SYMPOSIUM P

In-Situ Studies of Gas/Solid Surface Reaction Dynamics

March 29 - 31, 2005

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* Invited paper
SESSION P1: Semiconductor Surface Reactions and Oxidation

Chairs: Stacey Bent and Frances Ross
Tuesday Morning, March 29, 2005
Room 3006 (Moscone West)

8:30 AM *P1.1
In-situ Observation of Oxidation Reactions at Si(001) Surfaces using Synchrotron Radiation Photoelectron Spectroscopy. Yasuhiro Hasegawa, Kousuke Shirai and Kenji Terakura; Synchrotron Radiation Research Center, Japan Atomic Energy Research Institute, Kouto, Japan.

For the recent fabrication of gate-oxide films with a few atomic layers in Si based electronic devices, it is essential to understand the chemical reactions between O2 and Si surfaces to control not only film thickness but also those chemical compositions. In order to succeed in in-situ observation of such a high-speed reaction, monitoring the time evolution of adsorption states during reactions, we employ photoelectron spectroscopy combining with synchrotron radiation (SR-PES) to identify elements, chemical bonds, and electronic states. SR has many advantages such as high brilliance, high energy resolutions with variable photon energies etc. In this talk, I would like to show a usefulness of SR-PES for in-situ real-time observation of surface chemical reaction. As examples, the studies of thermal oxidation at Si(001) surfaces induced by translational kinetic energy (Ek) of O2 at room temperature will be presented. All experiments are performed at the end-station specially constructed for surface chemical reaction analysis at the soft x-ray beamline, BL23SU, in the SPring-8. Ek of O2 is controlled by a supersonic molecular beam (SSMB) technique. Ek of O2 can be controlled up to about 2.3eV by exploiting the high temperature nozzle (Max: 1400K). Real-time SR-PES monitoring is performed under an O2 gas atmosphere up to 10^-4 Torr, allowing us to examine the reaction mechanisms on O2 chemisorption processes on Si(OOl) surfaces. We observed the time evolution of Si oxidation states (Si^+; n=1,2,3,4) at Si(001) surfaces during SSMB (2.2eV) irradiation at room temperature. We found out the following results; (i) Si atoms at the top layer start to form Si^+; thus Si2O is unfomed at the initial oxidation stages. (ii) Si^+ and Si^2+ densities in a two-dimensional surface unit mesh are unchanged even with the progress of oxidation. (iii) Si^2+ changed to Si^4+. The oxidized films with lower than 0.6nm can be formed even at room temperature. From the results of the in-situ observation of Si oxidation states depending on the Ek of O2, the dynamical aspects of O2 chemisorption processes on Si(001) surfaces will be discussed.

9:00 AM *P1.2
Real-time Monitoring of Chemical Composition, Surface Structure and Morphology, Surface Electronic State and Work Function during Thermal Oxidation on Si(001) Surfaces. Syuichi Ogawa and Yuji Takakawa; Tohoku University, Sendai, Miyagi, Japan.

Reflection high energy electron diffraction combined with Auger electron diffraction (RHEED-AES) and ultraviolet photoelectron spectroscopy (UPS) were used to investigate the surface reaction dynamics of the thermal oxidation of Si(001) surface. In the RHEED-AES measurement, O KLL Auger electrons excited by a 10-keV primary electron beam for RHEED observation are detected during oxidation, making it possible to monitor in real time the amount of adsorbed oxygen together with the surface structure and morphology. UPS measurements using a He resonance line (21.22 eV) can be also performed under an O2 gas atmosphere up to 10^-4 Torr, allowing us to examine the amount of adsorbed oxygen, unoxidized surface states, and work function simultaneously by monitoring in real time the O 2p intensity, surface state intensity due to dimer dangling bonds and low-energy cutoff of secondary electrons, respectively. For the surface oxidation scheme of two-dimensional oxide island growth at high temperatures above 900°C, which was clearly identified from the time evolution of O-KLL Auger electron intensity, the RHEED half-order spot intensity showed a periodic oscillatory behavior, proving that layer-by-layer etching progressed on the surface. The measurement of oxide coverage and etching rate during oxidation is achieved by means of RHEED-AES. Furthermore, the RHEED spot intensity of bulk diffraction appeared upon etching of more than two Si layers and increased with oxide coverage, indicating the development of protrusions at the oxide/Si(001) interface. On the other hand, the almost linear correlation between the changes of work function and O 2p intensity implies that the oxide with a similar chemical composition grows two-dimensionally in coverage. In the case of Langmuir-type adsorption occurring at temperatures below 600°C, the RHEED intensity ratio between half-orders (1x1/2x1) and (0 1/2), which is proportional to the 1x2/1x2 domain ratio, changed with oxide coverage, complicatedly depending on temperature and 2x1/1x2 domain ratio of the clean surface before oxidation. The correlation of the 2x1/1x2 domain ratio with the oxide coverage can be quantitatively interpreted in terms of epitaxial growth of emitted Si atoms resulting from the elastic strain due to the volume expansion of oxidation. At the completion of first oxide layer growth, the interface morphology was rather flat without apparent bulk diffusion. Under this oxidation condition, the change of work function showed a nonlinear correlation to the O 2p intensity, meaning that the chemical composition of oxide changes with increasing reaction temperature. Consequently it is concluded that the combined information on the chemical composition, surface structure and morphology, and surface electronic state obtained by the real-time monitoring methods is very useful to investigate the thermal oxidation dynamics on Si surfaces.

9:30 AM *P1.3
A Comprehensive Study of Adsorption, Dissociation and Diffusion Processes Occurring on the PH3 Dosed Si(001) Surface. Neil Jonathan Cursen1,2, Steven R. Schofield3, Oliver Warszchlow1,4, Nigel A. Marks1,4, Hugh F. Wilson1,4, Marian W. Rady2, Phil V. Smith1,4, David R. McKenzie1,4, Thilo G. Reuschi1,4, and Michelle Y. Simmons1; 1Centre for Quantum Computing Technology, University of New South Wales, Sydney, New South Wales, Australia; 2School of Physics, University of Sydney, New South Wales, Sydney, New South Wales, Australia; 3School of Mathematical and Physical Sciences, University of Newcastle, Callaghan, New South Wales, Australia; 4School of Physics, University of Sydney, Sydney, New South Wales, Australia.

We use scanning tunnelling microscopy (STM), supported by first principles density functional theory (DFT) calculations, to characterise the species formed on the Si(001) surface after PH3 dosing and to follow the evolution of the adsorption system as a function of time and temperature. After dosing with PH3, the dissociation of O2 chemisorption, the following results are obtained: (i) Si1+ is observed without any oxidation states which means that SiO2 is uniformed at the initial oxidation. (ii) Oxidation states is consecutively change (Si1+, Si^2+, Si^3+, Si^4+) according to the thermal activation for surface migration and enhancement of SiO2 formation. Comparing the kinetics of O2 adsorption and dissociation time evolution of Si oxidation states, we will discuss the reaction mechanism and adsorption process on Si(001) surfaces. We observed the time evolution of Si oxidation states (Si^1+, n=1,2,3,4) in Si(001) surfaces during SSMB (2.2eV) irradiation at room temperature. We found out the following results; (i) Si atoms at the top layer start to form Si^1+; thus Si2O is unfomed at the initial oxidation stages. (ii) Si^1+ and Si^2+ densities in a two-dimensional surface unit mesh are unchanged even with the progress of oxidation. (iii) Si^2+ changed to Si^4+. The oxidized films with lower than 0.6nm can be formed even at room temperature. From the results of the in-situ observation of Si oxidation states depending on the Ek of O2, the dynamical aspects of O2 chemisorption processes on Si(001) surfaces will be discussed.

10:15 AM P1.4
Angular Distributions of Hydrogen Molecules Produced in the Abstraction Reaction of Incident Hydrogen Atoms on Hydrogenated Si(100), Si(111) and a-Si. Regis Bisson, Laurent Philippe and Marc Chatelet; LPICM - Ecole Polytechnique, Palaiseau, France.

In order to get a better understanding of the dynamics of atomic hydrogen interacting with hydrogenated silicon, we have carried out a hydrogen-surface scattering experiment. We have measured, by mass spectrometry, angular distributions of hydrogen molecules coming out from hydrogenated silicon surfaces, which have been exposed, to a hydrogen atomic chopped beam under fixed incidence angle. First of all, on Si(100) at 520K we get an exceptionally wide angular distribution of H2 molecules with a peak at 0° with n=1; this is typical of a non-activated mechanism assisted by a precursor. We interpret this new result by a non-activated reaction involving a transition state similar to the inter-dimer 4H pathway which has been recently proposed by several authors in H2/Si(100)-2x1 system under high coverage. The suggested mechanisms on monohydride passivated Si(100)-2x1 are collision induced desorption, since this process is efficient on Si(100), and localised hot atom abstraction, involving two neighbors inside a dimer column. Then, we have measured angular distribution of H2
(D2, HD) molecules created by impinging H (D, H+D) molecules on Ge and Si substrates at 600K, 450K and 300K, to evaluate the surface reconstruction effect on adsorption pathwork. Finally, similar experiments on Si(111) and an angular distribution of HD molecules produced by atomic deuterium impinging on hydrogenated amorphous silicon are presented and mechanisms are discussed in light of the structure of the surface.

