

SYMPOSIUM P

In-Situ Studies of Gas/Solid Surface Reaction Dynamics

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* Invited paper

8:30 AM *P1.1

In-situ Observation of Oxidation Reactions at Si(001) Surfaces using Synchrotron Radiation Photoelectron Spectroscopy. Akitaka Yoshigoe, Kousuke Moritani and Yuden Teraoka; 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* analyzing adsorbed species on solid surfaces and moreover 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 in O₂ ambient and the oxidation at Si(001) surfaces induced by translational kinetic energy (E_k) 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. E_k of O₂ is controlled by a supersonic molecular beam (SSMB) technique. E_k of O₂ can be controlled up to about 2.3eV by exploiting the high temperature nozzle (Max: 1400K). Real-time SR-PES monitoring O-1s and Si-2p core levels measured in about 5 and 10s can be achieved even during exposing SSMB. It is known that the thermal oxidation is varied by both surface temperature and O₂ pressure. In the oxidation of Langmuir-type adsorption mode in which merely progresses with dissociative O₂ chemisorption, the following results are obtained; (i) Si¹⁺ is observed without any oxidation states which means that SiO₂ is unformed at the initial oxidation. (ii) Oxidation states consecutively change (Si¹⁺→Si²⁺→Si³⁺→Si⁴⁺). (iii) Higher oxidation numbers appear earlier at much higher temperature, we directly identify the thermal activation for surface migration and enhancement of SiO₂ formation. Comparing the kinetics of O₂ adsorption and time evolution of Si oxidation states, we will discuss the reaction mechanisms on thermal oxidation at Si(001) surfaces. We observed the time evolution of Si oxidation states (Siⁿ⁺; 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 Si¹⁺, thus SiO₂ is unformed at the initial oxidation stages. (ii) Si¹⁺ and Si³⁺ densities at unit oxide thickness are unchanged even with the progress of oxidation. (iii) Si²⁺ changed to Si⁴⁺. (iv) 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 E_k 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 Takakuwa; 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 initial oxidation on 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 clean surface area 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 600°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. Thus the simultaneous measurement of the 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-order spots (1/2 0) 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 diffraction spots. 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 significantly with oxide coverage. 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 Curson^{1,2}, Steven R. Schofield³, Oliver Warschcow^{1,4}, Nigel A. Marks^{1,4}, Hugh F. Wilson^{1,4}, Marian W. Radny³, Phil V. Smith³, David R. McKenzie^{1,4}, Thilo C. G. Reusch^{1,2} and Michelle Y. Simmons^{1,2}; ¹Centre for Quantum Computer Technology, University of New South Wales, Sydney, New South Wales, Australia; ²School of Physics, University of 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 tunneling 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 dominant species on the Si(001) surface are the PH₂ + H and PH + H₂ and hemihydrides, with other species such as P + 3H and isolated end-bridge bonded P atoms less prevalent. Monitoring the density of each species as a function of time or slight increase in sample temperature reveals qualitative information about the relative stability of the species. Additionally, dissociation reactions can be followed directly in sequences of STM images. For example the reaction sequence PH₂ + H to PH + H₂ to P + 3H is routinely observed at room temperature (RT), on the timescale of minutes, with the reaction products remaining bound to the surface. The reverse reactions are never seen. The majority of reactions that occur on the PH₃ dosed Si(001) surface are either the decomposition of a P containing molecule, such as the sequence described above or reaction of a PH₂ moiety with another species, due to the ability of the PH₂ moiety to diffuse along dimer rows at RT. With the aid of DFT calculations we can explain multi-step reaction sequences imaged by STM. Our results provide a comprehensive description of the surface chemistry of the PH₃/Si(001) system at room temperature and also infer the mechanism by which P atoms are incorporated into the surface as the temperature of the surface is increased.

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 for the H₂ desorbing molecules, which can be fitted by cosⁿθ 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 localized hot atom abstraction, involving two neighbors dimers inside a dimer column. Then, we have measured angular distribution of H₂

(D2, HD) molecules created by impinging H (D, H+D) atoms on hydrogenated (deuterated) Si(100) at 600K, 450K and 300K, to evaluate surface reconstruction effect on abstraction pathways. 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 *P1.5

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 from the gas phase at 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 coverage, temperature, and time. Recently, we have examined the role of both carbonyl and amine functionalities in the adsorption process by studying model aldehydes 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 dimer atom. At room temperature, 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. Formaldehyde, the simplest aldehyde, shows remarkably rich chemistry on the Ge(100)-2x1 surface. At room temperature, formaldehyde 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 molecule and oxidizes the other, 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 P1.6

Arrangement of SiC Islands after Formation of Si(001)-c(4x4) Structure Using Monomethylsilane. Masayuki Harashima, Kanji Yasui, Masasuke Takata and Tadashi Akahane; Nagaoka University of Technology, Nagaoka, Niigata, Japan.

Recently, fabrications of quantum dots made from IV column semiconductors such as SiGe and Ge on Si substrates have attracted much attention. For 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 10^{11} cm^{-2} has been achieved using pre-growth of sub-monolayer carbon [1]. However, formation of regularly arranged nano-dots, using only self-assembling technique, has never been reported so far. Authors have found that Si(001)-c(4x4) reconstructed surface, which has step-bunching and little defect, appeared after supply of monomethylsilane (MMS) on Si(2x1) surface and disappeared as SiC nucleates. AFM measurements showed that SiC dots were arranged along $\langle 010 \rangle$ 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 tunneling microscopy (STM). And the contribution of the step bunching to the arrangement of SiC islands was investigated. Si substrates, which were cut from n-type Si(001)-2° off wafers, were used. 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 1.3×10^{-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 were 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 $\langle 1-10 \rangle$ -2° off substrates, steps run straight along $\langle 110 \rangle$ axis. At 700°C, c(4x4) surface with 45nm step separation was formed. After annealing the surface at 675°C for 13 h, SiC islands about 40nm in diameter were formed and arranged along $\langle 110 \rangle$ axis, which coincide with step separation and step direction, respectively. These results indicate that the degree of the step-bunching influenced to the density and the size of SiC islands. [1]

M. Stoffel, L. Simon, J. L. Bischoff, D. Aubel, L. Kubler and G. Castelein, Thin Solid Films 380 (2000) 32.

11:15 AM P1.7

Growth Kinetics and Relaxation Mechanism of Very Thin Epitaxial Si Films on (100) Germanium. Renaud Bonzom, Frederik Leys, Roger Loo, Olivier Richard, Danielle Vanhaeren, Jens Rip, Jan Van Steenberghe, Brice De Jaeger, Hugo Bender, Wilfried Vandervorst, Matty Caymax and Marc Meuris; IMEC, Leuven, Belgium.

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, TXRF, Auger spectroscopy and HRTEM. The stress 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 HRTEM and XRD. Surface roughness is obtained from AFM measurements. For growth at 575°C, the tensile 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 HRTEM. 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 3D growth that 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 through a mixed Stranski-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 P1.8

Synchrotron Radiation Photoemission Study of the Cs and O co-adsorbed InP(100) Surface for Applications in Negative Electron Affinity Devices. Dong-Ick Anthony Lee^{1,4}, Zhi Liu^{3,4}, Shiyu Sun^{3,4}, Samuel P. A. Peterson^{2,4}, William E. Spicer⁴ and Piero Pianetta^{2,4}; ¹Materials Science and Engineering, Stanford University, Stanford, California; ²Electrical 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-adsorbed layer on InP(100) and its role are realizing a 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 undertaken to follow 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 InP occurs at the same time due to unavoidable adsorption of oxygen from the residual 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, 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 more rapid at the interface between Cs/O complex and the substrate than at the surface.

