Surface Science
Room: Exhibit Hall B2 - Session SS-TuP

Surface Science Poster Session

SS-TuP1 In-situ Observation of Chemical State of a Si Electrode Surface during a Galvanostatic Oscillation in Fluoride Electrolytes Using Infrared Absorption Spectroscopy, ***Y. Kimura***, *J. Nemoto, M. Niwano*, Tohoku University, Japan

Electrochemical etching of silicon (Si) is an important technique for the fabrication of micro- and nano-structures on Si, and therefore, it has been extensively investigated theoretically and experimentally. It is well known that when an anodic potential below about 1 V is applied to a Si electrode, porous silicon (PS) forms in the vicinity of the surface. Interestingly, when a higher anodic potential, several volts or more, is applied to a Si electrode, an oscillation in the anodic potential or the anodic current density takes place. Previously, the oscillation has been interpreted as being due to alternative formation and removal of silicon oxide on the Si electrode surface. However, the chemistry of a Si electrode surface during galvanostatic oscillation has not been fully understood. In this study, we have investigated a galvanostatic oscillation phenomenon during anodization of a silicon (Si) crystal electrode in fluoride electrolytes using infrared absorption spectroscopy in multiple internal reflection geometry (MIR-IRAS). We confirm that the electrode surface is covered with a thin oxide layer during the course of galvanostatic oscillation. We observe a weak oscillation of the oxide thickness that synchronizes with the oscillation of an anodic potential. We also find that when the anodic potential falls to its minimum, hydrogen-substituted oxide (suboxide, $Si(O_3)$-H) forms on the electrode surface. We propose a model of galvanostatic oscillation in which it is assumed that an decrease in the anodic potential is due to the formation of pits in the oxide over layer and low-quality oxides containing $Si(O_3)$-H species are preferentially formed at the pit sites. We suggest that formation of an inhomogeneous oxide layer plays a crucial role for the galvanostatic oscillation phenomenon.

SS-TuP2 What Governs the Si(100) Low Temperature Phase ? - Study by STM and LEED, ***S. Yoshida***, *O. Takeuchi, K. Hata, H. Shigekawa*, University of Tsukuba, CREST, Japan

Through the recent intensive study on the low temperature phase of Si(100) by Scanning Tunneling Microscopy (STM) and Non-Contact Atomic Force Microscopy, symmetric dimmer, c(4x2)/p(2x2), and c(4x2) phases have been confirmed to exist below 30K, giving rise to the controversy on the ground state of Si(100). In addition to these structures, we recently succeeded in observing a single p(2x2) phase by STM at 10K for the first time, and have studied the conditions for the appearance of all these phases. For example, although c(4x2) phase easily appears in the case of p-type Si(100), particular sample conditions are necessary for the observation of the p(2x2) single phase; (1) n-type, (2) high dope, and (3) very low defect density. Furthermore, for the n-type Si(100) surface, we have succeeded in the direct observation of the phase transition between p(2x2) phase (lower temperature side) and c(4x2) phase (higher temperature side) by STM and LEED measurements. These obtained results suggest the great importance of the dopant and defect influences on the Si(100) surface phase transitions. Tip induced effect will also be discussed.

SS-TuP3 Stability Studies of Monolayers on Scribed Silicon to Water, Air, and X-ray, ***G. Jiang***, *T.L. Niederhauser, S.D. Davis, M.R. Linford*, Brigham Young University

The stability of alkyl monolayers on scribed silicon to air, water, and/or X-rays was investigated. Monolayers were prepared by scribing silicon surfaces in the presence of reactive liquids (1-pentene, 1-decene, 1-hexadecene, methyl iodide, 1-iodopetane, 1-iododecane, 1-butanol, 1-bromopentane, and 1,4-dibromobutane) with a computer-controlled diamond-tipped instrument. In all cases some initial oxidation of the underlying silicon surface was observed by X-ray photoelectron spectroscopy (XPS), which increased with time until the O1s/Si2p XPS ratio reached a stable level (after 100 - 200 hours). In the case of silicon scribed under the iodoalkanes, the iodine to silicon ratio by XPS decreased with time until it also reached a stable value. The C1s/Si2p XPS ratios for all surfaces remain essentially constant after all exposures to air and water, which indicates that monolayers of 1-alkenes and 1-haloalkanes on scribed silicon are quite stable. Kinetics measurements using water contact angles on scribed patches and water capacity measurements of hydrophobic corrals on silicon show trends similar to the XPS results. In general, hydrophobic corrals retained much of their capacity to hold water. Surface oxidation is shown to take place at the silicon surface. It is suggested that iodine is lost by hydrolysis of surface Si-I bonds. Finally, no change in the amount of C, O, or Br at the surfaces was observed by XPS after 3 - 4 hr of illumination with monochromatic Al Ka X-rays, indicating that XPS analyses can be performed on monolayers on scribed silicon without substantially damaging them.