10:30 AM *Pl1.5

Time-Dependent Behavior in the Adsorption of Model Organic Compounds on Ge(100)-2x1. Michael A. Filler, Albert Keung and Stacey Bent; Chemical Engineering Dept, Stanford University, Stanford, California.

Organic functionalization of semiconductor surfaces has potential application in a number of technological areas, including semiconductor processing, biomaterials, molecular electronics, and chemical sensors. The key step for vacuum-based functionalization is the adsorption of organic molecules onto the solid surface. In order to identify reaction pathways and elucidate mechanistic themes for these gas phase adsorption processes, we have investigated a series of simple organic molecules at the Ge(100)-2x1 surface. In situ vibrational spectra of adsorbed species were obtained via multiple internal reflection Fourier transform infrared (MIR-FTIR) spectroscopy as a function of temperature, coverage, and time. Recently, we have examined the role of both carbonyl and amine functionalities in the adsorption process by studying aldehyde and amides. All the tertiary amides studied were shown to react via a dative-bonded structure, similar to a coordinate covalent bond, where the carbonyl oxygen donates electron density to an electrophilic germanium atom from oxygen. This adsorption product desorbs on the timescale of minutes, remaining on the surface long enough to be observed by MIR-FTIR. The temporal behavior varied for different amides, suggesting the importance of coverage-dependent binding energies. Formicdehyde, the simplest aldehyde, shows remarkably rich chemistry on the Ge(100)-2x1 surface. At room temperature, formicdehyde initially adsorbs in two different dative-bonded precursor states. Subsequent reaction between these two adsorbed species over a timescale of minutes at room temperature appears to lead to a surface-bound methoxy and an aldehyde functional group. This conversion, which reduces one oxygen to two oxygen atoms, is analogous to the Cannizzaro reaction in solution phase organic chemistry. The time-dependent behavior will be discussed in the context of general adsorption mechanisms at the germanium surface.

11:00 AM Pl1.6

Arrangement of Si Islands after Formation of Si(001)-c(4x4) Structure Using Monomethylysilane. Masayuki Harashima, Kanji Yosi1, Masasuke Takata and Tadashi Akihune; Nagoya University of Technology, Nagakute, Nigiuta, Japan.

Recently, fabrications of quantum dots made from IV column semiconductors such as SiGe and Ge on Si substrates have attracted much attention, and the formation of the dots, control of density, size and their arrangements are essential. As regards the density of dots, formation of Ge dots with a density of 1011 cm-2 has been achieved using pre-growth of sub-monolayer carbon [1]. However, formation of regularly structured quantum dots, using this technique, has never been reported so far. Authors have found that Si(001)-c(4x4) reconstructed surface, which has step-bunching and little defect, appears after supply of monomethylysilane (MMS) on Si (2x1) surface and disappeared as SiC islands. AFM measurements have been undertaken to follow the evolution of the SiC islands at various stages of growth. AFM measurements showed that Si dots were arranged along <010> direction. One of this mechanism is speculated that the c(4x4) surface behaved as a template for SiC nucleation. In this study, the variation in the surface structure during the formation of c(4x4) structure and SiC nucleation was measured using scanning tunnel microscopy (STM). The contribution of the step bunching to the arrangement of Si islands was investigated. The reaction was set at 1.3x10-4 Pa. After the formation of 2x1 clean surface, the substrate was set at temperatures between 650 and 775°C, and MMS was supplied. Source gas pressure during the reaction was set at 1.3x10-4 Pa. During the reaction, the change of the surface structure was observed in situ by RHEED. The surface structure was observed at several reaction stages by STM. After MMS supply, both c(4x4) formation and step-bunching occurred. From the STM measurements for the samples prepared at various temperatures, it was found that the strength of step-bunching, which was determined from the step separation, increased with substrate temperature. In the case of c(1-10)-2''off substrates, steps run straight along the <110> axis. At 700°C with 45nm step separation was formed. After annealing the surface at 775°C for 13 h, SiC islands about 40nm in diameter were formed and arranged along <110> axis, which coincide with step separation and step direction, respectively. The organic indicates that the degree of the step-bunching influenced to the density and the size of SiC islands. [1]


11:15 AM Pl1.7


We examine the initial stages of the growth of epitaxial Si on (100) Ge surfaces from the pyrolysis of silane in a horizontal AP/RP-CVD single-wafer reactor between 500- and 600°C. We show that, using the proper growth conditions, 2-dimensional layer-by-layer growth is possible up to a thickness of at least 4 monolayers (ML). The thickness of the layers is determined using various techniques, including ARXPS, TARF, Auger spectroscopy and RHEED. The step flow in the layer as a consequence of the lattice mismatch and its influence on the growth mode is monitored at various stages of growth using cross-section RHEED and XRD. Surface roughness is obtained from AFM measurements. For growth at 575°C, the substrate strained Si layers were found to relax in a very early stage through the formation of a very dense, regularly spaced, dislocation network in the Si layer. The cross-hatch pattern resulting from these dislocations at the surface is studied with AFM and plane-view RHEED. A detailed discussion of the dislocations is given. Since the layers grown at 575°C are already highly relaxed after 4ML, we do not expect island growth to occur at higher thicknesses. It is important to note that this relaxation mechanism is fundamentally different from the 2D growth on SiC, which is expected theoretically and which was confirmed experimentally using solid-source MBE. Tsu et al. [1], who studied Si on Ge growth using gas-source MBE from disilane, also found layer-by-layer 2D growth to occur, but only up to 1.5ML, after which growth occurred. The mixed Strasinski-Krastanov mode. No dislocations were reported. A discussion on these differences, together with some possible explanations, is given. References (1) R. Tsu et al. J. Appl. Phys. 75, 240 (1994) and references therein.

11:30 AM Pl1.8

Synchrotron Radiation Photoemission Study of the Cs and O co-deposited InP(100) Surface and its Application to Negative Electron Affinity Devices. Dong-Ick Anthony Lee1,4, Zhi Liu1,4, Shinya Sumii1,4, Samuel P. A. Peterson2,4, William E. Spicer4 and Piero Pianetta2,4; 1Materials Science and Engineering, Stanford University, Stanford, California; 2 Electrical Engineering, Stanford University, Stanford, California; 3Physics, Stanford University, Stanford, California; 4Stanford Synchrotron Radiation Laboratory, Menlo Park, California.

The activation of InP(100) by Cs and O (Cs/O) co-deposition is critical to the achievement of Negative Electron Affinity (NEA) for applications in infrared detectors and photo-cathodes. The physical and electronic structure of the Cs/O co-deposited layer on InP(100) and its role in realizing the NEA state where the vacuum level is brought below the conduction band minimum in the bulk, is not yet fully understood. In order to better understand the surface chemistry, Synchrotron Radiation Photoemission Spectroscopy (SR-PES) measurements have been performed to follow in real-time the evolution of the valence band and core levels at different photon energies and at different incidence angles. The polarization dependent behavior of valence band PES along with the extent of the chemically shifted O1s component in the core level spectra leads us to believe that after activation at room temperature, the resulting Cs/O complex layer on InP(100) contains molecular oxygen peroxide species sandwiched between Cs layers and oriented parallel to the surface normal. This polar layer gives rise to the surface dipole which results in the achievement of a NEA surface. We propose that with time the peroxide species evolves to superoxide species and also oxidation of the underlying bulk In occurs at the same time due to unavoidable adsorption of oxygen from the residual gas pressure and these two phenomena are mainly the reasons of the decay of quantum yield which we have observed. The decay of quantum yield is reversible in the early stage of a decay process where the change of orientation in the Cs/O complex is a dominant effect, but it becomes irreversible when the oxidation of a substrate has significantly progressed. In the early stage of the chemical evolution of the Cs/O complex, the change is rapid at the interface between Cs/O complex and the substrate than at the surface.

SESSION P2: Metal Oxidation
Chairs: Jeff Eastman and Akikata Yoshigoe
Tuesday Afternoon, March 29, 2005
Room 3006 (Moscone West)

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Oxidation of strained, coherent thin films may proceed much differently than oxidation of the corresponding bulk material. These alternate pathways offer unique opportunities for both passivation of surfaces and creation of nanoscale structures. We are investigating the early-stage oxidation of a thin film of Co on Cu using advanced x-ray techniques.

2:00 PM 2P.2.2

We have measured strains in thermally grown oxides, in-situ, as the oxides develop and evolve. Extensive measurements have been acquired from Al2O3 and Cr2O3 grown in air, CuO grown in CO, TiO2 grown in CO, and thin films of CuO grown in CO. Strains have also been measured in thin-film and bulk single crystal samples, suggesting that substrate constraints are influencing oxidation behavior.