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

1:30 PM *P2.1

In-Situ Studies of the Oxidation of Strained, Coherent Cu (001) Films. Paul Fuoss, J. A. Eastman, G.-W. Zhou, L. E. Rehn, P. M. Baldo, L. J. Thompson and D. D. Fong; Materials Science Division, Argonne National Laboratory, Argonne, Illinois.

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 behavior of the Cu (001) surface at the Advanced Photon Source via in-situ x-ray diffraction techniques. Single crystal (001) Cu thin films grown on (001) SrTiO₃ substrates are oxidized to form crystallographically aligned Cu₂O nano-islands on the Cu surface. By measuring oxide island growth kinetics as a function of oxygen partial pressure, the thermodynamic limit between oxide growth and reduction has been determined for several temperatures and film thicknesses. We find the Cu/Cu₂O phase boundary for the nano-islands at a much larger oxygen partial pressure than predicted by bulk phase equilibria, and also find that the temperature dependence of this phase boundary is smaller than expected. Large reversible changes in the oxide lattice parameter of up to 0.5% in response to controlled variations in oxygen partial pressure in the chamber are also observed, possibly indicating an unexpectedly large stoichiometric range in Cu₂O nano-islands compared with bulk Cu₂O. Significant differences are seen between thin film and bulk single crystal samples, suggesting that substrate constraints are influencing oxidation behavior.

2:00 PM *P2.2

In-Situ X-Ray Measurement of Strains in Thermally Grown Oxides. Boyd W. Veal¹, Arvydas P. Paulikas¹, Peggy Y. Hou², Arun Reddy³, Arthur H. Heuer³, Manfred Ruhle⁴, Peter M. Baldo¹, Robert C. Birtcher¹, Guy Jennings¹ and Jennifer A. Linton¹; ¹Argonne National Laboratory, Argonne, Illinois; ²Lawrence Berkeley National Laboratory, Berkeley, California; ³Case Western Reserve University, Cleveland, Ohio; ⁴Max-Planck-Institut für Metallforschung, Stuttgart, Germany.

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 on single and polycrystalline NiAl, as well as Fe-Cr-Al, Ni-Cr-Al and Fe-Ni-Cr alloys. Measurements have also been acquired from Cu₂O grown on Cu and Cu-Au alloys. Using synchrotron X-rays (Advanced Photon Source, Beamline 12BM, Argonne National Laboratory), Debye-Scherrer diffraction patterns from the thermally grown oxides were recorded every 5 minutes during oxidation and subsequent cooling. The diffraction patterns were analyzed to determine strain in the oxides, as well as phase changes and degree of texture, as the oxides developed and evolved. As specimens were cooled to room temperature, the buildup of residual strain resulting from thermal expansion differences between oxide and substrate was followed. Debonding during cooldown was monitored. Generally, compressive growth stresses were observed in oxides isothermally formed on FeCrNi, FeCrAl and Cu alloys suggesting that oxide growth tends to occur internal to existing oxide as a result of the metal/oxygen cross diffusion process. For the alumina formers, strains in the early alpha-Al₂O₃ are typically tensile, a consequence of the transformation of transition aluminas to the stable alpha-phase, which involves a significant volume contraction. Occasionally, strains were simultaneously measured for both the alpha-Al₂O₃ (tensile) and for the transition alumina (compressive). The rate of transformation (e.g., at 1100 C) is strongly dependent on the presence of substrate components such as Fe or Cr, and the orientation of the crystallographic face being oxidized. For alpha-Al₂O₃ on beta-NiAl, after transformation, growth stresses at 1100 C are less than ~300 MPa and may be tensile or compressive depending on substrate composition (Ni₅₀Al, Ni₄₀Al, and Ni₅₀Al-Zr). Implications to growth mechanisms will be discussed. Creep was studied by monitoring strain relaxation after applying a stress to the oxide. This was accomplished by imposing an abrupt temperature change, exploiting the thermal expansion difference between oxide and substrate. For alpha-Al₂O₃ on beta-NiAl, it appears that creep is governed by grain boundary diffusion as described by the Coble model. Work supported by DOE-BES under contract number W-31-109-ENG-38

2:30 PM P2.3

Thermal Stability and Decomposition Mechanism of Very Thin Oxide on Ti(0001) Surface Studied by Real-Time Photoelectron Spectroscopy. Yuji Takakuwa¹, Syuichi Ogawa¹, Masayuki Ohira¹, Shinji Ishidzuka², Kousuke Moritani³, Akitaka Yoshigoe³, Yuden Teraoka³, Yoshiyuki Mizuno⁴, Hideki Tonda⁵ and Teiichi Homma⁶; ¹Tohoku University, Sendai, Japan; ²Akita National College of Technology, Akita, Japan; ³Japan Atomic Energy Research Institute, Sayo-gun, Japan; ⁴Stanford University, Menlo Park, California; ⁵Kumamoto University, Kumamoto, Japan; ⁶Chiba

Institute of Technology, Narashino, Japan.

A very thin TiO₂ layer grown by thermally oxidizing Ti metal surfaces with O₂ is of practical importance not only as a surface passivation layer but also as a surface functional layer with the photocatalyst capability, biocompatibility and so on. Although the bulk TiO₂ crystal is thermally stable up to 1800°C, it is known that a native oxide layer on Ti metal surfaces is easily decomposed at temperatures as low as 200-300°C. In this study, therefore, the growth and subsequent decomposition kinetics of very thin oxide on the Ti(0001) surface was monitored in real time by valence-band and core-level photoelectron spectroscopy to clarify the thermal stability and decomposition mechanism of very thin oxide based on the obtained information on the oxygen uptake, oxidation state, oxide thickness, density of states near the Fermi level and work function. Ti 2p and O 1s photoelectron spectroscopy using synchrotron radiation at photon energies of 662 eV (surface sensitive) and 1549 eV (bulk sensitive) was performed using a surface reaction analysis chamber (SUREAC2000) at the beamline BL23SU of the SPring-8, Mikazuki-cho, Japan. Under the oxidation condition at 400°C and 6x10⁻⁵ Pa of O₂ pressure, an oxide layer grew rapidly up to 100 Å in thickness and the oxide with thickness of 100 Å was mainly composed of TiO₂ at the subsurface, but the oxidation state of TiO, Ti₂O₃ and Ti₃O₅ remained near the interface with a comparable amount to that of TiO₂. It was confirmed by RHEED and LEED that the resultant oxide surface showed a $\sqrt{3} \times \sqrt{3}$ structure, indicating that the epitaxial growth of oxide on the Ti(0001) surface progresses successfully up to 100 Å. As soon as O₂ gas supply was stopped with keeping the substrate temperature at 400°C, the oxygen uptake curve showed a significant, monotonous decrease with decomposition time for the bulk sensitive observation, while it changed with repetitions of an almost saturation and a rapid decrease for the surface sensitive observation. Corresponding to the changes of the decrease rate in oxygen uptake, the amount of TiO, Ti₂O₃ and Ti₃O₅ showed an oscillatory behavior with different periods and phases, while the amount of TiO₂ decreased monotonously. As a result, it turns out that TiO₂ is rather unstable even at 400°C and the oxidation state can change in both the directions of Ti₂O₃ → TiO and Ti₂O₃ <- TiO during decomposition. Thus thermal decomposition of the very thin oxide proceeds with the complicated changes of oxidation state, oxygen uptake and oxide thickness. These results are further discussed based on the decomposition time dependence of the work function, O 2p intensity and density of states near the Fermi level obtained by valence-band photoelectron spectroscopy using a He-I resonance line (21.22 eV) to clarify the chemical state of the topmost surface, which is closely concerned with O₂ desorption during decomposition.