SS-TuP4 Bevel Crater SIMS for Auger Analysis of Laterally Oxidized AlGaAs/GaAs Multilayers, ***S.A. Wight***, *G. Gillen, P. Chi, A. Fahey, A. Roshko, K. Bertness*, National Institute of Standards and Technology

Recently, in support of a project to engineer strain in compound photonic semiconductors, we employed a combination of Secondary Ion Mass Spectrometry (SIMS), Auger Electron Spectroscopy (AES), and Scanning Electron Microscopy (SEM) to characterize MBE grown, laterally wet-thermal oxidized, $Al_{.98}Ga_{.02}As$ layers in an attempt to determine compositional uniformity through the oxide layers. Typical samples for this study consist of alternating layers of $Al_xGa_{1-x}As$ (where x is between 0.90 and 1.0) and GaAs. Each AlGaAs layer is 80.0 nm thick and is separated from adjacent layers by 150 nm of GaAs. The surface is capped with 200 nm of GaAs. Each sample has a series of trenches (spaced 100 µm apart) etched through the multilayer to expose the buried AlGaAs layers. The lateral extent of oxidation was designed to be 25 µm from the trench edge. An external raster waveform was used in place of the standard digital raster to produce bevel craters on a commercial SIMS instrument. Beveled samples were analyzed using O2+ and Cs+ microbeam imaging in the SIMS and by AES/SEM in a commercial scanning Auger instrument. Bevels were cut in AlGaAs samples using Cs, O and Ga + primary ion beams at several different energies. Both Cs+ and Ga+ beveling produced very distorted bevels resulting from the large sputter rate differences between oxidized and unoxidized regions and a high degree of surface topography as determined by SEM imaging. Best results were obtained by using O2+ bombardment for bevel production. Currently, we are using Ar+ sputtering at a few keV impact in the Auger instrument to remove the primary beam oxygen before analysis.

SS-TuP5 Oxygen Reactivity of Clean and Au-induced High-Index Si Surfaces, *J.C. Moore,* ***J.L. Skrobiszewski***, *A.A. Baski*, Virginia Commonwealth University

We have studied the oxygen reactivity of the clean high-index Si(5 5 12) surface, as well as nearby Au-induced facet planes. The (5 5 12) surface is oriented approximately midway between the (001) and (111) planes and forms a single-domain, row-like reconstruction. When submonolayer coverages of Au are deposited and annealed on Si(5 5 12), the surface undergoes significant restructuring to form a variety of nearby facet planes. In this work, we use scanning tunneling microscopy to investigate the O_2 reactivity of these various surfaces for a range of temperatures (600 to 800 °C), pressures (10^{-7} to 10^{-6} Torr), and exposures (50 to 200 Langmuirs). At lower temperatures (<700 °C), O_2 exposure of the clean (5 5 12) surface results in disordered oxide growth, similar to that previously observed for the low-index Si surfaces. At higher temperatures (>700 °C), etching is observed via step retraction and subsequent pinning by small islands, presumably due to oxide growth. The density of these islands decreases at higher temperatures (800 °C), indicating that oxide etching dominates in this temperature regime. With regard to the Au:Si(5 5 12) system, for oxygen exposures of ~100 L and moderate temperatures (700 to 750 °C), oxide island formation is seen on the lower Au coverage (337) facets, but no etching or oxidation is observed on higher coverage facets such as (5 5 11). This behavior indicates enhanced stability of the higher coverage Au-induced surfaces, which is consistent with the passivating nature of this adsorbate.

SS-TuP6 The Origin of the Metallic States on Ge(100) Surface, ***C. Jeon***, Sungkyunkwan University, Korea, *C.C. Hwang, K.-J. Kim, T.-H. Kang, B. Kim,* PAL, POSTECH, Korea, *C.-Y. Park,* Sungkyunkwan University, Korea

Semiconductor surfaces exhibit a temperature-induced metallization upon raising temperature. Photoemission spectroscopy (PES) and low-energy electron diffraction (LEED) studies on Ge (100) surface, Kevan and Stoffel, observed a metallic state above 130K whose intensity increases as temperature rises.[1] At the same time, a c(4x2) LEED pattern was observed to convert to a 2x1. A similar increase in metallicity with temperature (up to about 900K) on the Si(100) was reported in a recent study.[2] In this work, angle resolved ultra-violet PES was utilized to investigate the metallization on the Ge(100) surface from room temperature up to 900K. The metallic state was observed at about 580 K around two symmetric points without any change in LEED pattern. Based on these results, we'll discuss the difference and similarity between the origin of the metallic surface states of the Ge and Si(100) surfaces.

[1] S. D. Kevan, N. G. Stoffel, Phys. Rev. Lett. 53, 702, 1984

[2] C. C. Hwang et al., Phys. Rev. B 64, R201304, 2001

SS-TuP7 Two-dimensional Electronic Excitations in a Metallic Monolayer on a Semiconductor Surface