2:45 PM 2P.4

Plasma oxidation of thin aluminum films is a commonly used technique to form thin aluminum oxide barriers for application in the fabrication of tunnel junctions (typically 1 nm). In the present study, plasma oxidation is performed using Ar plasma discharge in oxygen (P = 5-12 W, p = 5-40 Pa) is used to oxidize ultrathin sputtered aluminum films. In contrast to thermal oxidation, the oxidation process is faster and provides high values of tunneling magnetoresistance (TMR) but at the cost of higher resistance-area products (RxA). However, whereas thermal oxidation of thin aluminum films is well understood in terms of the original model of Cabrera, where the oxidation rate is limited by field-assisted thermal vaporization of aluminum ions into the oxide, the detailed mechanism of plasma oxidation of thin aluminum films is still unknown. To unravel the mechanism in situ measurements of the oxidation rate and plasma parameters such as the ion and oxygen density are performed. The oxidation rate is determined from the increase in tunnel junction resistance and the plasma studies are performed using Langmuir probes, actinometry using optical emission spectroscopy, and two photon absorption laser induced fluorescence (TALIF). From these measurements, we have concluded that the interplay of plasma ions and the presence of dissociated oxygen is responsible for the increase in plasma oxidation rate. The results can be explained within a modified Cabrera model of oxidation in which the oxidation rate is enhanced due to the thermal spike of an impinging ion.
Understanding the microscopic processes controlling the oxidation of metal surfaces has practical importance in many fields including corrosion, heterogeneous catalysis, and dielectric growth. Oxidation of oxide layers has been observed on many metallic systems, and models have been proposed based on the transport of ionic species through a thick and continuous oxide film. Such previous studies have not followed the earliest stages of oxidation beginning with island nucleation and growth, however. We report here our investigations of the kinetics of early stage oxidation of Cu and Cu-Au alloys using in situ UHV-TEM. We examined the dynamic responses of thin films to variations in physical and chemical variables such as temperature, oxygen pressure, strain, and crystallographic orientation. The kinetics of the nucleation and growth of three-dimensional oxide islands demonstrate that oxygen surface diffusion is the rate-limiting mechanism for oxide growth, and that the appearance of an oxide island until saturation island density is reached, is significantly faster for Cu-Au alloys as compared to Cu. The nucleation behavior will be discussed in terms of the Gibbs free energy required for the oxide growth; the oxidation of (100)-oriented Cu-Au alloys with low Au content at ~ 600°C results in the formation of Cu2O oxide islands with a dendritic morphology and a non-uniform lateral distribution of island sizes. The distribution of the shape and size of the oxide islands can be quantitatively analyzed and is providing fundamental insights into the complex kinetics and energetics of oxidation and reduction. Models based on surface orientation, strain development, and diffusion will be discussed to qualitatively explain the formation of some of the novel oxide nano-structures.

We use low-energy electron microscopy (LEEM) to directly image how the kinetics of early stage oxidation of Cu and Cu-Au alloys using in situ UHV-TEM. Guangwen Zhou, Liang Wang, Robert C. Hwang, and Robert A. Brotherton. The oxidation of Ru(0001) and formation of epitaxial RuO2(llO)/Ru(0001) has attracted significant research interest recently. RuO2(llO)/Ru(0001) is a particularly interesting and important system for two reasons: (1) It is an exceptional CO oxidation catalyst and substrate for new catalyst systems; and (2) this system is the canonical example of how the perceived "pressure gap" in catalysis research can be overcome, leading to a direct coupling of fundamental science to applications. Yet, the oxidation pathway of Ru(0001), and in particular the role of surface structures (steps, defects, or decoration with other metals) on the formation of RuO2 remain poorly understood. Real-time microscopy during the exposure of Ru(0001) to oxygen has the potential to provide a comprehensive understanding of the mechanisms of Ru oxidation.

Observing the Chemistry of RuO2(llO) and RuO2(ll0)/Ru(0001) by Low-Energy Electron Microscopy, Kevin F. McCarty 1,2, J. P. Pierce 1, Materials Science Division, Argonne National Laboratory, Argonne, Illinois; 2Department of Materials Science and Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania.

We use low-energy electron microscopy (LEEM) to directly image how a hot NiAl crystal oxidizes when exposed to oxygen. At high temperatures, discrete oxide islands nucleate and grow on the (110) surface. Using selected-area electron diffraction, we establish that the islands are crystalline and that two different oxide phase forms. Each phase has a distinct epitaxial relationship with the substrate. One phase forms as rod-shaped islands whose lengths can be in excess of several microns. Since the heights and widths are quantized, respectively, in units of 2 A, we refer to this as the "nano-rod" phase. Real-time imaging reveals important aspects of how the nano-rods self assemble. They lengthen across virgin areas of the substrate at a constant rate. The rods thicken vertically by adding one atomic layer at a time – a new layer of oxygen nucleates on top of the nano-rod. This layer then grows along the rod's axis, causing the height of the entire rod to increase by about 2 A.

The second oxide phase that we observe is a type of alumina, which forms only where islands on the NiAl surface. Domains develop within the islands as they grow. The lattices of the domains are offset relative to each other. Usually such antiphase domains are assumed to form during film growth by the impingement of neighboring islands that are shifted with respect to each other. However, we observe antiphase domains forming within isolated islands. We will show that this process occurs so the oxide can reduce its strain with the substrate. Finally, we measure the thermal stability of both the thin-oxide nano-rod phases. At a fixed temperature, the pressure of oxygen in equilibrium with the oxide phase is determined by finding the pressure at which individual oxide islands neither shrink nor grow. Based on thin-film aluminum oxide, these nano-scale phases are remarkably less stable than bulk alumina. We attribute this reduced stability to the fact that the oxide film phases are strained and extremely thin. J. M. Libuda et al., Surf. Sci. 318 (1994) 61. This work was supported by the Office of Basic Energy Sciences, Division of Materials Sciences of the U.S. DOE under Contract No. DE-AC04-94AL85000.

Observation of the Oxidation of Ru(0001) by Low-Energy Electron Microscopy, Peter Sutter 1, Jan Hrbek 1, Robert A. Brotherton 1, and Robert C. Hwang 1, 1Center for Fundamental Nanomaterials, Brookhaven National Laboratory, Upton, New York; 2Department of Chemistry, Brookhaven National Laboratory, Upton, New York.

The oxidation of Ru(0001) and formation of epitaxial RuO2(llO)/Ru(0001) has attracted significant research interest recently. RuO2(llO)/Ru(0001) is a particularly interesting and important system for two reasons: (1) It is an exceptional CO oxidation catalyst and substrate for new catalyst systems; and (2) this system is the canonical example of how the perceived "pressure gap" in catalysis research can be overcome, leading to a direct coupling of fundamental science to applications. Yet, the oxidation pathway of Ru(0001), and in particular the role of surface structures (steps, defects, or decoration with other metals) on the formation of RuO2 remain poorly understood. Real-time microscopy during the exposure of Ru(0001) to oxygen has the potential to provide a comprehensive understanding of the mechanisms of Ru oxidation.
The reaction of $O^+$ with a self-assembled organic monolayer serves as a prototype system for understanding the degradation pathways suffered by polycyclic satellite materials in the low-earth orbit (LEO) space environment. For example, dodecanethiol adsorbs on gold to produce a densely packed SAM composed of $S(CH_{2})_{11}CH_{3}$ chains, tilted at 34° relative to the surface normal. Unlike bulk polyethylene, a SAM presents a well-ordered hydrocarbon film that does not undergo electronic charge when bombarded with an ion beam. In a UHV scattering chamber, we target 5-20 eV $O^+$ ions on a dodecanethiolate SAM. The scattered ionic products are collected with energy-, angle-, and mass-resolved detection. For 5-20 eV $O^+$ bombardment of a dodecanethiolate SAM, we have used X-ray photoelectron spectroscopy to measure the erosion yield and degree of oxidation in the hydrocarbon layer as a function of $O^+$ dose. To learn about the site-specificity to hydrogen abstraction in this system, we have deposited SAM layers for which the hydrogen atoms located on the C-12, C-11, or C-10 positions of 1-dodecanethiol have been substituted with deuterium atoms. Comparing the yields of OH to OD emerging from the three isotopomers provides a direct measure of the relative rates at which oxygen ions abstract hydrogen bound to the terminal carbon versus the secondary carbon sites just below it. In addition, STM images of the irradiated SAM reveal that ions preferentially attack the film domain boundaries. In contrast, molecules located within a sizeable structural domain remain largely unaffected by the impinging 5-eV $O^+$ ions.

**SESSION P3: Atomic Oxygen and Organic Materials**

**Chair: Dennis Jacobs and Tim Minton**

**Wednesday Morning, March 30, 2005**

**Room 3006 (Moscone West)**

**8:30 AM **

*P3.1*

**Reaction of Hyperthermal Energy Oxygen Ions with Hydrocarbon Self-Assembled Monolayers.**

Dennis Christopher Jacobs, Tochko Tzetkov, Xiangdong Qin and Xin Liu; Chemistry and Biochemistry, University of Notre Dame, Notre Dame, Indiana.

The reaction of $O^+$ with a self-assembled organic monolayer serves as a prototype system for understanding the degradation pathways suffered by polycyclic satellite materials in the LEO space environment. For example, dodecanethiol adsorbs on gold to produce a densely packed SAM composed of $S(CH_{2})_{11}CH_{3}$ chains, tilted at 34° relative to the surface normal. Unlike bulk polyethylene, a SAM presents a well-ordered hydrocarbon film that does not undergo electronic charge when bombarded with an ion beam. In a UHV scattering chamber, we target 5-20 eV $O^+$ ions on a dodecanethiolate SAM. The scattered ionic products are collected with energy-, angle-, and mass-resolved detection. For 5-20 eV $O^+$ bombardment of a dodecanethiolate SAM, we have used X-ray photoelectron spectroscopy to measure the erosion yield and degree of oxidation in the hydrocarbon layer as a function of $O^+$ dose. To learn about the site-specificity to hydrogen abstraction in this system, we have deposited SAM layers for which the hydrogen atoms located on the C-12, C-11, or C-10 positions of 1-dodecanethiol have been substituted with deuterium atoms. Comparing the yields of OH to OD emerging from the three isotopomers provides a direct measure of the relative rates at which oxygen ions abstract hydrogen bound to the terminal carbon versus the secondary carbon sites just below it. In addition, STM images of the irradiated SAM reveal that ions preferentially attack the film domain boundaries. In contrast, molecules located within a sizeable structural domain remain largely unaffected by the impinging 5-eV $O^+$ ions.