2:45 PM P2.4

In Situ Oxidation and Plasma Studies for Magnetic Tunnel Junctions: The Mechanism of Plasma Oxidation of Ultra-Thin Aluminum Films Unravelled. Karel Knechtel, Henk J. M. Swagten, Bert Koopmans, Wim J. M. de Jonge and Richard M.C.M. van de Sanden; Applied Physics, Eindhoven University, Eindhoven, Netherlands.

Plasma oxidation of thin aluminum films is a commonly used technique to form thin aluminum oxide barriers for application in magnetic tunnel junctions (typically 1 nm). In this technique a glow discharge in oxygen ($P = 5-12$ W, $p = 5-40$ Pa) is used to oxidize ultrathin sputtered aluminum films. In comparison with thermal oxidation the process is faster and provides high values of tunneling magnetoresistance (TMR) but at the cost of higher resistance-area products ($R \times A$). 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 "hops" 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 single wavelength ellipsometry 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 temperature is locally enhanced due to the thermal spike of an impinging ion. Additionally, due to the presence of atomic oxygen in the plasma, the field over the oxide during oxidation is enhanced by the increased adsorption of atomic oxygen on the oxide surface. Including both effects in an adjusted equation for the oxidation rate provides a good agreement between model and experiments. The model provides new insights into plasma based oxidation of ultra thin films and offers opportunities to further control the quality of the tunnel barrier.

3:30 PM *P2.5

Early-Stage Oxidation of Cu and Cu-Au Alloys Investigated by In Situ UHV-TEM. Guangwen Zhou¹, Liang Wang², Robert C. Birtcher¹, Judith C. Yang², Pete M. Baldo¹, John E. Pearson¹ and Jeff A. Eastman¹; ¹Materials Science Division, Argonne National Laboratory, Argonne, Illinois; ²Department of Materials Science and Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania.

Understanding the microscopic processes controlling the oxidation of metal surfaces has practical importance in many fields including corrosion, heterogeneous catalysis, and dielectric growth. Growth 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 thermodynamic 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 during initial oxidation in dry oxygen. Compared with the behavior of Cu films, the oxidation of Cu-Au alloys shows more complexity, such as a dependence of the kinetics and oxide morphology on the Au composition. For example, increasing Au content in the alloys decreases the nucleation and growth rate of the oxide islands, and increases the apparent activation energy required for the oxide growth; the oxidation of (100)-oriented Cu-Au alloys with low Au content at $\sim 600^{\circ}\text{C}$ results in the formation of Cu₂O oxide islands with a dendritic morphology and a non-uniform lateral distribution of Au around the islands. Evolution 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 quantitatively explain the formation of some of the novel oxide nano-structures.

4:00 PM P2.6

Energetics and Kinetics of Cu-Au Alloy Oxidation Studied by *in situ* UHV-TEM. Liang Wang¹, Guang-Wen Zhou², Jeff A.

Eastman² and Judith C. Yang¹; ¹Department of Materials Science and Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania; ²Materials Science Division, Argonne National Laboratory, Argonne, Illinois.

Elucidating the initial oxidation mechanisms of alloys has great impact on many diverse fundamental and engineering problems, from corrosion, to passivation properties, and to synthesis of self-assembled nano-oxide arrays for optical, magnetic or catalytic applications. *In situ* ultrahigh vacuum transmission electron microscopy (UHV-TEM) has been demonstrated to be a powerful tool in visualizing this transient regime of pure metal oxidation. Since most engineering materials are alloys, it is critical to understand how the oxide nucleation and growth processes of a metal are affected by the presence of secondary elements. In this report we use Cu_{1-x}Au_x (001) single crystal alloys to model the oxidation behavior of alloys with one oxidizing component and one inert component. We systematically examined the effect of Au concentration (x equals 5%, 15%, 38% and 50%), and reaction temperature on oxide nucleation rate, island density, growth kinetics, etc. A comparison to the oxidation behavior of pure Cu (001) thin films is made. For both Cu and Cu-Au alloys, an incubation time exists where no oxide formation is noted, then epitaxial Cu₂O islands rapidly nucleate until a saturation island density is reached, and finally these islands grow 3-dimensionally until coalescence. A longer incubation time is noted for the Cu-Au alloys as compared to Cu, but the nucleation rate, i.e. the time from the first 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. The Cu₂O islands have a slower growth rate on the alloy thin films than on pure Cu samples, which could be due to Cu diffusion through Cu_{1-x}Au_x as compared to Cu. Quantitative insights on the energetics of the early stages of oxidation will be discussed.

4:15 PM P2.7

Observing the Dynamics of Metal Alloy Oxidation using Low-Energy Electron Microscopy. Kevin F. McCarty and J. P. Pierce; Materials Physics Department, Sandia National Laboratories, Livermore, California.

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 phases form. 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 Å and 6 Å, 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 and metal cations 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 Å. The second oxide phase that we observe is a type of alumina,¹ which forms oblong 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 thermodynamic stability of both the alumina and nano-rod phases. At a fixed temperature, the pressure of oxygen in equilibrium with the oxide phases is determined by finding the pressure at which individual oxide islands neither shrink nor grow. Both the thin-film alumina and the nano-rod phase are remarkably less stable than bulk alumina. We attribute this reduced stability to fact that the oxide film phases are strained and extremely thin.¹J. 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.

4:30 PM P2.8

Observation of the Oxidation of Ru(0001) by Low-Energy Electron Microscopy. Peter Sutter¹, Jan Hrbek^{2,1} and Robert Hwang¹; ¹Center for Functional 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(110)/Ru(0001) has attracted significant research interest recently. RuO₂(110)/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 general 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. Using dynamic observations by low-energy electron microscopy (LEEM), we find the formation of two oxidation products, an ordered epitaxial oxide and a rapidly nucleating nanocrystalline phase, when exposing Ru(0001) to NO₂ as a source of atomic oxygen. The relative abundance of these two products depends strongly on the substrate morphology (e.g., step density, defects), and can be tailored by altering the local supply of surface oxygen, e.g., by decorating steps with metal adatoms. Under conditions that favor ordered growth, we have investigated the nucleation, autocatalytic growth, and coalescence of epitaxial RuO₂(110) islands. Our work provides a demonstration of novel pathways towards control of the nucleation and growth of RuO₂, e.g., as a nanostructured substrate for oxide supported metal nanocrystal catalysts.

4:45 PM P2.9

Redox Processes in Ceria and Ceria-Zirconia. Ruigang Wang³, Yong Jiang³, Renu Sharma¹, James B. Adams^{3,2} and Peter A. Crozier¹; ¹Center for Solid State Science, Arizona State University, Tempe, Arizona; ²Chemical and Materials Engineering, Arizona State University, Tempe, Arizona; ³Science and Engineering of Materials Program, Arizona State University, Tempe, Arizona.

Three way catalysts using ceria-based oxides are extensively used to reduce pollutants from automobile exhaust systems. The ceria-zirconia (Ce_xZr_{1-x}O₂) catalysts are composed of nanometer-sized particles and show dramatic variations in redox properties which depend on oxide composition and aging. Environmental transmission electron microscopy (ETEM) is being used to make atomic level in situ observations of structural and chemical changes in the nanometer-sized particles under reducing/oxidizing atmospheres at elevated temperatures. We are synthesizing a number of different high-surface area cerias and ceria-zirconia catalysts. Our goal is to use ETEM to understand the chemistry of individual catalyst particles (5-50 nm) under reaction conditions and to identify the most reactive particles/surfaces with respect to size, shape, structure and composition by combining high-resolution imaging with electron energy-loss spectroscopy. Our measurements confirm the formation of a superlattice due to oxygen vacancy ordering in ceria during reduction. The influence of Zr on the superlattice formation will also

be evaluated. We are also developing appropriate density functional methods to understand how reducing/oxidizing conditions (oxygen partial pressure and temperature) affect CexZr1-xO2 particles, including the effect on crystal structure, surface energies and vacancy formation energies. We will present results from both the experimental and theoretical work on CeO2 and CexZr1-xO2.