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There exists a surface-state band at the Si(111)-($\sqrt{3}$x$\sqrt{3}$)-Ag surface created by depositing a monolayer of Ag on the Si(111) surface. An electron system in this band forms a realistic two-dimensional (2D) conduction-electron system. Recently, 2D plasmons (PLs) in this electron system have been clearly observed by high-resolution electron energy-loss spectroscopy in a broad wave-number range including PL decay due to electron-hole pair (EHP) excitations. In the present work, by means of the local-field-correction (LFC) theory, we evaluate the exchange-correlation (X-C) effects on the above electronic excitations. We compare three cases, namely, (i) random-phase approximation, (ii) Hartree-Fock approximation, and (iii) STLS approximation formulated by Singwi, Tosi, Land, and Sjölander. The X-C effects are neglected in (i), only the X effect is considered in (ii), and both the X and C effects are taken into account in (iii). We determine the electron density and the electron effective mass so that the calculated results in (iii) accord with the experimental ones. Our calculations give a good description of the experimental results of the energy dispersion and the energy-loss intensity of the 2DPL. When the X or both the X and C are switched on, with increase in wave number q, the dispersion curve begins to shift downward, and decays away due to EHP excitations at a smaller q value. Simultaneously, the integrated resonance intensity of the 2DPL in the energy dependence of the energy-loss function declines more quickly at smaller q values. This effect is more conspicuous in (iii) than in (ii). Our electron system has a large effective Bohr radius, and consequently a high effective density, because our electron system lies on a semi-infinite dielectric medium. However, owing to low dimensionality, the X-C effects appear remarkably in the 2DPL with increase in q.

SS-TuP8 Formation pf Platinum Silicides on Si as followed by AES and XRD

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Auger electron spectroscopy was used for depth profiling of platinum silicide thin layer formed as a result of annealing of 43 nm platinum layers deposited on Si (111). The factor analysis was utilized for interpretation of Auger spectra. The stoichiometry of silicide layers was determined by X-ray diffraction in both Bragg-Brentano and grazing incidence (at angles 0,5°, 1°, 1.5° and 2°) geometries in order to distinguish the depth distribution of intermediate platinum silicide phases (Pt_3Si, Pt_2Si, PtSi).

SS-TuP9 Experimental and Computational Studies of the Adsorption of Allyl Alcohol on the Si(100) Surface

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In order to determine which mechanism, oxygen-addition or cycloaddition, plays a dominant role in governing the adsorption of organic molecules on silicon surfaces, the adsorption of a bi-functional molecule, allyl alcohol, on the Si(100)-(2x1) surface was investigated experimentally using Auger electron spectroscopy (AES), thermal desorption spectroscopy (TDS), and low-energy electron diffraction. The AES studies show that the surface adsorption of allyl alcohol is similar to the adsorption of the mono-functional molecule n-propanol, and is different from the adsorption of propene, based on final coverage comparisons. TDS results show that both allyl alcohol and n-propanol have no desorbing parent molecular species, while propene desorbs molecularly from this surface. Both allyl alcohol and propanol display desorption products consistent with the loss of water during decomposition. Computational studies were also performed using density functional theory and cluster models of the surface, in order to compare with the results from the experimental studies. Both the computational and experimental studies indicate that the oxygen-addition mechanism is most likely the favored path over [2+2] cycloaddition-type reactions with the Si(100) surface.

SS-TuP10 Stochastic Motion of 7x7 Kinks at Monoatomic Step Edges

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Control of steps on the surface have been regarded as one of the promising technique for future electronic devices.[1] Synthesis of artificial step arrangement can be achieved by photolithographically patterned substrates followed by thermal treatment. Because an individual step movement is governed by the detail balance between attachment and detachment of surface adatoms at step edges, the study of adatom kinetics is a crucial issue for understanding and controlling of step configuration. Here we propose a method for measuring migrating adatoms and step movements below the 7x7-"1x1" transition temperature.. Microscopically, meandering steps consist of long straight segments with well defined orientations and short segments called kinks. On the Si(111) surface, these kinks are expected to be quantized by the 7x7 reconstruction and their widths and strides are limited within the 7x7 period. Even in thermal equilibrium, these kinks will stochastically fluctuate by attaching or detaching adatoms. So, the individual kink can be regarded as one dimensional "Brownian particle". In this study, we made an in situ measurement of the kink motion by the high-temp. STM and found the kink is really Brownian particle. Because the chemical potential around the kink is uniform in thermal equilibrium, there is no net mass transport between the surface adatoms and the kink site. The Brownian kink, therefore, will not diffuse but restore its position. The kink velocity follows gaussian distribution and its standard deviation is a measure of the diffusion constant of the kink, which is closely connected to the adatom diffusion constant. The temperature dependence of the standard deviation showed an activation type behavior with an energy of ~0.87 eV, compared with the adatom diffusion energy of 0.75±0.2 eV on the Si(111) 7x7 surface.[2]

[1] T.Ogino et al., Appl. Surf. Sci. 107 (1996) 1.

[2] Voigtlander et al., Phys. Rev. B51 (1995) 7583.

SS-TuP11 Atomic Structure of Bare Si Dimer on H/Si(100) Surface

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When H adsorbs on the Si(100) surface, H bonds preferentially to Si dangling bonds and can form monohydride, Si-H. The structural, electronic, and chemical properties of the Si(100) surface are considerably modified by H adsorption. Recently, partially H-desorbed Si(100)2x1-H surfaces by thermal annealing or photon irradiation have received much attention, for example, due to its increasing chemical reactivity to H_2.[1] The modified chemical property could be strongly related to the atomic structure of bare Si dimer. It has been reported from scanning tunneling microscopy experiments that untilted dimers, which are different from those on the clean 2x1, are responsible for the exotic phenomenon. Contrary to this assertion, our synchrotron radiation photoemission spectroscopy results obtained at PAL in Korea[2] show that bare Si dimers are tilted and similar to those on the clean Si(100)2x1 surface. In this presentation, we will provide Si 2p core level and valence band spectra from partially H-desorbed surfaces and discuss possible origins of the chemical reactivity.