**9:00 AM **

*P3.2*

**Atomic Oxygen Reactions with Self Assembled Monolayers and Polymeric Substrates.**

Howard Fairbrother, Chemistry, Johns Hopkins University, Baltimore, Maryland.

The surface reactions of atomic oxygen (AO) play a central and often determinant role in many important plasma processes such as etching and the sterilization of biologically contaminated surfaces. In respect to polymers, AO is used to study the chemical conformation of the reactive part of the polymer is treated with a mixed quantum mechanics/molecular mechanics potential energy function in which the reactive part of the polymer is treated with a mixed quantum mechanics/molecular mechanics potential energy function in which the reactive part of the polymer is treated with a mixed quantum mechanics/molecular mechanics potential energy function in which the reactive part of the polymer is treated with a mixed quantum mechanics/molecular mechanics potential energy function in which the reactive part of the polymer is treated with a mixed quantum mechanics/molecular mechanics potential energy function in which the reactive part of the polymer is treated with a mixed quantum mechanics/molecular mechanics potential energy function in which the reactive part of the polymer is treated with a mixed quantum mechanics/molecular mechanics potential energy function in which the reactive part of the polymer is treated with a mixed quantum mechanics/molecular mechanics potential energy function in which the reactive part of the polymer is treated with a mixed quantum mechanics/molecular mechanics potential energy function in which the reactive part of the polymer is treated with a mixed quantum mechanics/molecular mechanics potential energy function in which the reactive part of the polymer is treated with a mixed quantum mechanics/molecular mechanics potential energy function in which the reactive part of the polymer is treated with a mixed quantum mechanics/molecular mechanics potential energy function.
conventional inorganic materials such as metals, semiconductors and oxides. A key difference involves the presence of strong covalent and ionic bonding in the latter class of materials. Inorganic materials are often bound by rather weak dispersion (van der Waals) forces. In addition, many organic materials are often known to crystallize in different phases, separated in total energy by amounts on the order of a few tenths of an eV. As a consequence, considerable promise exists in the use of energy tunable molecular beams for the deposition of organic thin films. In this talk we will review our efforts in using supersonic molecular beams as sources for film deposition, in particular, for the growth of thin films of pentacene, a representative organic semiconductor. Pentacene, which possesses a very low vapor pressure, presents a number of experimental challenges that must be overcome in order to generate energy tunable beams. First, using time-of-flight quadrupole mass spectrometry we have characterized supersonic molecular beams of pentacene generated using carrier gases of N₂, He and H₂. We demonstrate that for these beams, kinetic energies over the range of 0.006 to 0.0066 eV are present and the molecular fluxes are on the order of 10⁻²⁵ molecules·cm⁻²·s⁻¹. Next, we will present recent results concerning the deposition of pentacene on SiO₂ surfaces with these energetic sources. We find that beam energy affects a number of phenomena, namely nucleation in the monolayer regime, and both the kinetics of thin film deposition and the microstructure in the multilayer regime, evidenced by results from AFM. Closer examination of the data indicates that the dynamics of deposition in the monolayer regime is driven by graphene layers, by comparison to the higher order nucleation probability of pentacene, which decreases with increasing energy. However, in this same regime the trapping probability is found to increase with more glancing angles of incidence, a result inconsistent with so-called normal energy scaling. Finally, we have conducted an analysis of the evolution of the thin film microstructure of these films, as it provides further insight into the mechanisms of deposition through the use of scaling arguments. Here again energy plays a role, and we find that both the incident kinetic energy and the angle of incidence can affect the microstructure.

11:15 AM P3.6

Atomic-Scale Imaging of Carbon Nanofiber Growth.

By means of in situ high resolution transmission electron microscopy (HR-TEM) observations we address the gas-surface reaction dynamics involved in the growth carbon nanofibers. Time-resolved, high-resolution imaging directly reveals that graphitic nanofibers formed by catalytic decomposition of methane over supported nickel nanoclusters develop through a reaction-induced reshaping of the nickel nanocrystals. The dynamic shape of the nickel nanocrystals assists the alignment of graphene layers into graphitic nanopillars. Specifically, the graphitic layers are observed to couple to a dynamic formation and restructuring of mono-atomic step edges at the nickel surface. The finding that metallic step sites act as growth centers is attributed to the stronger bonding of carbon atoms to step sites than to facet sites. From interplay with density functional theory calculations, the observations of nickel step-edge dynamics are consistently explained by a new growth mechanism involving surface diffusion of nickel and carbon atoms.


11:30 AM P3.7

Fabricating Inorganic-Organic Interfaces for Use in Molecular Electronics.
Abhikheer Dubey1, Manish Sharma1, Andrew Chadney2, Peter T. Wolczanski2 and James R. Engstrom1; 1School of Chemical and Biomolecular Engineering, Cornell University, Ithaca, New York; 2Department of Chemistry and Chemical Biology, Cornell University, Ithaca, New York.

Most modern electronic devices are solid state devices, the active components of which are constructed essentially entirely of inorganic materials. To date, and excepting important applications such as photo-resists in lithography, organic materials have played a rather secondary role in this technology. This trend is changing and considerable efforts have been devoted over the past 50 years concerning the use of small molecules in active components of electronic circuitry—the field is known as molecular scale electronics or molecular electronics. In all cases involving the use of organics, communalities and nanofabrication have frequently dominated the research, for example, the ability to move charge through metal wires, thus contacts are required. Whereas self-assembly (chemically specific adsorption) has been used successfully make the first, so-called “bottom” contact (e.g. alkanethiol on gold), often more crude means are adopted to form the second, “top” contact. In the case of metallic top contacts, evaporation or sputter deposition of elemental metal has been employed due to its simplicity, but penetration of the organic film often occurs with this approach. Our approach towards addressing this issue is to make use of transition metal coordination complexes to initiate top contact formation. In this approach it is important to tailor the tail group of the molecule such that the reaction is both specific and self-limiting, and the kinetics of formation of tetraakis(dimethylamido) titanium (TDMAT), a precursor for titanium nitride (TiN), with self-assembled monolayers of molecules with conjugated backbones. In particular, we have synthesized conjugated thiophene molecules possessing terminal amine groups and used these to form self-assembled monolayers (SAMs) on polycrystalline gold. These SAMs were subsequently characterized using ellipsometry, and contact angle measurements. Following characterization, the SAMs were inserted into ultrahigh vacuum for additional analysis using x-ray photoelectron spectroscopy (XPS), as well as exposure to TDMAT. We have found that the reaction of TDMAT with these SAMs is self-limiting, and the kinetics of adorption are in reasonable agreement with first-order Langmuir kinetics. Angle resolved XPS (ARXPS) has been used to probe the nature of the SAMs, both before and after exposure to TDMAT. ARXPS of the SAMs themselves verifies that the thiophenes bind to the gold surface via a Au-S bond and that the amine termination is at the surface. ARXPS conducted after reaction of the SAMs with TDMAT shows clearly that reaction occurs cleanly with the amine group, that the reaction is, in fact, diamolecular in nature, and that we had observed in previous work on trichlorosilane SAMs assembled on silicon oxide. Finally, XPS has also been used to deduce the stoichiometry of the adlayer and these results will be discussed in context of using this strategy for top contact formation.

SESSION P4: Surface Reactions/Chemical Vapor Deposition

Chairs: Paul Faccio and Renu Sharma
Wednesday Afternoon, March 30, 2005
Room 3006 (Moscone West)

1:30 PM P4.1

Eley-Rideal and Hot Atom Reactions on Metal and Graphite Surfaces. Brest Jackson, Chemistry, University of Illinois, Urbana, Massachusetts.

In an Eley-Rideal reaction, a particle reacts directly with another particle adsorbed onto a surface. We have theoretically examined the Eley-Rideal reactions of H atom beams with H and Cl atom adsorbed on a metal and graphite surfaces. Electronic structure methods based on DFT are used to compute the potential energy surfaces for these reactions. Both quantum and classical methods are then used to study the reaction dynamics. For reactions on transition metal surfaces it is found that the cross section per direct Eley-Rideal formation of molecular hydrogen is very small, and that most of the incident H atoms trap to form highly mobile hot atoms. These hot precursors tend to relax and stick, but can also react with other adsorbates to form surface products. Our results are in excellent agreement with several experimental studies. H atom reactions with H adsorbed onto graphite are very different. We demonstrate that H can chemisorb to the graphite surface if the bonding carbon is allowed to pucker out of the surface plane. The Eley Ridal cross section for reaction with this H atom is very large. These predictions have been verified by recent experiments.

2:00 PM P4.2


In this talk we examine the origin of the unique reactivity of the Au(100) surface toward the electroreduction of oxygen in the basic electrochemical environment. It has been understood for many years that oxygen electroreduction proceeds incompletely, with the electron pathway on all the low Miller index faces of Au in acid and on the (111) and (110) faces of Au in base. However, the Au(100) surface exhibits four electron reduction activity. We present the results of electrochemical, vibrational spectroscopic, and ultra high vacuum based measurements directed at understanding this reactivity. In particular, OH shows unique reactivity on Au(100) relative to the other faces and exhibits an ordered adlattice when constructed by depositing water onto a K-modified Au(100) surface at UHV at low temperature. Calculations and vibrational spectroscopic measurements are then used to show how this unique OH reactivity translates into enhanced capacity for the four electron electroreduction of oxygen.