SESSION P3: Atomic Oxygen and Organic Materials

Chairs: 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 Tzvetkov, 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 polymeric satellite materials in the low-earth orbit (LEO) space environment. For example, dodecanethiol adsorbs on gold to produce a densely packed SAM composed of Au-S(CH₂)₁₁CH₃ chains, tilted at 34° relative to the surface normal. Unlike bulk polyethylene, a SAM presents a well-ordered hydrocarbon film that does not electrostatically 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-eV O⁺ bombardment of a decanethiolate 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 at the 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, the reactions of AO, specifically O(³P) are the principal factor that determines the longevity of coatings on spacecraft vehicles in low Earth orbit. However, the elementary reaction steps that accompany the interaction of AO with organic substrates are poorly understood. To address this issue we have studied, *in situ*, the interaction between AO, generated from a thermal gas cracker and chemically distinct self assembled monolayers (SAMs) as well as polymeric substrates. The reactions of AO with n-alkanethiolate SAMs is initiated at the vacuum/film interface where H-atom abstraction from C-H bonds leads to the formation of oxygen-containing carbon functional groups. Subsequent reactions of these species with AO form volatile species (e.g. CO₂). This leads to the formation of a steady state etch front that is responsible for the loss of carbon from the film. After prolonged exposure, AO penetrates to the film/substrate and oxidizes thiolate S atoms. In contrast to n-alkanethiolate SAMs, the reactions of semi-fluorinated SAMs with AO are characterized by an initial induction period where no reactivity is observed and the chemical composition of the film remains unaltered. This induction period is ascribed to the inertness of both C-C and C-F bonds to AO and the dense, well-ordered structure generated by the SAM. After longer exposures, AO permeates through the fluorocarbon overlayer to the film/substrate interface. This leads to the oxidation of sulfur atoms and the concomitant desorption of intact adsorbate chains. Experimentally, this is evidenced by a loss of carbon and fluorine from the film while the chemical distribution of residual carbon as well as the C:F ratio remains nearly unchanged. In conjunction with the data obtained for n-alkanethiolate SAMs, these results highlight the influence that the SAMs chemical composition plays in controlling the elementary reactions that accompany the interaction of AO with organic films. Results will also be presented on the reactions of AO with hydrocarbon substrates that were modified by phosphorous ion implantation. These studies are motivated by the development of

phosphorous containing polymers with improved resistance to AO induced erosion. To develop a molecular level understanding of this phenomenon, the surface reactions of molecular and atomic oxygen with polyethylene substrates modified by phosphorous ion implantation have been studied. Reactions with AO produce selective etching of carbon from the surface and an increase in the degree of phosphorous oxidation; this ultimately produces a phosphonate structure at the surface. The selective etching of carbon from the surface by AO is also accompanied by significant morphological transformations as evidenced by AFM.

9:30 AM *P3.3

QM/MM Studies of Polymer Degradation by Hyperthermal Atomic Oxygen. Diego Troya, Lipeng Sun and George C. Schatz; Northwestern University, Evanston, Illinois.

We present theoretical studies of the degradation of polymers by several eV atomic oxygen that mimic the the erosion of polymers by hyperthermal oxygen in low earth orbit conditions. The theory is based on a mixed quantum mechanics/molecular mechanics potential energy function in which the reactive part of the polymer is treated with semiempirical electronic structure methods, and more distant regions are treated with the MM2 empirical force field. Classical molecular dynamics methods are then used to study reactions of O atoms with the polymers. The surface is modeled as an octane thiol self assembled monolayer on gold (111). Both hydrocarbon and perfluorinated hydrocarbons are considered. We also study the effect of a POSS (polyoligomeric silsequixane) cage.

10:30 AM *P3.4

Atomic Beam-Surface Scattering Studies of the Combined Effects of VUV Radiation and Hyperthermal O or Ar Atoms on the Erosion of FEP Teflon Surfaces. Amy Leigh Brunsvold and Timothy K. Minton; Chemistry and Biochemistry, Montana State University, Bozeman, Montana.

Surfaces of spacecraft flying in low Earth orbit (LEO) are exposed to an environment containing atomic oxygen, electromagnetic radiation, ions, electrons, and high-energy-charged particles. Atomic oxygen and molecular nitrogen are the major constituents in the residual atmosphere at LEO altitudes, and they collide with spacecraft surfaces at relative velocities of ~7.8 km s⁻¹. These high relative velocities lead to gas-surface collisions with many electron volts of collision energy in the center-of-mass reference frame. The energy associated with these hyperthermal collisions is in excess of many bond dissociation energies and may help promote materials degradation by allowing barriers to reaction or to collision-induced dissociation (CID) to be overcome. Spacecraft in LEO are also exposed to high fluxes of vacuum ultraviolet (VUV) radiation, which might contribute to the degradation of materials present on spacecraft surfaces. Fluorinated ethylene-propylene copolymer (FEP Teflon) is commonly used as a thermal blanketing material to provide protection for spacecraft from direct solar heat. It has been reported that FEP Teflon erodes under the combined exposure of VUV light and atomic oxygen, while the erosion by atomic oxygen alone is negligible. The sensitivity of polymer erosion rates to simultaneous and sequential exposure of VUV light has not yet been quantified. We have conducted a beam-surface scattering experiment that probed products scattered from a FEP Teflon surface that was bombarded by various combinations of atomic oxygen (in the ground O(³P)), Ar atoms, and VUV light. A laser-detonation source was used to create hyperthermal beams of atomic oxygen and argon. A deuterium lamp provided a source of VUV light. FEP Teflon that was exposed to VUV light alone yielded volatile reaction products (C_nF_m fragments) that were detected with a mass spectrometer. O(³P) atoms with 5 eV of translational energy did not react with a pristine FEP Teflon surface, but scattered reaction products were observed when VUV light also bombarded the surface. A hyperthermal Ar beam was used to determine if CID plays a role in the erosion of FEP Teflon through inelastic energy transfer. We detected scattered products when Ar atoms, with translational energies greater than ~9 eV, were directed at a pristine surface, indicating that energetic collisions (through CID) alone may lead to mass loss from FEP Teflon. The scattered CID product signal increased significantly when VUV light was present. Therefore, it appears that VUV light plays an important synergistic role in the mass loss of FEP Teflon by creating reactive sites and by producing relatively light fragments that can be dislodged from the surface by energetic gas-surface collisions.

11:00 AM P3.5

Deposition of Organic Thin Films using Energy Tunable Molecular Beams. Aravind S. Killampalli, Todd W. Schroeder and J. R. Engstrom; School of Chemical and Biomolecular Engineering, Cornell University, Ithaca, New York.

The deposition and growth of organic materials for applications in electronics and photonics differs fundamentally from that of more

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, whereas organic 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 $k_B T$. 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 shall review our efforts in using supersonic molecular beams as sources for film deposition, in particular, for the deposition of thin films of pentacene, an 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 N_2 , He and H_2 . We demonstrate that for these beams, kinetic energies over the range of $E_i = 1.4$ - 10.6 eV are possible, whereas incident molecular fluxes are on the order of 10^{15} molecules- $cm^{-2}s^{-1}$. Next, we will present recent results concerning the deposition of pentacene on SiO_2 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 determined by the trapping probability of pentacene, which decreases with increasing energy. However, in this same regime the trapping probability is found to decrease 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.

Bjerne S. Clausen, Stig Helveg, Jens Sehested, Poul L. Hansen and Jens R. Rostrup-Nielsen; Haldor Topsoe A/S, Nymoelevvej 55, DK-2800 Kgs. Lyngby, Denmark.