[1] E. J. Buehler and J. J. Boland, Science 290, 506 (2000).

[2] C. C. Hwang et al., Phys. Rev. B 64, R201304 (2001).

SS-TuP12 Shape Transformation of Silicon Trenches during Hydrogen Annealing

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In trench gate MOSFETs, trench corner rounding, which is caused by surface self-diffusion during heat treatments, is significant for the gate oxide reliability. Though the evolution of a crystal shape through surface self-diffusion during heating in vacuum has been extensively investigated, it has not been sufficiently studied in specific ambient, which is applicable to semiconductor process. In this work, we have studied the shape transformations of silicon trenches through surface self-diffusion during annealing in hydrogen ambient. The trench stripes on Si(001) with a depth of 3µm were fabricated by RIE technique with HBr contained gas plasma, where the trench sidewall surface orientation was chosen to be (110) and (-110). Then the samples were annealed at 1000°C in hydrogen ambient at various hydrogen pressures. The cross-sectional profiles of the trenches were observed by SEM after cleaving the substrates along the trench stripes. The observed time evolution of trench shapes was well reproduced by numerical simulation based on Mullins' continuum theory.[1] Thus we confirmed that the evolution of the trench-shape was due to Si surface self-diffusion. From comparison between the time scales in the experiment and the simulation, the diffusion coefficient was estimated to be about 2x10^{6}nm^2/sec at 5.3kPa, which is smaller than that at vacuum ambient.[2] It was found that the rate of shape transformation decreased with increasing hydrogen pressure, showing strong pressure dependence of the diffusion coefficient. In the symposium, we are going to discuss the dependence of silicon surface on hydrogen pressure in detail. In addition, the behavior of atomic steps on the trench sidewall surfaces, which was observed by AFM, will be also discussed.

[1] W.W.Mullins, J.Appl.Phys.28,333(1957)

[2] Yang et al., Surf.Sci.356,101(1996).

SS-TuP13 Adsorption and Photodissociation of 4-Haloanilines on GaN(0001)-(1x1), ***V.M. Bermudez***, Naval Research Laboratory

Photochemical reactions of organic molecules on semiconductor surfaces are of interest as a means of synthesizing patterned structures with specific chemical functionalities. The adsorption of 4-chloro- and 4-iodoaniline on the GaN(0001)-(1x1) surface, and the effects of subsequent exposure to near-UV or vacuum-UV radiation, have been studied using primarily UV photoemission and electron energy loss spectroscopies, supported by ab initio quantum-chemical modeling. Both 4-haloanilines adsorb via the molecular NH_2 group, with the phenyl ring intact, as does aniline itself.[1] Like aniline, both are very reactive with the clean GaN(0001)-(1x1) surface, requiring only a small dose to achieve saturation coverage (ca. 0.29 molecules/surface site). 4-Iodoaniline is photochemically active as an adsorbate on GaN, as expected from its apparent behavior in non-polar solvents. UV radiation promotes dissociation of the molecular C-I bond, leading to the transfer of I to available sites on the GaN surface. The molecular C-I bond is intact prior to irradiation, as suggested by the changes in ELS and UPS data seen to result from UV exposure. The photochemical activity of 4-chloroaniline adsorbed on GaN is at present uncertain, but it appears to be relatively inert, again consistent with its behavior in non-polar solvents. Similar results were obtained for both n- and p-type GaN, suggesting that the photochemistry is not mediated by excited carriers from the GaN substrate.

[1] V.M. Bermudez, Surf. Sci. 499 (2002) 109, 124.

SS-TuP14 RHEED and STM Study of Initial-stage Structural Change of Si(100) Surface Induced by Exposure to Ethylene Gas and Annealing, ***T. Takami***, Visionarts Inc., Japan, *I. Kusunoki*, Tohoku University, Japan

The initial stage of the structural change in clean Si(100) - 2 X 1 surface induced by annealing at 913 K and exposure to ethylene gas has been studied by reflection high-energy electron diffraction (RHEED) and scanning tunneling microscopy (STM). Transmitted bulk Si and particle SiC spots appeared on the RHEED patterns of the ethylene-exposed Si(100) surface. The obtained STM images were in accordance with the respective RHEED patterns. At the flat area of the exposed surface where the RHEED pattern showed twice the periodicity of surface spots and transmitted bulk Si spots, the STM image showed 2 X n (n=6,7,8,9,10,11,12) reconstruction. The obtained 2 X n STM image depended on the bias voltage.

SS-TuP15 Structure of Stable Si(6 9 17) Facet on Si(5 5 12), *Y.Z. Zhu, S.H. Cho, W.X. Quan,* ***J.M. Seo***, Chonbuk National University, Korea

Up to now, it has been known that the stable facet parallel to the atomic row of Si(5 5 12) is Si(113). In the recent structural studies on Si(5 5 12) using STM, it has been found that there exists another stable facet, Si(6 9 17), whose azimuthal angle is 97 degree-off from the atomic row and polar angle is 6.2 degree-off from Si(5 5 12). As this (6 9 17) facet appears at differently inclined surfaces, it is not simply due to miscutting. Although Si(6 9 17) facet is nearly vertical to the atomic row, it consist of 1.92 nm wide (337) terraces and single (011) steps, of 0.195 nm height, connecting such narrow (337) terraces. The unit cell of (6 9 17) contains a pair of tetramers and π-7 chain which is quite similar to those of (337) subsections composing of Si(5 5 12). As the (6 9 17) facet is always accompanied by defects like grain boundaries, it can adapt smoothly-bending facets as well as straight facets. It can be concluded that it is essential to form such flexible (6 9 17) facets in combination with straight (113) facets in order to relieve the local strain with various directions.

