub 3@-NO-SiN@sub 2@O, and (d) O-N(-Si)@sub 2@, respectively.

SS-ThP13 Study of Step Stability on the Fe@sub 3@O@sub 4@ (100) Surface*, *H.-Q. Wang, E.I. Altman, V.E. Henrich,* Yale University

The atomic structure along steps on metal oxide surfaces is crucial to the growth of overlayers. Yet no experimental techniques are capable of resolving that sturcture. Ab initio calculations of step structures on metal oxides are complex and have not been reported to date. By considering both the ionic and covalent components of interatomic bonding in metal oxides, we have developed a method of predicting the relative stability of different step structures.@footnote 1@ Fe@sub 3@O@sub 4@ (magnetite) is a ferrimagnetic metal that is of interest as substrate for growing complex oxides and for spintronics applications. Our STM observations on Fe@sub 3@O@sub 4@ (100) surfaces show step edges along both [110] and [1-10] directions; the step edges are found to be straight for steps heights of 4.2 ± 0.3 Å, but alternating smooth and jagged for step heights of 2.1 ± 0.2 Å. The straight (jagged) step edges are parallel (perpendicular) to the octahedral iron rows on the upper terrace. By evaluating the coordinative unsaturation of step-edge ions and the excess charge along a step, we show that steps parallel to the octahedral iron rows on the upper terrace are expected to be more stable than those perpendicular to them, in agreement with our STM observation. This step stability criterion is found to be independent of both terrace structure and step height. @FootnoteText@ *This research is partially supported by U.S. Department of Energy Grant No. DE-FG02-00ER45844, NSF Equipment Grant No. DMR-0075824, and NSF Grant MRSEC DMR-0520495.@footnote 1@V.E. Henrich and S.K. Shaikhutdinov, Surf. Sci. 574, 306 (2005).

SS-ThP14 Self-Assembled Monolayers as Templates to Control Electrochemical Metal Deposition, *C. Shen,* University of StAndrews, UK*; M. Buck,* University of StAndrews, UK, United Kingdom

Tailoring electrode activity by self-assembled monolayers (SAMs) of thiols is the basis of a promising scheme to generate electrode structures. It consists of a cycle which involves SAM directed electrochemical deposition of a metal pattern and subsequent transfer to an insulating substrate.@footnote 1@ The process relies on a favourable combination of properties of SAMs, i.e., the possibility to control both adhesion and interfacial charge transfer. With the availability of techniques to pattern SAMs on length scales down to nanometers the process offers the perspective to generate small scale electrode structures in a very simple way. However, with increasingly smaller dimensions of patterns the control of structures and properties of SAMs and electrochemical metal deposition becomes increasingly demanding. Some of the key challenges are the exact control of metal nucleation on a SAM modified electrode and the minimisation of defects in those types of SAMs which serve to suppress metal deposition. We report on our studies of alkane thiols and @omega@-(4'-methyl-biphenyl-4-yl)-alkane thiols which, using electrochemical characterisation and scanning tunneling microscopy, show

how variations in the SAM structure affects metal nucleation and that a non-equilibrium annealing process substantially improves the passivating properties of thiol SAMs. @FootnoteText@ @footnote 1@ I. Thom, G. Haehner, and M. Buck, Appl. Phys. Lett. 87, 024101 (2005).

SS-ThP15 Tuning the Exchange Reaction between a Self-Assembled Monolayer and Other Molecules by Electron Irradiation, *N. Ballav, A. Shaporenko, M. Zharnikov,* Universität Heidelberg, Germany
The molecules comprising a self-assembled monolayer (SAM) may exchange gradually when exposed to solutions containing other molecules, which are capable to build a SAM on the given substrate. This replacement offers a route to generate a new organic surface on a substrate already supporting a SAM. The rate and extent of replacement depend on a number of parameters, including the identity of the molecular chain, chain length, degree of order, and topography/roughness of the substrate. Taking SAMs of non-substituted and @omega@-substituted alkanethiolates (AT) as test systems, we studied the effect of an additional factor - electron or X-ray irradiation. We show that, in view of the exchange process, such a treatment is especially effective at a relatively low irradiation dosage, below 1 mC/cm@super 2@. Staying under this limit and varying the dosage, we were able to change the rate and extent of the exchange reaction continuously and to a noticeable extent. In particular, in the case of a non-substituted AT SAM and -OH and -COOH substituted alkanethiols in the solution, the rate of the exchange reaction could be increased by an order of the magnitude, and about 60-70% of the primary SAM molecules could be substituted after a preliminary irradiation (it was less than 10% without the irradiation). The suggested combination of e-beam patterning and substitution reaction can be used for the fabrication of molecular gradients of any particular form with the resolution down to several nanometers.