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 nanocluster 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 nanofibers. Specifically, the nucleation and growth of the graphene 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. References: (1) S. Helveg, C. Lopez-Cartes, J. Sehested P. L. Hansen, B. S. Clausen, J. R. Rostrup-Nielsen, F. Abild-Pedersen, J. K. Norskov, *Nature* 427, 426 (2004). (2) H. S. Bengaard, J. K. Norskov, B. S. Clausen, L. P. Nielsen, A. M. Molenbroek, J. R. Rostrup-Nielsen, *J. Catal.* 209, 365 (2002).

11:30 AM P3.7

Fabricating Inorganic-Organic Interfaces for Use in Molecular Electronics. Abhishek Dube¹, Manish Sharma¹, Andrew

Chadeayne², 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 interest has been developed in the past 5-10 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, communication with the macroscopic world requires the transport of electrical 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. alkanethiols 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. In this study we have studied the reactions of tetrakis(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 adsorption 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, and that there is no penetration of the monolayer, which 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 Fuoss 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. Bret Jackson, Chemistry, University of Massachusetts, Amherst, 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 atoms adsorbed onto 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 for 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 hot products. Our conclusions 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 terrace if the bonding carbon is allowed to pucker out of the surface plane. The Eley Rideal cross section for reaction with this H atom is very large. These predictions have been verified by recent experiments.

2:00 PM *P4.2

Reduction of Oxygen on Au(100) in Base: Lessons from the Gas-Solid Interface. Andrew A. Gewirth, Chemistry, University of Illinois, Urbana, Illinois.

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) via a two 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 in 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. Monika Margarete Biener^{1,3}, Juergen Biener² and Cynthia M. Friend^{1,3}; ¹Chemistry Department, Harvard University, Cambridge,

Massachusetts; ²Nanoscale Synthesis and Characterization Laboratory, Lawrence Livermore National Laboratory, Livermore, California; ³Division of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts.

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 [J. Vac. Sci. Technol. A 12, 192 (1994), Langmuir 2001 17, 4919 (2001)]. 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 S_n at higher coverages [J. Am. Chem. Soc. 125, 276 (2002)]. In our work, the interaction of sulfur with Au(111) was studied by real-time scanning tunnelling microscopy (STM) using sulfur dioxide as a source of sulfur. We will demonstrate the formation of a two-dimensional gold sulfide accompanied by a dynamic rearrangement of the surface. At early reaction times, adsorbed sulfur atoms (< 0.1 ML) lift the herringbone reconstruction of the Au(111) surface. At a sulfur coverage of 0.33 ML a ($\sqrt{3} \times \sqrt{3}$)R30° 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 monoatomic step height and small clusters develop. After a cumulative SO_2 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. Large vacancy islands of monoatomic depth form by coalescence of the pits generated by SO_2 exposure at 300 K. High resolution STM images reveal the formation of a well-ordered two-dimensional gold sulfide. Annealing the surface beyond 500 K leads to irreversible loss of sulfur 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

In-Situ Studies of Reversible Hydriding in Palladium Thin Films. Dillon Fong, J. A. Eastman, P. H. Fuoss, G. W. Zhou, L. E. Rehn, P. Baldo and L. J. Thompson; Materials Science Division, Argonne National Laboratory, Argonne, Illinois.

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 $SrTiO_3$ (001) substrates (0.4% misfit strain) and 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 in both the Pd-matrix and the Pd-hydride was 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 strain state. For films coherently strained to the $SrTiO_3$, we observe the formation of nanoscale hydride precipitates with lattice parameters near those of bulk $PdH_{0.64}$. 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

In-Situ Observations of CO_2 Mineral Sequestration Process. Renu Sharma, Michael J. McKelvey, Hamdallah Bearat, Andrew V. G. Chizmeshya and Ray W. Carpenter; Center for Solid State Science, Arizona State University, Tempe, Arizona.

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 possible sequestration process component, and (iii) and its chemical and structural similarity to the more complex

serpentine ($Mg_3Si_2O_5(OH)_4$) minerals. Partially dehydroxylated $Mg(OH)_2$ (brucite) single crystal fragments exhibit substantially increased reactivity at room temperature. BET measurements of 91% dehydroxylated fragments indicate the high surface area ($120 \text{ m}^2/\text{g}$) directly contributing to the increased reactivity. Room temperature carbonation of freshly formed nanocrystals has been observed in-situ via ETEM 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 Gatan Imaging Filter (GIF). Natural brucite single-crystal 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 CO_2 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 hydroxide diffraction spot intensity became diffuse at 166 C and only {111}MgO spots with streaking could be observed by 307 C. At room temperature the product was found to be very reactive and CO_2 and H_2O 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 CO_2 and H_2O content of the reaction product. Although, some hydroxylation was observed, H_2O 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 both C_k and O_k -edges of the samples after reaction matched those obtained from $MgCO_3$ (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 $La_{1-x}Sr_xCoO_{3-\delta}$ ($x=0.1, 0.2, 0.5$ and 0.7) Determined via Oxygen Permeation Measurements. Frederic H. B. Mertins, Dave H. A. Blank and Henny 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 $La_{1-x}Sr_xCoO_{3-\delta}$ ($x = 0.1, 0.2, 0.5$ 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 ionic and electronic 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 material, provided that the electronic transference number 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 $La_{1-x}Sr_xCoO_{3-\delta}$ ($x = 0.1, 0.2, 0.5$ 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 expected behaviour are observed 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. Mizusaki, Y. Mima, S. Yamauchi and K. Fueki, Nonstoichiometry of the Perovskite-Type Oxides $La_{1-x}Sr_xCoO_{3-d}$, J. of 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 Kinetics of Hafnium Diboride and Zirconium Diboride from Single Source Precursors. Yu Yang^{1,3}, Sreenivas Jayaraman^{1,3}, Jennifer E. Gerbi^{1,3}, Do-Young Kim², Gregory S. Girolami^{2,3} and John R. Abelson^{1,3}; ¹Dept. of Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois; ²Dept. of Chemistry, University of Illinois at Urbana-Champaign, Urbana, Illinois; ³Frederick Seitz Materials Research Laboratory, University of Illinois at Urbana-Champaign, Urbana, Illinois.

Zirconium diboride and Hafnium diboride are metallic ceramic materials which have high melting points, high hardnesses and low electrical resistivities. ZrB_2 and HfB_2 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 low temperature (200-300°C) grown films are amorphous, dense and conformal; the potential applications include impurity diffusion barriers to separate Cu from Si, and hard coatings for MEMS devices. To achieve conformal coverage on complex structures like deep trenches and MEMS, a very low surface reaction probability is desired. We perform temperature programmed reaction experiments to study the interaction of the precursors with different surfaces in the low flux (dosing) regime. In this regime, the decomposition reaction starts at 190°C, and the reaction probability is independent of flux and increases with temperature with apparent activation energies of 0.28 and 0.45 eV for Zr(BH₄)₄ and Hf(BH₄)₄, respectively. We identified that the growth is nucleation limited on clean Si and SiO₂ surfaces. Faster nucleation can be achieved by transiently increasing the precursor flux to high values. This effect and the growth under surface saturation conditions (high flux regime) were studied by in-situ spectroscopic ellipsometry. A Langmuir type of surface reaction mechanism is proposed based on these studies. We will show that the growth condition can be chosen to achieve excellent conformity and a range of growth rates. Current investigations are focused on studying the surface chemistry involved in the growth process using in-situ FTIR spectroscopy.

4:15 PM P4.8

Cavity Ring Down Spectroscopy Investigation of Sulfur-Assisted Nanocrystalline Diamond Chemical Vapor Deposition. Madalina Buzaianu, Vladimir Makarov, Brad Weiner and Gerardo Morell; University of Puerto Rico, San Juan, PR, Puerto Rico.