SS-TuP16 Interfactant-mediated Growth of Ultrathin Bismuth Films on Si(111), ***J.T. Sadowski***, *T. Nagao, Y. Fujikawa, S. Kuwano, T. Sakurai*, Tohoku University, Japan

Semimetal bismuth (Bi) has quite distinctive electronic properties due to its covalent-like bonds, highly anisotropic Fermi surface and low carrier concentrations. The small carrier effective masses and the very long mean free path result in large MR effects observed in bulk single crystals of Bi. However, fabrication of high quality bismuth films with nanometer thickness, required for the technological applications, still appears to be difficult. Recently, we have found that ultrathin Bi layers deposited at room temperature on the Si(111)-7x7 surface exhibit 2D growth after forming initial rough transition layer, and self-organizes into a single crystal ultrathin film nearly perfectly aligned to the Si substrate. In this paper we report the scanning tunneling microscopy studies of the role of the interfactants of Au-induced surface superstructures in the growth of flat, very well ordered, ultrathin Bi films on Si(111) surface. The morphology of the Bi ultrathin film was found to be modified by the presence of interfactant surface superstructures since the growth kinetics is modified by the change in the diffusion length, nucleation density, and the interface free energy due to the modification in the atomic as well as domain-wall configuration. In the systematic study, the morphology and detailed atomic structure of the Bi layer grown on the various Au-induced surface superstructures such as 5x2, α-root3xroot3, and β-root3xroot3-Au will be discussed and compared with the results of the direct Bi growth on the Si(111)-7x7 surface, as well as with growth on otherwise modified interfaces such as α-root3xroot3 and β-root3xroot3-Bi superstructure.

SS-TuP17 Measurement of the Dependence of Bulk Defects on the Reactivity of the TiO_2(110) Surface, ***S.N. Thornburg***, *J.M. Burst, C.A. Ventrice, Jr.*, University of New Orleans, *U. Diebold*, Tulane University

Missing-atom point defects at metal oxide surfaces often enhance the reactivity of these surfaces towards the adsorption of simple molecules. A previous study of the adsorption of S on the TiO_2(110) surface found that the reactivity of this surface at temperatures >120°C was enhanced by the presence of bulk missing-oxygen defects.[1] This was determined by measuring the S 2p uptake with x-ray photoelectron spectroscopy as a function of reduction time. However, this was performed on a new TiO_2 crystal, so the influence of bulk impurities on the uptake of S was difficult to determine. A technique for reoxidizing dark blue, bulk-reduced, TiO_2 crystals has been developed that allows us to return these crystals to a defect free clear state. The degree of bulk reduction is monitored using optical spectroscopy and temperature dependent resistivity measurements with a four point probe. Optical spectroscopy measurements for both the dark blue and clear crystals show the same absorption edge at 3.0 eV, which corresponds to the bulk band gap of TiO_2. However, the dark blue crystals also show a strong absorption below 2.6 eV. Photoemission measurements of the S uptake, O reduction, and S peak shift at 250°C and room temperature have been performed on both dark blue and clear crystals. At room temperature, the S saturates at approximately one monolayer coverage for both clear and bulk reduced crystals. At 250°C, the adsorbed S replaces the first few layers of oxygen atoms. The rate of S adsorption is found to depend on bulk reduction, but at a reduced rate as compared to the measurements on a new crystal. This indicates that bulk contaminants in new crystals are also influencing the S adsorption rate.

[1] E. L. D. Hebenstreit et al., Surf. Sci. 486, L467 (2001).

SS-TuP18 FT-IR Investigation of Water Adsorbed on a-Al_2O_3 and MgO at 296 K, ***H.A. Al-Abadleh***, *V.H. Grassian*, University of Iowa

Fundamental studies of water adsorption on oxide surfaces are of great interest as the water/oxide interface plays an important role in many if not all environmental chemical processes. In these studies, transmission FT-IR spectroscopy is used to investigate the adsorption of water on α-Al_2O_3 (0001) and MgO (001) surfaces. The FT-IR spectra of the (0001) surface of α-Al_2O_3 and (001) surface of MgO single crystals are measured in the presence of 0.2 to 20 Torr H_2O vapor pressure corresponding to 1 to 95% relative humidity (RH) at 296 K. The adsorption of D_2O on the single crystal surfaces of on α-Al_2O_3 and MgO is also carried out in order to obtain additional insight into the behavior of adsorbed water. Water adsorption on nitrate-coated oxide single crystal surfaces are also carried out to investigate the effect of adsorbed ions on the hydrogen bonding network of water on oxide surfaces. The FT-IR spectra are analyzed so as to quantify the amount of water adsorbed on these oxide surfaces under ambient conditions and to determine more about the nature of the adsorbed water layer.