2:30 PM P4.3

Sulfur-Induced Corrosion of Au(111) Studied by Real-Time STM. Monica Margarete Biener1,2, Juergen Biener1 and Cynthia M. Friend1,2; 1Chemistry Department, Harvard University, Cambridge, Massachusetts; 2Materials Science Department, Harvard University, Cambridge, Massachusetts.

Sulfur-Induced Corrosion of Au(111) Studied by Real-Time STM.
The interaction of sulfur with gold surfaces has attracted considerable interest due to numerous technological applications such as the formation of self-assembled monolayers (SAMs), corrosion inhibition, and sensors. A recent investigation of the gold-sulfur interaction suggested that sulfur atoms prefer threefold-hollow positions at low coverages (<0.25 ML) and form polymer species Sn at higher coverages. We will demonstrate the formation of a two-dimensional gold sulfide accompanied by a dynamic rearrangement of the surface. At early reaction stages, the sulfide surface (0.1 ML) lift the herringbone reconstruction of the Au(111) surface. At a sulfur cover of 0.33 ML a (sqrt3xsqrt3)R30º LEED pattern is observed. A further increasing sulfur coverage leads to a weakening of the Au-Au bonds, and gold atoms are removed from regular surface sites and incorporated into the growing gold sulfide overlayer. Simultaneously, pits of monotonous step height and small clusters develop. After a cumulative SO2 exposure of ~1000 L, the surface is completely covered with a short-range ordered gold sulfide overlayer exhibiting a sponge-like structure and a total S coverage of 0.5 ML, based on AES data. Annealing the gold sulfide overlayer to 500 K yields a complex LEED pattern, and significant changes of the surface topography. Topographs of a film island (depicted by the areas of coalescence of the pits generated by SO2 exposure at 300 K. High-resolution STEM images reveal the formation of a well-ordered two-dimensional gold sulfide. Annealing the surface beyond 500 K leads to an irreversible decomposition as shown by AES. Using real-time STM, we observed that the Au(111) surface undergoes a dramatic restructuring while forming a two-dimensional AuS overlayer. This 2-D AuS film can be used as a template for metal sulfide growth.

2:45 PM P4.4

Growing interest in the use of metal alloys for hydrogen storage has created a need to understand the fundamental behavior of metal-hydrides. Since the volume of the hydride is often much larger than that of the host metal, strain is an important factor controlling hydride formation and decomposition. However, systematic studies of the effects of strain on hydriding and dehydriding are lacking. In an effort to understand these effects, we have carried out in situ x-ray scattering studies to investigate reversible hydriding in palladium, a prototypical metal-hydride-former. Epitaxial thin films of Pd were grown on SrTiO3(001), SrTiO3(110), Cu(111), and GaAs(001). Films studied during hydrogen absorption and desorption at room temperature and variable hydrogen partial pressures using a system specially built for in situ x-ray studies of gas-solid interactions. The hydrogen concentration, as monitored by x-ray spectra taken along in-plane and out-of-plane directions. From our investigation of both coherently strained and relaxed Pd films, we find the behavior of the hydride depends strongly on the Pd film. For films coherently strained to the SrTiO3, we observe the formation of nanoscale hydrides precipitates with lattice parameters near those of bulk PdH0.6. For thicker, relaxed Pd films, the hydride forms both as a precipitate strained to the Pd-matrix as well as a precipitate with bulk-like lattice constants. In all cases, the nanoscale hydride maintains a cube-on-cube-orientation with the film. The kinetics of hydriding and dehydriding will also be discussed.

3:30 PM P4.5

Mineral dehydroxylation generates highly reactive nanomaterials with applications in flue gas desulfurization, decontamination (e.g. rendering chemical warfare agents ineffective), and carbon sequestration technology. Mg-rich minerals containing hydroxide lamella (e.g. brucite and serpentine) are appealing candidate materials for carbon sequestration via mineral carbonation. Serpentine, in particular, is widely available at low cost. Herein, Mg(OH)2 is chosen as a prototype material to initiate investigation of the mechanisms associated with dehydroxylation and carbonation due to its (i) chemical and structural simplicity, (ii) interest in Mg(OH)2 gas-solid carbonation as a sequestration mechanism, and (iii) and its chemical and structural similarity to the more complex serpentine (Mg3Si2O5(OH)4) minerals. Partially dehydroxylated Mg(OH)2 (brucite) single crystal fragments exhibit substantially increased reactivity at room temperature. RBS and 91% dehydroxylated fragments indicate the high surface area (120 m2/g) directly contributing to the increased reactivity. Room temperature carbonation of freshly formed nanocrystals has been observed in situ via STEM to provide new insight into their highly reactive nature and the associated carbonation process. Experiments were performed using a PHILIPS-430 electron microscope operated at 300KV, fitted with a differentially pumped environmental-cell (E-cell) (ETEM) and a gaseous imaging filter (GIF). Fragments were dry loaded on holey-carbon Cu grids and heated to 465 C to complete the dehydroxylation. These samples were exposed 400 m Torr of humid CO2 at room temperature. A combination of imaging and electron energy-loss spectroscopy was used to investigate the carbonation process. The brucite crystals were observed to disintegrate into MgO nanocrystals during dehydroxylation. On heating, the hydride forms both as a precipitate strained to the film. At 166 C, only [111]MgO spots with streaking could be observed by 307 C. At room temperature the product was found to be very reactive and CO2 and H2O diffused through the grain boundaries of the nanocrystals during reaction, swelling the fragment. As the reaction progressed, a waxing and waning of the sample edge is observed consistent with local temperature fluctuations causing minor changes in the CO2 and H2O content of the reaction product. Although, some hydration was observed, H2O appears to primarily increase MgO mobility, enhancing carbonation in the process. Only diffuse rings were observed in SAED patterns indicating the non-crystalline nature of the carbonate formed. The electron energy-loss near-edge structure for C1s and O1s-edge energy dispersion have confirmed those obtained from MgCO3 (magnesite). Ex-situ studies have confirmed the formation of an amorphous carbonate phase. The mechanism deduced from time resolved video images will be presented.

3:45 PM P4.6
Ionic Conductivity of La1-xSrxCO3-d (x = 0.1, 0.2, 0.5 and 0.7) Determined via Oxygen Permeation Measurements. Frederick H. B. Moring, Dave H. A. Blank and Hendrik J. M. Bouwmeester; Faculty of Science and Technology & MESA+ Research Institute for Nanotechnology, Laboratory for Inorganic Materials Science, University of Twente, Enschede, Netherlands.

The perovskite materials La1-xSrxCO3-d (x = 0.1, 0.2, 0.5 and 0.7) are well-known mixed conductors. The concentration of point charge defects (electrons, holes and oxygen vacancies), resulting from charge compensation upon strontium doping, is dependent on the oxygen partial pressure [1]. According to the Nernst-Einstein relation, the ionic conductivity is proportional to the concentration of oxygen vacancies, increasing with x and decreasing oxygen partial pressure. Wagner [2] described the transport of oxygen through mixed conductors, assuming the bulk diffusion to be the dominant transport mechanism. This theory predicts the oxygen flux to be proportional to the ionic conductivity of the mate-rial, provided that the electronic transfer equals unity, which is an appropriate assumption for the perovskite materials under consideration. This study presents oxygen permeation measurements as a direct way of determining the ionic conductivity of La1-xSrxCO3-d (x = 0.1, 0.2, 0.5 and 0.7) as a function of the partial pressure of oxygen. The trend in the results is in agreement with the predicted behaviour obtained from the derivation of the Nernst-Einstein relation with respect to the non-stoichiometry. Locally, deviations from the predicted behaviour are obtained for high-strontium concentrations. This can be explained by different mechanisms, in particular the presence of a stagnant layer on the low oxygen partial pressure side of the membrane. A simple model is used to analyse the influence of this layer and its effect on the determination of the ionic conductivity. The results obtained are critically discussed and general conclusions are drawn. References: 1. J. Misono, Y. Mima, S. Yamauchi and K. Pueki, Nonstoichiometry of a Perovskite-Type Oxides La1-xSrxC03-d, J. J. Solid State Chem. 80, 102-111 (1989). 2. C. Wagner and W. Schottky, Beitrag zur Theorie des Anlaufvorganges, Z. Phys. Chem. 1930, B11, 25-41.

4:00 PM P4.7
Low Temperature Chemical Vapor Deposition Growth of Hafnium Diboride and Zirconium Diboride from Single Source Precursors. Y. Gao, S. Yang, S. Yu, S. Jacob, and J. L. Rehg; Department of Electrical Engineering and Computer Science, University of Michigan, Ann Arbor, Michigan.