The addition of trace amounts of sulfur, in the form of hydrogen sulfide, to the diamond chemical vapor deposition reaction produces profound changes in the gas phase chemistry. We have found a four-fold increase in the deposition rate, from 0.1 to 0.4 microns with 500 ppm of hydrogen sulfide, for films grown at 700°C, which is the typical substrate temperature. Further, for films grown under 0.3% CH₄ and 500 ppm H₂S, the Raman intensity increases by an order of magnitude as the substrate temperature is reduced from 900 to 400 °C. This is a strong indication of improved film microstructure as the substrate temperature is reduced when S is available. The changes induced in the gas phase reactions and composition by the addition of H₂S during CVD were studied by Cavity Ring Down Spectroscopy (CRDS). We report experiments designed to detect the HS radical concentration as a function of distance from the reactor filament. The experimental setup used for such measurements is arranged for observation of the 0-1(28010.72 cm⁻¹) transition of HS. Since the HS radical has high value of the rotation constants both in ground and excited states (BX = 9.461 and BA = 8.521 cm⁻¹), the rotation spectrum of this radical is resolved even at high temperature and bulk conditions. The preliminary results suggest that H₂S leads to the formation of CS in the heat-activated volume around the filament, which turns back into H₂S in the cooler region above the substrate, while leaving C atoms deposited on the substrate surface to form diamond.

4:30 PM P4.9

Real Time Monitoring of Surface Reactions During MOCVD Growth of GaN on SiC by Spectroscopic Ellipsometry. Maria Losurdo^{1,2}, Maria M. Giangregorio¹, Pio Capezzuto¹, Giovanni Bruno¹, Tong-Ho Kim² and April S. Brown²; ¹Chemistry, IMIP-CNR, Bari, Italy; ²Dept of Electrical and Computer Engineering, Duke University, Durham, North Carolina.

III-nitrides, AlN, GaN, InN and their alloys have gained considerable interest because of their applications for optoelectronic devices covering the Vis-UV wavelengths. Presently, metalorganic chemical vapour deposition (MOCVD) is widely applied for the deposition of high-quality nitride structures. However, MOCVD suffers from the lack of real time diagnostics because of the high pressure environment. Thus, for MOCVD applications there is an increasing need for real time monitoring during growth not only for controlling process and material quality but also for understanding the growth mechanism. Herein we apply in situ real time spectroscopic ellipsometry for the investigation of the gas-surface interaction during all steps involved in the growth of GaN on SiC using r.f. plasma assisted MOCVD (PA-MOCVD). We also present data on the structural and interfacial properties of GaN nucleation on 4H- and 6H-SiC(0001) substrates. Specifically, for the heteroepitaxial growth of GaN on SiC we apply and investigate (i) the interaction of the SiC substrate with a remote hydrogen plasma for the in situ cleaning and preparation of the SiC surface; (ii) the interaction of the cleaned SiC surface with a remote nitrogen plasma that we use for pre-conditioning the SiC surface to the epitaxial growth; (iii) the early nucleation stage of GaN on SiC using trimethylgallium (TMGa) and a N₂ plasma as precursors, and finally (iv) the epigrowth dynamics. The impact of the surface 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. It is shown that the temperature and H₂ and N₂ SiC preconditioning affect the interface roughness, the GaN nuclei size (from tens of nanometers to microns) and the nucleation mode (i.e., homogeneous growth, 2D, 3D, hemispherical or columnar island nucleation). The interface and subcutaneous SiC and GaN 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 the impact of the nucleation geometry on the final quality of the GaN epitaxial layer.

4:45 PM P4.10

Initial Growth Study of Plasma-Assisted Atomic Layer Deposition of TiN Films by in situ Spectroscopic Ellipsometry. W. M. M. Kessels, E. Langereis, S. B. S. Heil, A. Versteegh and M. C. M. Van de Sanden; Dept. of Applied Physics, Eindhoven Univ. of Technology, Eindhoven, Netherlands.

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 silicide formation 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 recombination 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 loss probabilities and ligand 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:
Chairs: Jeff Eastman and Judith Yang
Wednesday Evening, March 30, 2005
8:00 PM
Salons 8-15 (Marriott)

P5.1

Partial Oxidation of Alkanes Over Supported Metal Oxides: In-Situ DRIFT Studies. Gerald Macala, 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 atmospheric physics, astrophysics, and planetary astronomy. 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 while 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

presented and correlated. It is noted that significant differences are observed, particularly for the time dependence of the evolution of the gas phase molecules, between ices grown 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

Diagnostics of Hydrogen Plasma with Optical Emission Spectroscopy and in situ Silicon Probes. *Szetsen Steven Lee*, Chemistry, Chung Yuan Christian University, Taoyuan, Taiwan.

Hydrogen plasma has been generated with an RF source. Small silicon chips were placed at various locations inside a discharge tube for both the purposes of plasma treatment and in situ probes. In situ optical emission spectroscopy has been employed to probe plasma conditions such as number densities and temperatures. The hydrogen plasma-treated silicon surfaces were characterized with the contact angle measurement method. The spectroscopic information in plasma is correlated with the results of surface characterization. We have proposed plasma excitation and reaction mechanisms for the observed correlation between plasma temperatures and the wettability of the silicon surface.

P5.4

The Low Temperature Initial Oxidation Stages of Cu (100) Investigated by *In situ* UHV-TEM. *Li Sun*, Xuetian Han, Liang Wang and Judith C. Yang; Materials Science and Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania.

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 fuel cell reactions. Surprisingly, few studies exist concerning the initial oxidation stage-from the nucleation to the initial growth of metal oxides. Hence, we have used *in situ* 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 [1,2]. For the temperature range we examined (200 to 350 °C), epitaxial Cu₂O 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 Cu₂O 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 TFOx (Thin Film Oxidation), for deeper physical insights. [1] J. C. Yang, M. Yeadon, 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 (2003).

P5.5

Growth Kinetics of Germanium on (100) Germanium by Pyrolysis of Germane. *Renaud Bonzom*¹, Frederik Leys¹, Roger Loo¹, Kristof Dessein², Wilfried Vandervorst¹ and Matty Caymax¹; ¹IMEC, Leuven, Belgium; ²Umicore, Olen, Belgium.

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 350-750C. The Arrhenius plot for the growth rate shows a strong non-linear behavior and three important regions can be distinguished. Below 450C, the plot is linear and the growth rate strongly increases with temperature. Between 450- and 550C a much weaker temperature dependence is found and the curve levels off near the end of the region. Above 550C, the growth rate was 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 Jang 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- 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. The experimental results in this regime are analyzed using both one-site and dual-site chemisorption

models, where for the dual-site model we assume that the initial adsorption step consists of the dissociative chemisorption of GeH₄ into GeH₃ and H. Below 450C, an apparent activation energy of 27 kcal/mole is found, which is reasonably close to the 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 when calculating the surface coverage, which then leads to the well-known Langmuir-Hinshelwood type of growth rate equations (See, e.g. ref. 3). A brief comparison with predictions from other models, where Ge containing molecules are assumed to be the dominant species, is also given. References (1) S.-M. Jang and R. Reif, Appl. Phys. Lett., 59, 3162 (1991) (2) J. Holleman, A.E.T. Kuiper and J.F. Verweij: J. Electrochem. Soc., 140, 1719 (1993) (3) J. Holleman and J.F. Verweij: J. Electrochem. Soc., 140, 2089 (1993)

P5.6

TEG for CVD Surface Kinetic Studies. *Yukihiro Shimogaki*, Dept. of Materials Engineering, The Univ. of Tokyo, Tokyo, Japan.