SS-TuP19 Ozone Reactivity on Processed Mineral Oxide Particles, ***C.R. Usher***, *A.E. Michel, V.H. Grassian*, University of Iowa

Wind-blown mineral dust from arid and semi-arid regions can be transported over large distances in the troposphere. The reaction of dust with trace atmospheric gases can result in the presence of organic and inorganic surface coatings. These coatings will alter the surface chemistry of mineral dust with other tropospheric species. In this study the reactivity of ozone on mineral oxides (e.g. α-Al_2O_3 and SiO_2) that had been previously reacted with nitric acid, sulfur dioxide and organics has been measured. Comparison of the kinetics of ozone decomposition on previously reacted particles to particles that have not been reacted shows that the reactivity can either increase or decrease depending on the nature of the coating. Insight into these reactions is obtained by FT-IR spectroscopy of the coated oxide particle surface before and after exposure to ozone.

SS-TuP20 Adsorption of Vesicles to Titanium Dioxide: Effect of Vesicle Size and Lipid Composition, ***I. Reviakine***, University of Houston, *F. Rossetti*, ETH Zurich, Switzerland, *A.N. Morozov*, University of Leiden, The Netherlands

Adsorption of intact vesicles has been shown to be the first step in the formation of supported phospholipid bilayers.[1,2] While the process of supported bilayer formation has been investigated in significant detail, that of vesicle adsorption has received much less attention. Experimental[2] and theoretical[3] studies indicate that the extent of deformation of the adsorbed vesicles determines whether they will form a Supported Vesicular Layer

(SVL) or a Supported Phospholipid Bilayer (SPB). Bending rigidity of the bilayer and vesicle size control the extent of vesicle deformation on a given surface. This study has therefore focused on investigating the effect of these two parameters on the properties of an SVL formed on the surface of TiO_2, where vesicles used in this study adsorbed but did not form SPBs. A combination of spectroscopic (Quartz Crystal Microbalance with Dissipation measurement, QCM-D) and microscopic (Atomic Force Microscopy) techniques was used to follow the adsorption process. Voight model was used to interpret QCM-D response [4] and the results were compared with the Random Sequential Adsorption model.

[1] Keller and Kasemo, Biophys J. 1998, 75, 1397.

[2] Reviakine and Brisson, Langmuir 2000, 16, 1806.

[3] Seifert U., Adv. Phys. 1997, 46, 13.

[4] Voinova et al., Physica Scripta 1999, 59, 391.

SS-TuP21 Perchlorate Reduction on Irradiated Titania Studied by LITD-FTMS, XPS, and IC

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Inorganic contaminants in water supplies have been a concern for decades, due to possible deadly health effects. Perchlorates, in particular, have posed a major concern as of late due to their irreversible and damaging effects on the human thyroid, long residence time in water sheds, and resistance to existing catalysts used in water treatment. However, preliminary studies have shown that oxidized surfaces of titanium exposed to ultraviolet radiation reduce perchlorates in aqueous solutions effectively. The reaction mechanism of this reduction has been studied using laser induced thermal desorption- Fourier transform mass spectroscopy, x-ray photoelectron spectroscopy, and ion chromatography. A new chamber that allows for the rapid introduction of samples reacted in aqueous solution into UHV for analysis was used for the LITD-FTMS studies. Reacting the perchlorate solutions with the titania catalyst at atmospheric pressures allows for a more inclusive reaction mechanism due to the incorporation of atmospheric water, carbon dioxide, nitrogen, and oxygen. Surface species are seen both in the LITD-FTMS experiments as well as in the XPS studies, while species that do not adhere to the catalyst surface can be seen in the IC solution studies. Studies show that LITD-FTMS of perchlorate and its oxy-chloride derivatives do not have distinct enough fragmentation patterns to be studied by LITD-FTMS. XPS and IC studies have indicated that titania, in a thin film form, is a slow, but effective catalyst for the reduction of perchlorate. Higher surface area titania, like nano-particulate titania, may prove faster in the reduction of perchlorate to chloride.

SS-TuP22 Electron- and Photon-stimulated Desorption of Alkali Atoms from a Lunar Sample and a Model Mineral Surface[1]

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To investigate mechanisms for the origin of alkali atoms in the atmosphere of the Moon, we are studying the electron- and photon-stimulated desorption (ESD and PSD) of K atoms from a model mineral surface (SiO_2 film), and ESD and PSD of Na atoms from a piece of lunar basalt. X-ray photoelectron spectroscopy demonstrates the existence of traces of Na in the lunar sample. To permit increased signal for detailed measurements of desorption parameters (appearance thresholds, yields, energy distributions), a fractional monolayer of Na is predeposited onto the lunar sample surface. An alkali atom detector based on surface ionization and a time-of-flight technique are used for ESD/PSD measurements, together with a pulsed electron gun, and a mechanically-chopped and filtered mercury arc light source. We find that bombardment of the alkali covered surfaces by UV photons or by electrons with energy $E>4$ eV causes desorption of "hot" alkali atoms. The results are consistent with the model developed to explain our previous measurements of sodium desorption from a silica surface[2] and desorption of K atoms from water ice:[3] charge transfer from the substrate to the ionic adsorbate causes formation of a neutral alkali atom in a repulsive configuration, from which desorption occurs. The data support the suggestion that PSD by UV solar photons is a dominant source process for alkalis in the tenuous lunar atmosphere.