Zirconium diboride and Hafnium diboride are metallic ceramic materials which have high heat conductivity and strength, and which are used as low electrical resistivity. ZrB2 and HfB2 thin films can be grown at...
temperature as low as 200°C by chemical vapor deposition from the single source precursors Zr(BH4)4 and Hf(BH4)4. In previous studies, we found that the temperature and of the H2 and N2 pretreatments on the SiC/GaN interface, on the GaN nucleation and on the GaN surface modifications is discussed through the analysis of kinetic data acquired using ellipsometry. Chemical vapor deposition (CVD) growth at 100°C, and the T and N2 SIC pre-conditioning affect the interface roughness, the GaN nucleation, and surface reactivity during the GaN growth are found to be dependent on the nucleation geometry. Real time ellipsometric data are corroborated with atomic force microscopy, Kelvin probe microscopy, which are used for the study of their impact of the nucleation geometry on the final quality of the GaN epilayer.

4:45 PM P4.10

Plasma-assisted atomic layer deposition (PA-ALD) opens up new routes in thin film growth by combining the benefits of ALD with those offered by low-temperature plasma processing. The full exploitation of PA-ALD demands, however, knowledge about the relevant plasma species, gas-surface interaction, and the elemental surface reactions taking place. In situ spectroscopic ellipsometry has therefore been applied to the PA-ALD process of TiN films in which TiCl4 precursor dosing and H2-N2 plasma exposure are alternated. By collecting ellipsometry data over the photon energy range of 0.7 to 5.0 eV after each ALD cycle, information on the growth rate as well as on the film properties such as electrical resistivity and mass density has been obtained. Moreover, the data have revealed important insight into initial film growth on different types of substrates (chemical and thermal oxides, H-terminated Si) and surface pre-treatments (annealing, plasma exposure). The role of surface species such as hydroxyls and siloxane bridges for the initial surface reactions as well as for nucleation delays and silicidation will be discussed. Insight into the surface reactions such as ligand abstraction by atomic H and nitridation by atomic N is also obtained from studies of the temperature dependence of TiN growth revealing information about activation barriers. Furthermore, the influence of surface reconstructions of H and N atoms has been investigated by 2D-Monte Carlo simulations as PA-ALD differs from conventional ALD by the fact that radical species can be lost on surfaces by ligand abstraction reactions as well as by recombination. Qualitative information about the surface radical abstraction probabilities is obtained by comparing simulated and experimental deposition profiles of TiN deposited in high-aspect ratio (20:1) structures.

SESSION P5: Poster Session

P5.1
Partial Oxidation of Alkanes Over Supported Metal Oxides: In-Situ DRIFT Studies. Gerald Macke; Chemistry, UCSB, Santa Barbara, California.

Selective partial oxidation of alkanes to oxygenates and alkenes remains an important challenge. In particular, selective and efficient conversion of natural gas to more valuable and more easily transportable feedstocks is a problem with strong environmental and economic motivation. Conversion has been reported over supported metal oxides and can be tuned by varying oxide composition, temperature, and other factors. Representative reactions have been studied using In-Situ Diffuse Reflectance FTIR to identify surface species which may yield mechanistic information.

P5.2
Photochemical Processing of Solid Carbon Dioxide. T. Randy Dillingham, David Cornelison, Joe Dinius, Joshua Martin and Tim Porter; Physics and Astronomy, Northern Arizona University, Flagstaff, Arizona.

The investigation of the photochemical processes that can occur in solids like carbon dioxide have important applications in astrophysics, astrobiology, and planetary science. In this study, carbon dioxide ices are grown at various temperatures using a closed-cycle helium cryostat. The ices are characterized using x-ray photoelectron spectroscopy and Fourier transform infrared spectroscopy, and the chemical changes are monitored by the solids are irradiated with x-rays for periods of up to six hours. A quadrupole mass spectrometer was also used to monitor the gas phase species evolving from the ice surface during photoprocessing. The XPS and FTIR results are consistent with previous studies...
presented and correlated. It is noted that significant differences are observed, particularly for the time dependence of the evolution of the gas phase model at 77 K as compared to those grown at 20 K and at intermediate temperatures. *Supported by the NAU Intramural Grants Program and the NASA Space Grant Program.

P5.3


The Low Temperature Initial Oxidation Stages of Cu (100) Investigated by Insitu UHV-TEM.

The fundamental understanding of oxidation mechanisms is essential, because these processes play crucial roles in numerous engineering applications, including environmental stability, gate oxides, catalytic reactions, and corrosion. Surprisingly, few studies exist concerning the initial oxidation stage from the nucleation to the initiation of metal oxides. Hence, we have used insitu ultra high vacuum transmission electron microscopy (UHV-TEM), to study the initial stages of oxidation, in order to gain insights into the oxidation kinetics with controlled surface conditions. These studies mainly focus on the oxidation of Cu (100) below 350 °C in order to extend our previous studies, which centered on oxidation mechanisms that occurred at temperatures at and above 350°C. For the temperature range we examined (200 to 350 °C), epitaxial CuO islands form with a triangular in cross-section shape that had rounded edges when Cu(100) was exposed to dry oxygen at 5x10^-4 torr in situ. Our initial analysis on the nucleation and growth of these three-dimensional CuO islands agree well with the heteroepitaxial model of surface diffusion of oxygen, which was originally developed by Yang et al. [1]. The growth behavior of these oxides will be simulated by a recently developed kinetic Monte Carlo (KMC) program, called TPOx (Thin Film Oxidation), for deeper physical insights. [1] J. C. Yang, M. Yeadin, B. Kolasa and J. M. Gibson, Scripta Materialia, 38 (8) 1237-1242 (1998). [2] G.W. Zhou, J.C. Yang, Appl. Phys. Lett. 210, 165 (2002).

P5.5

Growth Kinetics of Germanium on (100) Germanium by Pyrolysis of Germane.

The growth kinetics of Ge on (100) Ge by pyrolysis of GeH4 under H2 ambient was studied in a horizontal single-wafer Atmospheric Pressure/Reduced Pressure-Chemical Vapor Deposition reactor over a broad range of GeH4 and H2 partial pressures in the temperature range 350-790°C. The Arhenius plot for the growth rate shows a strong non-linear behavior and three important regions can be distinguished. Below 450°C, the plot is linear and the growth rate strongly increases with temperature. Between 450- and 550°C a much weaker increase in temperature is evident, and above 550°C, the growth rate is found to decrease weakly with increasing temperature. The low and intermediate temperature regions are well known from Si-CVD and represent a surface reaction dominated region and a gas-phase mass flow dominated region respectively. The decrease in growth rate at high temperature was already noted by Jiang and Reif (1), who studied the influence of increasing Ge content on the SiGe growth rate. We start the analysis with a phenomenological approach, determining the apparent activation energy for the three regions assuming a simple Boltzmann-like temperature dependence for the growth rate. A comparison with similar experimental values found in literature is given and discussed. Although the intermediate temperature and high-temperature regime are briefly discussed and a possible explanation for the decrease in growth rate in the third region is given, the main focal point of the present paper is the analysis of the surface reaction dominated regime. These models, where for the dual-site model we assume that the initial adsorption step consists of the dissociative chemisorption of GeH4 into Ge and H, an apparent activation energy of 32 kcal/mole reported by Holleman et al. (2) for H2-desorption from a Ge surface. In our growth model for this region, we therefore assume H to be the dominant species in the surface coverage, which then leads to the well-known Langmuir-Hinshelwood type of growth rate equations. A brief comparison with predictions from other models, where Ge containing molecules are assumed to be the dominant species in the surface coverage, is also given. [1] S.-M. Jiang and R. Reif, Appl. Phys. Lett. 59, 3192 (1991) (2) J. Holleman, A.E.T. Kuiper and J.F. Verweij, J. Electrochem. Soc., 140, 1718 (1993) (3) J. Holleman and J.F. Verweij: J. Electrochem. Soc., 140, 2906 (1993).

P5.6

TEG for CVD Surface Kinetic Studies.

The surface reaction mechanisms of CVD processes involves various steps, like as adsorption, surface diffusion, desorption, and surface reaction of adsorbed species. Several experimental techniques to observe these surface chemistries had been developed, but they sometimes require special reaction condition that may be different from actual deposition conditions. On the other hand, deposition rate profile in a test structure gives messages of surface chemistries. For example, growth rate, non-uniformity of selective MOVPE for InP and GaAs based compound semiconductor can extract the actual surface reaction rate constant of film forming species even if the growth rate is measured by the differential measurement of precursor. Specially designed mask pattern for selective MOVPE growth may be an effective tool to discuss the surface kinetics including reaction probability and surface diffusion of incoming species. The growth rate non-uniformity in a micromachined trenches and holes, i.e., step coverage, will give us information on reactive sticking probability for various kinds of CVD processes. The comparison of step coverage profile in trenches with different aspect ratio may be a powerful tool to extract the reactive sticking probability of film forming species and it is also possible to discuss how many chemical species are contributing to the deposition. Several examples to examine the surface reaction kinetics using step coverage analysis will be discussed, including ZnO2, SiO2, and SiCVD. The test structure having various aspect ratio for examining the kinetics of deposition and etching of plasma processes. The contribution of ion and neutral species can be easily distinguished from the deposition profile analysis using Monte Carlo based simulation. The plasma enhanced deposition of amorphous fluorinated carbon films from C4F8 and dry etching of SiO2 by C2F2/O2 chemistry was analyzed by this test structure. These test structures, may be called TEG (Test Element Group) for CVD surface kinetics, are effective tool to study various surface reaction dynamics.

P5.7

Dynamics of Gas-Surface Interaction involving ZnO Probed in Real Time: Impact of Surface Polarity and Nanostructure.