SS-ThP16 Tribological Properties of Micro Patterned Surface, *M. Nakano, K. Miyake, T. Murakami, Y. Ando, S. Sasaki,* AIST, Japan
Recently, the tribological properties of micro-patterned surfaces have been investigated and it has been shown that the feature of surface can affect the friction behavior of lubricated surface. In this study, the micro-patterned surface was prepared by photorisography, plasma ethcing and evaporation of NiFe alloy on Si surface in order to investigate the effect of the surface texture on the tribological properties under lubrication condition. The size of pattern was from 10 μm to 100 μm and the depth was about 10 μm. The friction test was carried out using pin-on-plate tribometer. The normal load was varied from 10 mN to 100 mN and the sliding speed was from 1mm/sec to 10 mm/sec. The commercial lubricants and the pins made of cast iron were used. The patterned surface showed less variation of friction force with the variation of the normal load than the flat surface. Moreover, the friction force of the patterned surface became lower. On the other hand, in the case of dry condition, the friction coefficient was high and the friction behavior was independent of surface feature. Therefore, it was considered that the surface texturing affect the lubricant film thickness and the frictional behavior.

SS-ThP17 Multivariate Analysis as an Enabling Method for Structure-to-Property Studies of Fuel Cell Electrocatalysts, *S. Pylypenko, T.S. Olson, M. Dowlapalli, K. Artyushkova, J.E. Fulghum, P. Atanassov,* The University of New Mexico
Understanding the surface chemistry and structure of electrocatalysts, and linking structure to properties is important for optimization of catalyst performanace and elucidation of failure mechanisms. Characterization of the changes in surface chemistry that occur as a function of catalyst production, modification and aging requires identification of subtle changes in a complex system. X-ray photoelectron spectroscopy (XPS) in combination with multivariate analysis (MVA) was used to study a number of materials, including non-platinum electrocatalysts, based on pyrolysed porphyrins, and carbon blacks used as catalyst supports. Analysis of chemical bonding information from XPS spectra frequently utilizes deconvolution of the spectra into multiple peaks, resulting in significant interpretational ambiguities. Multivariate analysis techniques, in combination with conventional curve fitting, facilitate both interpretation of the data and the development of structure-property correlations. Principal component analysis (PCA) was applied to the XPS curve fit results from the catalysts and supports, enabling identification of chemical species, grouping of chemical species as a function of catalyst treatment, and correlation with electrochemical performance. The methodology applied in this study can be effectively used to identify active catalytic sites responsible for oxidation/reduction process, detect chemical species

responsible for corrosion of the catalyst material, and assist in design of optimized electrocatalysts.

SS-ThP18 Isotope Effect in Chemicurrent Experiments, *D. Krix, R. Nuenthel, H. Nienhaus,* University of Duisburg-Essen, Germany
During exothermic reactions of atomic hydrogen or deuterium on a silver surface hot charge carriers are produced which have been observed by using Ag/Si(111) Schottky diodes. Thin film devices provide a means to bring a charge detector as close to the reaction site as the mean free path of the charge carriers. In the case of a p-doped substrate the Schottky barrier works as a high-pass energy filter for hot holes. We have therefore produced large area Schottky diodes with film thicknesses of up to 30 nm varying the thickness to rule out any influence of this device parameter. Those diodes were then exposed to beams of hydrogen atoms and deuterium atoms produced in a hot-capillary source. Gas exposures do not affect the Schottky barrier height significantly. While exposing the samples to defined atom fluxes the closed-loop current was monitored in real time. It shows that the current is proportional to the amount of flux supplied as long as the total flux is low and sticking is independent of hydrogen coverage. We have found hydrogen to generate more than three times the amount of hot holes than are created during reactions with deuterium. Theoretical predictions of non-adiabatic energy dissipation using the electronic friction model agree well with the experimental results.