[1] supported in part by NASA

[2] B. V. Yakshinskiy and T. E. Madey, Surf. Sci. 451(2000) 160

[3] B. V. Yakshinskiy and T. E. Madey, J. Geophys. Res. 106, E12(2001) 33303.

SS-TuP23 The Periodically-Stepped NiO(100) Surface and the Adsorption of Bromobenzene

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Periodically-stepped NiO(100) was prepared and characterized the surface with Low Energy Electron Diffraction, (LEED), Auger Electron Spectroscopy, (AES), and X-Ray Photoelectron Spectroscopy, (XPS) to model surface defects relevant to heterogeneous chemical processes. All solid materials, including single crystal surfaces, possess irregular steps and other defects. These step defects, model undercoordinated sites that initialize catalytic and other chemical behavior. The NiO(100) single crystal was cut, polished, and oriented with regular repeating steps of seven-atom terrace width. LEED diffraction patterns are characteristic of an ordered step array with appropriate terrace and step height dimensions. Preliminary results show bromobenzene adsorbs onto stepped NiO(100) surface at 133K. The XP spectra of 515L of the adsorbate give two distinct carbon peaks separated by 4.5eV and the Ni 2p region peaks exhibit minimal structure loss. Thermal Desorption Spectrometry, (TDS), shows the majority of physisorbed bromobenzene desorbing molecularly by 190K and smaller adsorbed ring fragments around 280K. Studying a surface of characterizable defects of known density helps further the understanding of the first initial steps occurring in a chemical reaction and in the fabrication of nanostructure materials.

SS-TuP24 MCS and KMCS of Adsorption Probabilities: The Auto-catalytic Adsorption Phenomenon

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An increase in the coverage, Θ, dependent adsorption probability, $S(\Theta)$, with increasing coverage, i.e. an auto-catalytic adsorption phenomenon which is called for now adsorbate-assisted adsorption, has frequently been observed for the adsorption of prototype molecules on quite different surfaces. However, the effect has rarely been addressed theoretically. We present a steady-state Monte Carlo (MCS) version of the modified Kisliuk model which is consistent with the energy, E_i, dependence of the phenomenon and includes the effect of surface defects on $S(\Theta)$. Although steady-state MCS lead already to a better understanding of the microscopic scenario than analytical models, the influence of the adsorption temperature, T_s, on $S(\Theta)$ can in principle not be studied. We therefore present additionally first results of a time-dependent (kinetic) Monte Carlo simulation scheme (KMCS) which can account in principle also for the T_s dependence of $S(\Theta)$. The MCS schemes are tested for different adsorption scenarios (such as the Kisliuk and Langmuirian dynamics) and especially for the auto-catalytic adsorption. Furthermore, a comparison of the simulations with experimental data for CO adsorption on both polar (O- or Zn-terminated) ZnO surfaces [Th. Becker, et al., JCP 113 (2000) 6334] will be shown. Although the scheme can be applied to other adsorption systems, the polar surfaces of ZnO are a perfect test system for the algorithm which is mainly based on the differences in the mass-mismatch of the adsorbate (CO) and the surface atoms (O or Zn).

SS-TuP25 Synchrotron Radiation X-ray Photoelectron Spectroscopy Study of Thermal Effects on Nb Surface Oxides[1]

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We report a recent x-ray photoelectron spectroscopy study of thermal effects on the oxides grown in air on crystalline Nb surfaces. Both angle-resolved and glancing-incidence x-ray photoelectron spectroscopy techniques were used in this study. The samples were annealed at 430 °K and 540 ° K for various lengths of time. We will demonstrate that the reduction of the insulating Nb_2O_5 layer to lower oxidation states is primarily an interface-mediated reaction. Annealing at 430 °K produces a semiconducting, layered oxide with a composition of NbO_x that changes from $x = 2.5$, 2.0, 1.5, 1.0, to 0.5 across the oxide. Annealing at 540 °K produces a metallic oxide layer with a composition that is mainly $NbO_{0.5}$, but changes continuously and rapidly near the oxide surface. A photoelectron diffraction effect is observed on the 540-K annealed surface, which possibly indicates the formation of an ordered, but faceted, oxide layer. Oxygen readily diffuses into the Nb substrate by annealing at 540 °K. However, oxygen diffusion proceeds predominantly within the oxide in the case of annealing at 430 °K.

[1] This work is supported by the U.S. Department of Energy, Office of Basic Energy Sciences, under Contract No. W-31-109-ENG-38.

SS-TuP26 Active Sites of Photocatalyst for Water Decomposition of RuO_2-dispersed p-block Metal Oxides Involving In^{3+}, Ga^{3+}, Sn^{4+} and Ge^{4+} with d^{10} Configuration