Hexagonal zinc oxide, ZnO, is a II-VI semiconductor of considerable technological interest for optics and optoelectronics due to its wide band gap of 3.4 eV, a strong excitonic feature even at room temperature and lasing properties at room temperature suitable for ultraviolet laser applications. A number of other applications of ZnO-based systems are known in catalysis and for gas-sensor applications. Furthermore, it is also a suitable substrate for the heteroepitaxial growth of III-nitride (GaN, AIN,) by MOCVD and MBE. For all the above applications, it is of interest to study the interaction of hydrogen and oxygen with ZnO surfaces. Although a number of theoretical studies have been devoted to the investigation of the interaction of hydrogen and oxygen with ZnO very few experimental investigations reported the real time monitoring of the interaction of O-polar and Zn-polar ZnO surfaces with hydrogen, oxygen or atomic species and/or they do not characterize the different reactivity of the O- and Zn-polar ZnO. Specifically, the crystal structure of ZnO is wurtzite with two inequivalent sequences of atomic planes along the 1001 axis with the (00-1) O-polar face and the (100) face. The present contribution is aimed at studying the kinetics of the interaction of O-polar and Zn-polar surfaces of single crystal ZnO with atomic hydrogen, nitrogen and oxygen produced by remote plasmas of H2, N2 and O2, respectively, monitored in real time using spectroscopic ellipsometry. It is shown that the surface reaction of atomic hydrogen, nitrogen and oxygen with ZnO is sensitive to ZnO polarity, being the Zn-polar surface more reactive toward atomic hydrogen and nitrogen than the O-polar ZnO surface. The study extends from crystalline ZnO to nanocrystalline...
ZnO films by MOCVD. The impact of the nanostructure on the kinetics of the gas-surface reaction is fingerprinted by ellipsometry, which yields information on the surface density and reactivity of hydrogen and nitrogen on the various ZnO nanostructures. The chemistry of the surface modification of ZnO upon gas interaction is investigated using XPS. The change of the surface morphology upon interaction is highlighted by HEEM. A correlation between polarity, nanostructure of ZnO and its reactivity to hydrogen, nitrogen and oxygen is presented and discussed.

P5.8 Abstract Withdrawn

P5.9 Thermogravimetry of Gas/Solid Interactions. Lawrence L. Cook 1, Winnie Wong-Ng 2 and Siu-Wai Chan 1; 1 Ceramics, NIST, Gaithersburg, Maryland; 2 Materials Science, Columbia University, New York, New York.

Thermogravimetry provides a sensitive tool for investigating the interaction of gaseous species with solid surfaces through in-situ measurement of mass changes at the sub-microgram level. With simultaneous instrumental and data analysis the detection of mass changes of < 50 ng has become possible, while the sample is maintained at temperatures from -150 °C up to 2400 °C. In many instances, the experimental geometry will allow the sensitivity can be magnified, if necessary, by treating larger sample sizes. This capability has broad application in the materials science of solid surfaces, including catalysis, corrosion, passivation, hydration, adsorption, and oxidation/reduction. We will discuss selected examples from our current research on the surface stability of CoO2-x, and the oxidation of Ag in mettalization in electronic ceramics.

P5.10 Measurements of Water Adsorption on HfO2 and ZrO2 Surfaces using a Novel Design for Gas Adsorption Microcalorimetry. Sergey V. Usakov, Misojung Wang and Alexandra Navrotsky; Thermochemistry Facility and NEAT ORU, University of California at Davis, Davis, California.

Direct calorimetric measurement of heats of gas-solid interaction is a powerful technique for elucidation of thermodynamic controls of reactions and understanding energetics of various adsorbates. Many such measurements used Calvet type microcalorimeters which offer very good stability of the baseline. However, the laborious nature of such experiments employing custom built manual dosing systems restricted application of this technique. We developed a novel instrumental design, which gives the advantage of automated operations and allows for versatile applications. It employs a modified surface area analyzer (Micromeritics ASAP 2020) for sample preparation, surface area determination and as an automated dosing system for the adsorbing gas. A Calvet-type twin microcalorimeter (Setaram DSC 111) is used in isothermal mode for direct measurements of heats of adsorption. It enables measurement of heats of gas-solid interaction at temperature range from 4 °C to 350 °C. Experimental methodology will be discussed and the results of measurements of heats of water adsorption on ZrO2 and HfO2 surfaces will be reported. We successfully measured water adsorption enthalpies on monolayer quantities of samples with total surface area of several square meter. For monoclinic zirconia (1.6 m²/g) and hafnia (6.4 and 65 m²/g) samples annealed at 800 °C in vacuum, heats of water adsorption on most energetics sites were found to be in the range 274-291 kJ per mole of water.

P5.11 Novel Nitrogen Radical Cleaning Technique for UHV Chamber Wall. Masaru Ebitani 1, Seigo Tsukishima 2, Masaru Hori 2, Shoji Den 1 and Hiroshi Kano 1; 1 Foresight Techno Co., Ltd., Tokyo, Japan; 2 Department of Engineering, Nagoya University, Nagoya, Japan.

We have proposed the novel radical cleaning technique in which N radicals were employed for deduction of contaminant(H2O, H2, N2) from the wall surface in an ultrahigh vacuum chamber. So far various techniques have been made. For example, the temperature of the chamber was increased to 200-250°C and kept for a long time, and hereby contaminants released from the wall with the thermal desorption could be exhausted with a vacuum pump. In this technique, however, there has been a serious problem that the function parts of the UHV chamber were deteriorated because they were kept under the high temperature conditions for a long time. As the other technique with He/Ar gas, it has been employed for producing active species. In this technique, there have been still problems as well. A function part's surface was much damaged by the active species such as ion and electron of high energy. As a new technique to solve these problems, in this study, N radicals with high internal energy and high reactivity were irradiated to the chamber wall. The desorption through the chemical reaction between the radical and contaminants will be performed by the radical enhanced reactions which break off the molecule bonds of the solid surface. In the experiments to realize these new concept for the chamber wall cleaning, the contaminants were actually identified to be removed completely from the UHV chamber wall by the radical irradiation. The plasma parameters of the N radical source used in this experiment were investigated by VUVAS(vacuum ultraviolet absorption spectroscopy) method and double probe method. During N radical irradiation, the temporal gas desorption from the samples(SUS304/AI/SiO2 substrates were initially contaminated by H2O, and another were not contaminated) was analysed by using QMS, and the surface chemical structure of the sample was analysed by XPS. Contaminants were decreased, as a sample A(the contaminated sample was irradiated by N plasma) and sample B(the contaminated sample non-irradiated by N2 plasma) were heated and the presence of zinc oxide was observed. As a result, the out gas was able to be reduced in the sample irradiated by N radical. The measured electron density and temperature irradiated by the radicals were low levels not to influence the surface damage of sample. By XPS measurement, it was confirmed that the N radicals were absorbed on the surface of the sample through the N radical irradiation. These experimental results show the desorption of contaminants from the wall in the UHV chamber using N radical irradiation, which will open a new cleaning technology without any damage.

P5.12 Understanding of Surface Phenomena Responsible for the Selective Growth of Ge on Si over SiO2. During Molecular Beam Epitaxy. Qinling Li 1, Joshua L. Krauss 3, Stephen Hersee 2 and Sang M. Han 1; 1 Chemical & Cancer Engineering, University of New Mexico, Albuquerque, New Mexico; 2 Center for High Technology Materials / Electrical Engineering and Computer Engineering, University of New Mexico, Albuquerque, New Mexico; 3 Materials Science and Engineering, University of Wisconsin, Madison, Wisconsin.

We have previously demonstrated the growth of high-quality Ge through nanoscale openings in a patterned SiO2 template [Li et al., APL, 81(24), 5032 (2002)] as well as by "touchdown" of nanoscale (~7 nm) Ge pods through a thin layer of SiO2 [Li et al., APL, 81(11), 2087 (2002)] during molecular beam epitaxy. These two techniques are designed to square only on selective growth of Ge on exposed Si rather than on SiO2. In order to understand the surface phenomena responsible for the selective growth, we have experimentally measured the removal rate of Si (~1.2 nm) and the SiO2 (~1.5 nm) on Si(001) upon intermittent Ge exposure, using X-ray photoelectron spectroscopy. For the thin SiO2 layer, the Ge exposure creates openings through the SiO2 layer to the underlying Si. These openings grow laterally as a function of time, provided that the Ge lateral overgrowth is prevented with low Ge flux. The thickness of the remaining SiO2, however, remains constant according to the high-resolution, cross-sectional transmission electron microscopy images taken before and after the Ge exposure. Due to the thin opening size, the reaction rate accelerates with Ge exposure time. In contrast, the Ge exposure does not remove SiO2 from the thick layer. Based on the desorption rate of Ge from the thick SiO2 as a function of substrate temperature, we have determined that the reaction between Ge and Ge2O3 on SiO2 takes place with an activation energy of 42 ± 3 kJ/mol, which is on the order of Van der Waals force, rather than a strong chemical bond. That is, the weak interaction between Ge and SiO2 and therefore the high desorption rate of Ge are responsible for the selective growth of Ge on Si, rather than on SiO2. We surmise that the difference between thin and thick SiO2 stems from Ge diffusion through the pinholes that exist in a thin layer of SiO2 and a subsequent reaction, Ge + SiO2 + Si → GeO2 + SiO1, where the products are highly volatile at the growth temperature.