SS-ThP19 Tunable Frequency Alternating Current Scanning Tunneling Microscope for Surface Excitation in the Microwave Frequency Range, *A.M. Moore, P.S. Weiss,* The Pennsylvania State University
We have built a scanning tunneling microscope (STM) capable of measuring the response of surfaces excited with microwave frequencies (up to 20 GHz) at sub-nanometer resolution. Two frequencies are applied to the STM tip and the nonlinearity of the tunnel junction mixes the frequencies, generating new signals including at the difference of the frequencies applied. This ultrahigh resolution (<1 nm) profiling tool enhances and complements what is obtained through current metrology tools and will support semiconductor processing as the size scale of devices continues to decrease. It will allow us to study single molecule rotations excited at microwave frequencies and also allow us subsurface properties of thin films and cluster-assembled materials.

SS-ThP20 Purification of Otho-Hydrogen by Adsorption Separation Method Combined with Thermal Desorption Process, *K. Niki, T. Kawauchi, M. Matsumoto, K. Fukutani, T. Okano,* The University of Tokyo, Japan
Separation of ortho-hydrogen from normal hydrogen, a mixture of ortho H@sub 2@ (o-H@sub 2@) and para-H2 (p-H@sub 2@), has been carried out by using an adsorption separation method, which exploits the difference between the activation energies of desorption of o-H@sub 2@ and p-H@sub 2@. @footnote 1@ The optimum value of the separation coefficient S was empirically determined and analyzed based on adsorption equilibrium data of o-H@sub 2@ and p-H@sub 2@. Recently, we developed rotational state-selective thermal desorption spectroscopy (TDS) for hydrogen molecules. Grains of activated alumina were contained in a sample cell attached to the cold head of a mechanical refrigerator. After the activated alumina was exposed to normal hydrogen for a certain time, it was heated at a constant rate. The desorbing hydrogen molecules were ionized from selected rotational quantum status by resonant-enhanced multiphoton ionization (REMPI). The TDS peak temperatures were measured as 18K and 16 K for o-H@sub 2@ and p-H@sub 2@, respectively. In previous reports on the adsorption separation process, the molecular process during the desorption period was not well-analyzed. Based on our state-selective TDS data, we calculated the enhancement of the separation coefficient by sampling the desorbing hydrogen molecules at an intermediate temperature during the TDS measurement. To prove this estimation of the enhancement of the separation coefficient, we constructed an o-H@sub 2@ purifier. The apparatus consists of two parts: an adsorption separation cell system and a REMPI detector system. Details of the experimental results of o-H@sub 2@ purification and the comparison with the calculation is to be presented. @FootnoteText@ @footnote 1@ C. M. Cunningham et al., J. Am. Chem. Soc. 80, 2382 (1957).

SS-ThP21 Energetic Gas-Phase Collisions with Alkanethiol Self-Assembled Monolayers, *N.A. Kautz, D.P. Fogarty, S.A. Kandel,* University of Notre Dame
The combination of a molecular-beam source with an ultra-high-vacuum scanning tunneling microscope allows the investigation of structural and chemical changes of octanethiol self-assembled monolayers resulting from energetic gas-surface collisions. In situ monitoring of the sample before,

during, and after collision shows that at the molecular scale, close-packed regions of the monolayer show very few changes even when bombarded by hyperthermal or reactive species. However, defects in the organic monolayer, which result automatically from the film deposition process, result in more reactive environments in which significant changes are seen.