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 limited by the diffusional movement 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 micron-sized trenches and holes, i.e., step coverage, will give an 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 ZrO₂, SiO₂, and Si CVD. The test structure having cantilever structure is good for examining the kinetics of deposition and etching of plasma processes. The contribution of ionic 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 C₄F₈/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 solid surface reaction dynamics.

P5.7

Dynamics of Gas-Surface Interaction Involving ZnO Probed in Real Time: Impact of Surface Polarity and Nanostructure. *Giovanni Bruno*¹, Maria M. Giangregorio¹, Pio Capezzuto¹, Maria Losurdo¹, Graziella Malandrino², Manuela Blandino² and Ignazio L. Fragala²; ¹IMIP-CNR and INSTM, Bari, Italy; ²Dipartimento di Scienze Chimiche, Università di Catania, Catania, Italy.

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, AlN,...) by MOCVD and MBE. For all the above applications, it is of interest the study of the interaction of ZnO with hydrogen, nitrogen and oxygen. 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 various gases and/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 c-axis, with the (0001) being the Zn-polar face and the (000-1) O-polar 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 coverage, in-diffusion and reactivity of hydrogen and nitrogen on the various ZnO nanostructure. 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 AFM. 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. Cook¹, Winnie Wong-Ng¹ and Siu-Wai Chan²;

¹Ceramics, NIST, Gaithersburg, Maryland; ²Materials 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 modern instrumentation 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, such as the surface stoichiometry of CeO_{2-x}, and the oxidation of Ag metallization in electronic ceramics.

P5.10

Measurements of Water Adsorption on HfO₂ and ZrO₂ Surfaces using a Novel Design for Gas Adsorption Microcalorimetry.

Sergey V. Ushakov, Miaojun 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 to probe energetics of surfaces. Many such measurements used Calvet type calorimeters 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 below room temperature to 800 °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 milligram quantities of samples with total surface area below one 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 energetic 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 Ebihara¹, Seigo Takshima², Masaru Hori², Shoji Den³ and Hiroyuki Kano⁴; ¹Foresight Techno Co., Ltd., Tokyo, Japan; ²Department of Engineering, Nagoya University, Nagoya, Japan; ³Katagiri Engineering Co., Ltd., Yokohama, Japan; ⁴NU-EcoEngineering Co., Ltd, Aichi, Japan.

We have proposed the novel radical cleaning technique in which N radicals were employed for deduction of contaminant(H₂O,HC's) from the wall surface in UHV(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, the DC glow discharge with He/Ar gases 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 energies. 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 N radical and contaminants will be performed through 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 N₂ plasma irradiation, the temporal gas desorption from the samples(SUS304/Al/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 pressure increment 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 nitrogen was not trapped 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 the 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. Qiming Li¹, Joshua L. Krauss³, Stephen Hersee²

and Sang M. Han¹, ¹Chemical & Nuclear Engineering, University of New Mexico, Albuquerque, New Mexico; ²Center for High Technology Materials / Electrical Engineering and Computer Engineering, University of New Mexico, Albuquerque, New Mexico; ³Materials 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, 83(24), 5032 (2003)] as well as by "touchdown" of nanoscale (~7 nm) Ge pads through a thin layer of SiO₂ [Li et al., APL, 85(11), 1928 (2004)] during molecular beam epitaxy. These two techniques squarely rely 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 thin (~1.2 nm) and thick (>150 nm) SiO₂ on Si(100) 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 growing opening size, the removal 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 desorption activation (*E_d*) energy is 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 + 2SiO₂ + Si → GeO↑ + 3SiO↑, where the products are highly volatile at the growth temperature.

P5.13

In situ and Real-Time Second Harmonic Generation During a-Si:H Thin Film Growth: Detection of Reactive Sites for SiH₃ Adsorption. I. M. P. Aarts, J. J. H. Gielis, M. C. M. van de Sanden and W. M. M. Kessels; Applied Physics, Eindhoven University of Technology, Eindhoven, Noord-Brabant, Netherlands.

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 wire 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 dangling bond defect states at the surface based upon molecular oxygen dosing experiments and real-time SHG experiments during growth. The ~ 1.5 eV peak is expected to represent a resonance at twice the pump photon energy (~ 3.0 eV) as concluded from a comparison between the nonlinear and the linear susceptibility of a-Si:H films as obtained by spectroscopic ellipsometry. Following a similar argumentation as for c-Si this strongly suggests that the resonance peak at ~ 1.5 eV is due to distorted or strained Si-Si bonds in the a-Si:H subsurface region. The results will be used to address and evaluate the SiH₃ gas phase surface interactions such as the adsorption of the SiH₃ radical on dangling bonds, the direct insertion of SiH₃ in strained Si-Si bonds and the creation of dangling bonds due to the abstraction of hydrogen by the SiH₃ 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, 865 (2003).

P5.14

Mapping Water Reactivity at Oxide Surfaces.

Jorge O. Sofo^{1,2,3} 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 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 chemisorption energy barriers, and by comparing 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 mappings 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 Dissociation on Si(100). Heather L. Abbott¹, David F. Kavulak² and Ian Harrison¹; ¹Chemistry Department, University of Virginia, Charlottesville, Virginia; ²Chemistry Department, University of California, Berkeley, Berkeley, California.

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 quantitative agreement with recent GGA-DFT calculations. A simple scheme for increasing the rate of chemical vapor deposition of silicon from SiH₄ at low surface temperatures is suggested.

SESSION P6/R9: Joint Session: Catalysis: In Situ and Nano-Characterization
Chairs: Juergen Janek and Judith Yang
Thursday Morning, March 31, 2005
Room 3001 (Moscone West)

8:00 AM *P6.1/R9.1

The Role of Atomic Resolution-In Situ Electron Microscopy in the Development of Nanomaterials for Green Chemical Catalysis and New Energy Carriers. Pratibha L. Gai, ¹Central Research and Development, DuPont, Wilmington, Delaware; ²Materials Science, University of Delaware, Newark, Delaware.

Global challenges of the 21st century include sustainable alternative energy sources, energy carriers and novel green routes to polymers. Today, our world faces a variety of challenges in creating alternative energy sources, reducing green house gases and toxic byproducts. The development of advanced methods in the design of molecular and nanomaterial systems are needed to meet these challenges. In situ atomic resolution-environmental electron microscopy (ETEM) is a powerful method in understanding and predicting how dynamic catalysis work at the atomic scale. In this presentation, I will describe the first in situ atomic resolution environmental-TEM (ETEM) developed in our laboratory to study dynamic gas adsorption on the surface of nanocatalysts and carbon nanostructures to engineer nanomaterials to meet these demands. The ETEM is capable of atomic resolution under gas pressures of a few mbar and temperatures up to 1000 C and gas-solid reactions can be monitored as they take

place. Probing reactions in wet environments is also possible. Most recently, our research is focused on the heterogeneous hydrogenation routes using nanocatalyst materials in clean polymer technology. In addition, we have investigated nanomaterial architectures based on doped-carbon nanotubes and related nanostructures as candidates for hydrogen gas adsorption. The results exemplify the pivotal role of advanced in situ electron microscopy methods in the design of optimum nanomaterials for catalysis and energy storage.

8:30 AM *P6.2/R9.2

Understanding Growth Mechanisms and Kinetics of Gas Solid Interactions at Nanoscale using Environmental Transmission Electron Microscope. Renu Sharma, Center for Solid State Science, Arizona State University, Tempe, Arizona.