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The development of solid photocatalysts to produce hydrogen from water has been among important issues. The photocatalysts discovered so far have been the transition metal oxides with d^0 configuration. In aiming at finding a new photocatalyst group, we have focused on the p-block metal oxides with d^{10} configuration.[1] In the present study, MIn_2O_4, MGa_2O_4, M_2SnO_4 (M = Mg, Ca, Sr, Ba), and Zn_2GeO_4 were employed, and the effects of M on the photocatalytic activities were examined. For photocatalytic decomposition of water, RuO_2 were loaded on p-block metal oxides by an impregnation method. MIn_2O_4 (M= Ca,Sr) have pentagonal-prism-like tunnel structures with two distorted InO_6 octahedra each. For M = Ca and Sr, hydrogen and oxygen were stably evolved in repeated run under Xe lamp light illumination, whereas little activity was observed for M= Ba. The activity of M_2SnO_4 (M= Ca, Sr, Ba) was remarkably large for M= Ca and M= Sr, but negligible for M= Ba. The SnO_6 octahedra of M= Ca and M=Sr were distorted, whereas those of M= Ba were normal, indicating the contribution of the deformed octahedra to photocatalysis. In MGa_2O_4 (M=Mg, Sr, Ba), the activity was observed for M=Sr and M=Ba, but not for M=Mg, for which there existed correlation between photocatalytic activity and distorted metal-oxygen units. The present study clearly demonstrates that the distorted metal-oxygen units play an important role in the photocatalysis, which is possibly related to the efficiency of photoexcited charge formation. The p-block metal oxides with d^{10} configuration is concluded to form a new photocatalyst group for water decomposition.

[1] J. Sato, N. Saito, H. Nishiyama, and Y. Inoue, J. Phys. Chem., 105, 6061 (2001).

SS-TuP27 How Thick is my Oxide?, ***D.D. Allred***, *S. Lunt*, Brigham Young University

"How thick is the oxide on this sample?" is a question is frequently heard in the lab. After a thin film is removed from the deposition system, exposing it to air on its top surface, it can begin to tarnish. I will review our work in determining the kinetic constants required to answer the question posed, to estimate the thickness of the tarnish layer as a function of time and temperature for several thin film metal exposed to laboratory air at temperatures near ambient for times up to several thousand hours. The thickness and composition of the tarnish layer is important, particularly when it is to be used in an application, such as for gate oxides for ULSI devices, for which understanding and controlling the thickness of ultrathin oxide layers is important. Our EUV optics deposition group also labors in an area where the thickness of ultrathin post deposition films is extremely important. We have looked for a single, or set of, papers which would help us answer this question for materials of interest for the extreme ultraviolet optics (EUV) community. Since the data could not be found in the literature, we resolved to measure and report them. We have studied the tarnishing of a variety of very thin metal films (typically 3-30 nm) including: Al, several of the 3-d metals (e.g. Sc, V, Cr, Fe), one each of the 4d (Ru) and 5d (W) metals and U, and UO2 in laboratory air at temperatures near ambient for several months. We have used spectroscopic ellipsometry, AFM, XPS, and low-angle x-ray diffraction in this work. The tarnish formed is not the familiar bulk oxide for Al and some other cases. We will focus particularly our progress in understanding the stages of oxidation in the 2-6 nm range, thicker than is usual for surface studies but thinner than most corrosion work. We will also show that EUV reflectance is itself a sensitive tool for measuring the thickness of ultrathin oxide films such as SiO2 and UO2.

SS-TuP28 New Insights into Self-Assembled Monolayer Structure and Dynamics, ***S.B. Darling****, *S.J. Sibener*, The James Franck Institute at The University of Chicago

We have studied the effect of adsorption of a low-density alkanethiol monolayer on the state of the Au(111) reconstruction. It is commonly believed that the substrate deconstructs following formation of a thiolate self-assembled monolayer, but our results suggest this is not always the case. Helium diffraction from 1-decanethiol (C10) and 1-octanethiol striped phase monolayers is exploited to establish the surface nearest-neighbor spacing and to illustrate a unit cell corresponding to the long dimension of the (23x√3) reconstruction. Complementary scanning tunneling microscopy data are also presented that show persistence of the reconstruction during growth of a decanethiol striped phase monolayer and no evidence for vacancy islands typically associated with deconstruction. Our model involving a still-reconstructed substrate is consistent with all of the available data. Furthermore, the low-energy surface vibrational structure of the (11.5x√3) striped phase of C10 has also been studied. Energy-transfer spectra for this system exhibit a dispersionless inelastic feature at 8 meV. We assign this to the frustrated translation of the entire molecule vibrating with polarization perpendicular to the surface. These results further the understanding of the forces that govern nanoscale self organization.

SS-TuP29 Oxygen Induced Reconstructions and Epitaxial Growth of MoO2(100) on Mo(112) : A Combined STM and LEED Study, ***B.K. Min****, *A.K. Santra*, *D.W. Goodman*, Texas A&M University

Oxygen chemisorption followed by oxidation of Mo(112) has been investigated in detail by the use of low energy electron diffraction (LEED) and scanning tunneling microscopy (STM). Oxygen-induced p(2x3)-O, p(1x2)-O and p(1x3)-O missing row reconstructed surface structures are observed using STM and are shown to be dependent on the substrate temperature during oxygen adsorption. Atomically resolved STM data explain the undulated LEED pattern observed for the p(1x3)-O surface. This is the first direct demonstration of the epitaxial growth of MoO2(100) on a Mo(112) surface where the p(1x3)-O reconstructed surface is shown to be the precursor. A new oxide surface has been observed that corresponds to the c(2x2) reconstruction of MoO2(100) and correlates with the onset of oxide formation. Oxidation at 1250K produces a mixture of MoO2 and MoO3 (3:1) as determined by XPS and AES.

***** Morton S. Traum Award Finalist

Authors Index

Bold page numbers indicate the presenter