SS-ThP23 Beam Damage on Drug Tablet during XPS Analysis, *C.A.J. Kemp, X. Dong,* Eli Lilly and Company

It is a well-known phenomenon that certain samples are susceptible to beam damage during XPS analysis. Dry-formulated drug products usually contain, in addition to the active pharmaceutical ingredient (API), multiple excipients. It is of great interest to understand the potential for inadvertent sample alteration during the analysis of drug products using XPS. In the current study, the potential beam damage to a drug tablet was evaluated. The preliminary results revealed the discoloration of the analytical area on the tablet after it was exposed to a 15kV X-ray beam for 2 hours. By ToF-SIMS analysis it was found that the characteristic mass peak of the excipient mannitol was relatively lower in the spectra of the discolored area than in the spectra of the control area, when compared to the characteristic peak of API. It suggests that mannitol is more susceptible to beam damage than API under the typical XPS analysis conditions. The effect of API level, and different XPS analysis conditions on the extent of beam-induced damage will be further investigated.

SS-ThP24 Motion of Water Droplets on Inclined Hydrophobic Surfaces in Flowing Air, *A. Hashimoto, J.-H. Song, M. Sakai,* Kanagawa Academy of Science and Technology, Japan*; S. Suzuki,* Kanagawa Academy of Science and Technology, and Tokyo Institute of Technology, Japan*; N. Yoshida,* Kanagawa Academy of Science and Technology, and The University of Tokyo, Japan*; Y. Kameshima, A. Nakajima,* Kanagawa Academy of Science and Technology, and Tokyo Institute of Technology, Japan

Recently, not only for water-repellent treatment, control of liquid droplets on solid surfaces has become important for advanced device systems such as MEMS or microscale chemical processing. So far, various investigations have been performed to examine the motion of a liquid droplet on a solid surface using external fields such as gravity, electric fields, photo-illumination and a heat gradient. However, investigation on the control of a liquid droplet using air flow is insufficient although it is indispensable for the design of industrial items such as windshield of automobiles. In the present study, we investigated effect of air flow on droplet shape and motion on hydrophobic surfaces using high-speed cameras. Three silanes were deposited on Si substrates by CVD method. Water droplets with different weight (10 ~ 50 mg) were placed on the surfaces, which were tilted at 0, 35, 45 and 60 ° in an open-circuit-type wind tunnel. We carefully observed the droplets by high-speed cameras changing a wind velocity (0 ~ 20 m/s). The droplet motion on inclined hydrophobic surfaces in air flow was classified into three categories by the competition between the forces of the wind and the gravity; sliding down, stopping and climbing up. Detailed relationship among these behavior, moving speed, droplet deformation, experimental condition and surface state will be discussed.

SS-ThP25 Computational Simulations on the Interaction of Water and Hydrophobic Surface, *Y. Kameshima, S. Suzuki,* KAST and Tokyo Institute of Technology, Japan*; M. Sakai, A. Hashimoto,* KAST, Japan*; N. Yoshida,* KAST and CCR, Tokyo University, Japan*; K. Okada,* Tokyo Institute of Technology, Japan*; A. Nakajima,* KAST and Tokyo Institute of Technology, Japan

Wettability is an important phenomenon of solid surfaces from theoretical, practical, and technological aspects. And the wettability of the solid surface is a characteristic property of materials and is controlled by the surface energy and roughness. If the wettability and the water repellency are simulated by the theoretical calculation, the obtained information is useful to design the hydrophobic surface. The interaction of water with hydrophobic surface was evaluated by the theoretical calculation. Molecular orbital (MO) calculations were used to determine the energy change of water molecular by their distance to typical model surface of hydrophobic coatings. Molecular dynamics (MD) calculations were used to study nanoscale water dynamics phenomenon. Clusters of $C_{13}H_{22}$ and $C_{13}F_{22}$ consisted by three hexagon of carbon were used for the model clusters for MO calculation. The water molecule was placed center of the substrate cluster. The distance of water molecule and the surface hydrogen or fluorine was set to be 1.0ï½z4.0â"«. On each system, the optimization of the structure was done so that the total energy of each system may become a minimum. As the result, the water molecule could not be separated from the surface of $C_{13}F_{22}$ cluster. CH_4 and CF_4 molecules in water cell were used for the typical model for MD calculation. Under 1 ns

calculations, there were no difference in radial distributions for CH4 and CF4 calculations.