The growth mechanism of amorphous semiconductors from gas phase deposition is not well understood, even for hydrogenated amorphous silicon (a-Si:H) which can be considered as a model system for fundamental research on surface processes during thin film growth [1]. To comprehend the interactions between gas phase species such as SiH3 radicals - known to be the key radicals for a-Si:H growth - and the surface, it is essential to identify experimentally the nature of possible active surface sites for radical adsorption. Using the surface-sensitive nonlinear optical technique of second harmonic generation (SHG) we present evidence for the existence of dangling bonds and Si-Si strained bonds in the surface region of a-Si:H. Spectroscopic SHG measurements on hot wafer chemical vapor
deposited a-Si:H thin films show two resonance peaks at a photon energy of ~1.2 and ~1.5 eV. We argue that the ~1.2 eV peak is associated with bond defects caused by molecular oxygen during experiments and real-time SiH experiments during growth. The ~1.5 eV peak is expected to represent a resonance at Si(100) due to strained Si-Si bonds and the creation of dangling bonds due to the abstraction of hydrogen by the SiH radical. [1] W.M.M. Kessels, J.P.M. Hoefnagels, P.J. van den Oever, Y. Barrell, and M.C.M. van de Sanden, Surf. Sci. Lett. 247, 805 (2003).

P5.14 Mapping Water Reactivity at Oxide Surfaces. Jorge O. Soto 1,2 and Elam A. Leed 1,2; 1Physics, Penn State, University Park, Pennsylvania; 2Materials Research Institute, Penn State, University Park, Pennsylvania; 3Materials Science and Engineering, Penn State, University Park, Pennsylvania.

A Density functional theory (DFT) modeling technique has been developed for mapping the spatial distribution of reactive sites on oxide surfaces. The technique examines the "hardness/softness" of surface sites to obtain a reactivity index for dissociative chemisorption of water. Validity of the reactivity index is given by comparison with calculated energy barriers and reactivity trends with varying composition against experimental results. The reactivity mappings are used to determine the most important sites for chemisorption, and to determine the effect of chemisorption on reactivity of neighboring sites. The method can also be converted to cumulative distributions of reactivity to facilitate direct comparison between surfaces of different oxides. A possible adaptation of the mapping method to investigate the reactivity of surfaces with respect to H2 is discussed.

P5.15 Nonequilibrium Activated Dissociative Chemisorption: SiH4 Reactions on Pt(111) Studies in Atomic Resolution Electron Microscopy. Sanwu Wang 1,2, Sergey N. Rashkeev 1,2, Sokrates T. Pantelides 2,1, Karl Sohlberg 1,2, and Elam A. Leed 2,3; 1Physics, Penn State, University Park, Pennsylvania; 2Materials Research Institute, Penn State, University Park, Pennsylvania; 3Materials Science and Engineering, Penn State, University Park, Pennsylvania.

A three-parameter local hot spot model of gas-surface reactivity is employed to analyze and predict dissociative sticking coefficients for SiH4 incident on Si(100) under varied nonequilibrium conditions. Two Si surface oscillators, and the molecular vibrations, rotations, and translational energy directed along the local surface normal are active degrees of freedom in the microcanonical kinetics. The threshold energy for SiH4 dissociative chemisorption is found to be 19 kJ/mol, in qualitative agreement with recent DFT calculations for aluminum oxide. A simple scheme for increasing the rate of chemical vapor deposition of silicon from SiH4 at low surface temperatures is suggested.
The Effect of Substrates/Ligands on Metal Nanocatalysts Investigated by Scanning Tunneling Spectroscopy and Microscopy

Surface Defects on TiO₂(110): From Atomic and Electronic Structure to Catalytic Activity.

Heterogeneous Photocatalysis of Oxidation of Acetaldehyde using Titanium Nanotubes.
The metal-oxide interface is of fundamental importance in many areas such as microelectronics, corrosion and catalysis. Magnetic and iron display an important role in industrial processes such as the production of hydrogen and the synthesis of ammonia. The ability of controlling the size and arrangement of Fe nanostructures may influence the way catalytic processes take place. Furthermore, the self-assembly of ordered arrays of metal nanoclusters is a particularly promising subject for microelectronics and ultra-high density recording. We have studied the formation of Fe nanostructures on the magnetite (111) surface of single crystals and thin films. The FeO3(111) surface exhibits an hexagonal 42 Å superstructure, when annealed in oxygen atmosphere [1]. We have shown that this highly regular pattern is useful as a template for the self-assembly of nanostructures. We have deposited Fe films of 0.2, 0.5, 1 and 2 Å thickness at room temperature by means of electron beam evaporation. STM images prove that ordered nucleation of nanoclusters takes place only on the patterned regions of the surface, while random nucleation takes place on the unpatterned regions. These results have been reproduced in the case of a 0.5 Å Cr film. The metal nanostructures are characterized by a very regular size distribution over a length of several hundreds nanometers. Our results demonstrate that the self-assembly of crystalline Fe and Cr nanostructures takes place on the preferential nucleation sites provided by the nanopatterned FeO3(111) surface. We suggest that ordered arrays of nanostructures could be grown on different oxides displaying long-range surface reconstruction, as recently demonstrated by the growth of ordered Pd clusters on ABO3 [2].

References:

11:15 AM P6.9/R9.9
In situ Observation of Electrode Reactions on Solid Electrolytes Probed by Microspectroscopy. Bjorn Luerssen, Holger Fischer and Juergen Janek; Physical Chemistry, Justus-Liebig-University Giessen, Giessen, Germany.

In-situ microspectroscopic investigations of metal (Pt) and oxide electrodes deposited on the ion conducting solid electrolyte YSZ (= yttria stabilized zirconia) contribute to the mechanistic understanding of the electrode processes under polarization conditions. In our experiments we use Photoelectron Emission Microscopy (PEEM) and Scanning Photoelectron Microscopy (SPEM) to investigate the behaviour of platinum electrodes upon anodic and cathodic polarization and to obtain local chemical information about the electrode and the electrolyte material. Three different types of electrodes were used: porous Pt paste electrodes, microstructured electrodes and dense Pt electrodes prepared via pulsed laser deposition (PLD). The results upon anodic polarization show (in contrast to the literature [1]) the formation of normal chemisorbed oxygen on the platinum surface [2]. Upon cathodic polarization reduction fronts are observed at the surface of the electrolyte which are interpreted as a local increase of the electron concentration due to the reduction of zirconium dioxide [3]. This reduction is almost complete in the case of polycrystalline YSZ, i.e. Zr(0) species can be identified in the XPS spectra. The lowest oxidation state of the single crystalline samples is (under our experimental conditions) Zr(1+). The dense electrodes allow the exact microscopic determination of the three phase boundary as the place of the oxygen evolution. For the first time, a surface reaction could be imaged with SPEM. The experimental results are presented together with mechanistic considerations on both the NEMCA effect (NEMCA = Non Faradaic Electrochemical Modification of Catalytic Activity) and the cathodic reduction of the solid electrolyte [4]. [1] S. Ladis, S. Kennou, S. Bebelis, C. G. Vayenas, J. Phys. Chem., 1993, 97, 8845 [2] B. Luerssen, S. Guenther, H. Marbach, M. Kiskinova, J. Janek, R. Imbihl, Chem. Phys. Lett., 2000, 316, 331 [3] B. Luerssen, J. Janek, R. Imbihl Solid State Ionics, 2001, 141-142, 701-707 [4] B. Luerssen, S. Guenther, M. Kiskinova, J. Janek, R. Imbihl Phys. Chem. Phys., 2002, 4, 2673-2679

11:30 AM P6.10/R9.10
In-situ Monitoring of Oxygen Spillover Ions on Pt/YSZ Electrodes. Juergen Janek1, Bjorn Luerssen1, Holger Fischer1 and Sebastian Guenther2; 1Physical Chemistry, Justus-Liebig-University Giessen, Giessen, Germany; 2Department Chemie, Ludwig-Maximilians- Universitaet Muenchen, Muenchen, Germany.

In-situ microspectroscopic investigations of metal (Pt) and oxide electrodes deposited on the ion conducting solid electrolyte YSZ (= yttria stabilized zirconia) contribute to the mechanistic understanding of the processes at the three phase boundary and thus of the catalytic processes under polarization conditions [1]. The general aim of our studies is the control of catalytically active surfaces via ion-pumping in electrochemical cells. In our experiments we use Photoelectron Emission Microscopy (PEEM) and Scanning Photoelectron Microscopy (SPEM) to investigate the behaviour of platinum electrodes (prepared by pulsed laser deposition) during anodic polarization and to obtain local chemical information about the electrode and the electrolyte material. The SPEM allows two working modes: acquiring spectra (with an energy resolution of ca. 0.2 eV) or images (on a specific kinetic energy with a spatial resolution of approximately 500 nm). By this means it was possible to image the surface diffusion of oxygen spillover ions in-situ by SPEM. As the diffusion process is too fast for a direct imaging in SPEM we chose an indirect way: Firstly, the electrode surface was covered with carbon. Afterwards, the polarization was started and the surface reaction C + 2 O(ad) -> CO2 was imaged [2]. References: [1] C. G. Vayenas et al., Electrochemical Activation of Catalysis, Kluwer Academic/Plenum Publisher, New York 2001 [2] B. Luerssen, H. Fischer, J. Janek, S. Guenther, In Situ Microscopy of Polarized Pt/YSZ Electrodes, Solid State Ionics: The Science and Technology of Ions in Motion, World Scientific, Singapore 2004, pp. 139-149