SS-ThP26 Deformation and Motion of a Droplet of Water-based Magnetic Fluid on a Hydrophobic Surface by Gravity and Magnetic Field, *A. Nakajima,* KAST (Kanagawa Academy of Science and Technology) and Tokyo Institute of Technology, Japan*; H. Asakura,* KAST and Tokyo Institute of Technology, Japan*; M. Sakai, A. Hashimoto,* KAST, Japan*; S. Suzuki, Y. Kameshima,* KAST and Tokyo Institute of Technology, Japan*; N. Yoshida,* KAST and CCR, Tokyo University, Japan*; K. Okada,* Tokyo Institute of Technology, Japan

Control of a liquid droplet on a solid surface has attracted much attention as an indispensable technology for various industrial items, especially for hydrophobic coatings. Recently, not only for water-repellent treatment, this technology has become important for microscale chemical processing systems. To date, various investigations have been carried out to examine the motion of a liquid droplet on a solid surface using external fields. However, investigations on the control of a solid and liquid mixture using an external field are limited. Magnetic fluid is a very common solid-liquid mixture, In the current paper, motion and deformation of a water-based magnetic fluid on a hydrophobic surface were investigated under gravity and a magnetic field. Surface energy and the resultant contact angle of magnetic fluid depend on the surfactant concentration. Viscosity of the fluid is mainly governed by magnetite concentration. The front edge of the droplet moved under a weak external field. The rear edge required a higher external field for movement. The force for moving of the front edge is almost identical between gravity and the magnetic field. However, that of the rear edge is different. The motion of magnetic fluid by an external field depends on the concentrations of surfactant and magnetic particles, external field, and experimental assembly.

SS-ThP27 Observation of Internal Fluidity in a Water Droplet during Sliding on Hydrophobic Surfaces by Particle Image Velocimetry, *M. Sakai, A. Hashimoto, M. Sugibuchi,* Kanagawa Academy of Science and Technology, Japan*; S. Suzuki,* Tokyo Institute of Technology and KAST, Japan*; N. Yoshida,* CCR, the University of Tokyo and KAST, Japan*; Y. Kameshima, A. Nakajima,* Tokyo Institute of Technology and KAST, Japan

Recently, the importance of dynamic hydrophobicity (sliding acceleration) is recognized in various industries. In the current paper, we evaluated the sliding behavior; acceleration, advancing-receding contact angles, and the shape of water droplets on various declined hydrophobic surfaces by a high-speed camera system with motion picture analysis. The intensity of the interaction between the solid surface and liquid dominated the sliding behavior of the water droplet. Moreover, during the droplet sliding on the hydrophobic surface, the rolling like a catapillar motion and the slipping on the contact line was observed from the motion of the indicator particle in the droplet. The sliding velocity in the water droplet can be described by the two elements. The cross-section images, which were obtained by a sheet laser (wave length: 488 nm), from the center of the droplet were precisely analyzed by the particle image velocimetry. We successfully confirmed the thickness of boundary layer for the hydrophobic surface by this method. We will discuss the effect of the velocity gradient around the boundary between liquid and the hydrophobic surface on the sliding behavior of water droplets.

SS-ThP28 Liquid Selection using Sliding Behavior of Droplets on Line-Patterned Hydrophobic Surfaces, *A. Nakajima,* Tokyo Institute of Technology, Japan*; S. Suzuki,* KAST (Kanagawa Academy of Science and Technology) and Tokyo Institute of Technology, Japan*; K. Tanaka,* Tokyo Institute of Technology, Japan*; M. Sakai, A. Hashimoto,* KAST, Japan*; Y. Kameshima,* KAST and Tokyo Institute of Technology, Japan*; N. Yoshida,* KAST and CCR, Tokyo University, Japan*; K. Okada,* Tokyo Institute of Technology, Japan

Technologies of hydrophobic coating have been important for various industrial items. The evaluation of a solid surface's hydrophobicity is divided into two branches: static hydrophobicity and dynamic hydrophobicity. For assessing solid surfaces' dynamic hydrophobicity, information related to the speed at which the droplet can be removed from the surface at a certain tilt angle is becoming important. Surface composition patterns using self-assembled monolayers (SAMs) were fabricated recently using photolithography. Wettability on well-defined micropatterned surfaces with different surface free energy has been specifically examined, although wetting behavior of droplets on homogeneous surfaces has mainly been studied. The relationship between heterogeneous patterned surface and dynamic hydrophobicity on patterned surfaces is not precisely reported. In the present paper, we

demonstrate liquid selection effect using sliding behavior of droplets on the line-patterned hydrophobic surfaces. A cleaned Si wafer was micro-patterned by fluoroalkylsilane (FAS) and octadecyltrimethoxysilane (ODS). When a Si wafer with the patterned lines was rotated to a certain angle in plane and inclined from horizontal position, droplets of water or ethanol solution slid down on the surface with some displacement to line direction with changing their sliding velocity. This behavior depends on not only surface energy and droplet mass but also a rotation angle and patterning structure. Detailed discussion on the relationship among these factors will be presented.

SS-ThP29 Optimization of Lithographic Parameters for Writing Thiolated Molecules via Nanografting and NPRW using an Open-Loop AFM System, *W. Serem, J.N. Ngunjiri, J.C. Garno,* Louisiana State University

The unique advantages and capabilities of nanografting and NanoPen Reader and Writer (NPRW) for writing arrays of nanopatterns (< 200 nm) of self-assembled monolayers (SAMs) using an open-loop AFM system will be presented. Both methods apply force to an AFM tip to write SAM nanopatterns in ambient environments. Nanografting is accomplished in a dilute solution of the molecules chosen for writing. The AFM tip is scanned at high force, displacing molecules of the matrix SAM under the tip. Fresh molecules from solution assemble onto the surface following the track of the scanning tip. For NPRW, the AFM tip is coated with SAM molecules for writing in air or water. During writing, the tip is scanned at a high force to write nanopatterns within a methyl-terminated matrix SAM resist. For both methods, the resolution of writing depends on the geometry of the AFM tip, easily achieving 10 nm dimensions with standard commercial cantilevers. Nanografting and NPRW are excellent for in situ studies and use the same tip for fabrication and imaging the designed nanostructures. Both methods offer flexibility and can be used to write n-alkanethiols with different terminal chemistries and chain lengths. When using an open-loop AFM scanner, the writing speed, direction and force must be optimized to achieve high-resolution writing. Vector movements which translate the tip in both the X and Y directions simultaneously are shown to produce problems with alignment and registry for nanopatterns. We will disclose the programming strategies for tip translation which lead to improvements in the uniformity, alignment and geometries of nanopatterns written using open-loop feedback control.

SS-ThP30 Mechanical Properties of Surfactant Aggregates at Liquid-Solid Interfaces: Molecular Dynamics Simulations, *P. Chiu,* University of Florida*; K. Shah,* Intel Corporation*; S.B. Sinnott,* University of Florida

There are a wide range of applications that use surfactants, including dispersion in such things as paints and detergents, controlled drug delivery systems, and chemical mechanical polishing (CMP) of silicon wafers. As a result, great strides have been made in using experimental methods to shed light on the behavior of surfactants in solution and at the solid-liquid interface. Those experimental studies, however, have produced little insight into understanding the behavior of surfactants at the molecular level, the mechanics of which are still to be explored. Consequently, new developments in molecular dynamics (MD) simulation have been directed towards this area of study. This research uses MD simulations to study the mechanical properties of surfactant aggregates, specifically the surfactant dodecyltrimethyl ammonium bromide (C$_{12}$TAB), at liquid-solid interfaces, such as at water-silica and water-graphite interfaces. Indentation simulations both normal to the substrate, at an angle, and laterally are considered. The aim is to understand the failure mechanisms of micelles, if any, during nanoindentation with different proximal probe tip indenters.

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