Transmission electron microscopy (TEM) has been the technique of choice for chemical and structural characterization of nanomaterials due to their infinitesimal size. Recent advances in the instrumentation have made it possible to obtain near atomic level information of the nanoscale synthesis processes in controlled gas pressures (up to 50 Torr) and high temperature (1000 C). These microscopes are commonly known as environmental transmission electron microscope (ETEM) and may be equipped with a field-emission gun (FEG). An ETEM is often used to understand the response of nanoparticles to gaseous environment and temperature at an atomic level and provides a powerful combination of in-situ imaging, diffraction and spectroscopy to obtain gas-solid reaction mechanisms of individual particles. Whereas high-resolution images and electron diffraction provide structural information, electron energy-loss spectroscopy (EELS) is used to obtain chemical information. Time and temperature resolved images and/or spectroscopic data provide the reaction rates that are used to obtain kinetic and thermodynamic data. Moreover, ETEM can also be used as a nanoscale cold-wall chemical vapor deposition (CVD) reactor, and is used to obtain nucleation and growth mechanism of nanomaterials during CVD process under diverse precursor pressure and deposition temperature. This unique combination of synthesis and characterization has tremendous time advantage over ex-situ synthesis and characterization. Practical applications of such microscope can be divided in to two broad categories: (1) transformation mechanism of nanostructures due to gaseous environment at elevated temperature and (2) controlled synthesis of nanomaterials. The first category includes examples of oxidation-reduction of catalysts e.g. three-way catalysts commonly used in catalytic converters of automobiles. The second category includes synthesis of carbon nanotubes, electron beam induced deposition of nanoparticles. Some examples from each category will be presented to elucidate different types of information that can be extracted from the in-situ data obtained using a FEG-ETEM.

9:00 AM P6.3/R9.3

Understanding Catalysis Through Aberration-Corrected STEM and Theory. Albina Y Borisevich¹, Andrew R. Lupini¹, Sanwu Wang², Sergey N. Rashkeev^{1,2}, Sokrates T. Pantelides^{2,1}, Karl Sohlberg³ and Stephen J. Pennycook^{1,2}; ¹Condensed Matter Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee; ²Department of Physics and Astronomy, Vanderbilt University, Nashville, Tennessee; ³Department of Chemistry, Drexel University, Philadelphia, Pennsylvania.

Aberration-corrected Z-contrast (HAADF) STEM offers unprecedented insights into the structure and functionality of heterogeneous catalysts due to its sub-Angstrom resolution and high sensitivity. Realistic catalysts such as high-surface area powders can be studied, and structural detail down to a single heavy atom (inside a lighter material or on its surface) can be detected. Such observations also provide a direct link to first-principles calculations, which can connect the structure of metal formations on oxide supports with the properties of the catalytic system. In the studies of La-doped γ -Al₂O₃ catalytic supports, the single-atom imaging and theoretical calculations allowed identification of isolated La atoms adsorbed on γ -Al₂O₃ surface as the instruments of the dopant-induced thermal stabilization [1]. In a related system, accurate measurements of the interatomic distances of the Pt₃ clusters on the surface of γ -Al₂O₃ and thorough theoretical analysis led us to discover that these units are capped with OH-groups, which affect electron density distribution within the clusters and, consequently, the catalytic activity of the system [2]. Simultaneously acquired electron energy loss (EELS) spectra were instrumental in characterizing distinct additive distribution for Cr₂O₃ on γ - and η -Al₂O₃. Additional possibilities open for the studies of bimetallic catalysts, where distribution of the two different metals can be addressed both by imaging (e.g. (Pt, Ru)/ γ -Al₂O₃) and by EELS (e.g. (Pt, Fe)/ γ -Al₂O₃ and MgO). Results on the study of three-dimensional structure of catalysts using a novel technique of depth slicing in STEM will also be discussed. [1] S. Wang, A. Y. Borisevich *et al.*, *Nature Materials* 3, 143 (2004). [2] K.Sohlberg *et al.*, *ChemPhysChem*, in press (2004).

9:15 AM P6.4/R9.4

The Effect of Substrates/Ligands on Metal Nanocatalysts Investigated by Quantitative Z-Contrast Imaging and High Resolution Electron Microscopy. Huiping Xu¹, Noel T. Nuhfer², Laurent Menard³, Anatoly Frenkel⁴, Ralph Nuzzo³, Duane Johnson³ and Judith C. Yang¹; ¹Dept of Mat Sci & Engr, University of Pittsburgh, Pittsburgh, Pennsylvania; ²Carnegie-Mellon University, Pittsburgh, Pennsylvania; ³University of Illinois at Urbana-Champaign, Urbana, Illinois; ⁴Yeshiva University, New York, New York.

Our direct density function-based simulations of Ru-, Pt- and mixed Ru-Pt clusters on carbon-based supports reveal that substrates can mediate the PtRu5 particles [1]. Oblate structure of PtRu5 on C has been found [2]. Nevertheless, the cluster-substrate interface interactions are still unknown. In this work, we present the applications of combinations of quantitative z-contrast imaging and high resolution electron microscopy in investigating the effect of different substrates and ligand shells on metal particles. Specifically, we developed a relatively new and powerful method to determine numbers of atoms in a nanoparticle as well as three-dimensional structures of particles including size and shape of particles on the substrates by very high angle (~96mrad) annular dark-field (HAADF) imaging [2-4] techniques. Recently, we successfully synthesize icosahedra Au13 clusters with mixed ligands and cuboctahedral Au13 cores with thiol ligands, which have been shown by TEM to be of sub-nanometer size (0.84nm) and highly monodisperse narrow distribution. X-ray absorption and UV-visible spectra indicates many differences between icosahedra and cuboctahedral Au13 cores. Particles with different ligands show different emissions and higher quantum efficiency has been found in Au11 (PPH3) SC12)2Cl2. We plan to deposit those ligands-protected gold clusters onto different substrates, such as, TiO2 and graphite, etc. Aforementioned analysis procedure will be performed for those particles on the substrates and results will be correlated with that of our simulations and activity properties. This approaching will lead to well understanding the cluster-substrate relationship for consideration in real applications. [1]. S. V. Khare, D.D. Johnson, A. Rockett, T. Martinez, A. I. Frenkel, R. G. Nuzzo, submitted (2004). [2]. J.C.Yang, S. Bradley, J.M. Gibson, Materials Characterization, 51, 101 (2003). [3] J.C. Yang, S. Bradley and J.M. Gibson, Microsc. Microanal., 6, 353 (2000). [4]. A. Singhal, J.C. Yang and J.M. Gibson, Ultramicroscopy, 67, 191 (1997). Supported by the Department of Energy (#DE-FG02-03ER15475).

9:30 AM P6.5/R9.5

Surface Defects on TiO₂(110): From Atomic and Electronic Structure to Catalytic Activity. Ken Taesung Park^{1,2}, Minghu Pan², Sergei Kalinin³, Vincent Meunier⁴, William Shelton⁴, Arthur P. Baddorf³ and E. Ward Plummer^{2,3}; ¹Physics, Baylor University, Waco, Texas; ²Physics and Astronomy, University of Tennessee, Knoxville, Tennessee; ³Condensed Matter Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee; ⁴Computer Science and Mathematics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

The chemical reactivity of solid surfaces is determined by the presence of active sites such as defects, vacancies, and step edges. Optimization of the catalytic and sensing properties of transition metal oxide based materials thus necessitates comprehensive studies of their surface atomic and electronic structure. We use the combination of high resolution Scanning Tunneling Spectroscopy and Microscopy with first principles density functional calculations to elucidate the electronic and chemical properties of one dimensional defects on a TiO₂(110) surface. Previously, Onish and Iwasawa reported that oxygen-deficient TiO₂(110) regenerates its (1x1) surface of the bulk-like termination, via "added rows of Ti₂O₃" [Phy. Rev. Lett. 76, (1996) 791]. We present a scanning tunneling microscopy/spectroscopy (STM/STS) study of the added rows on a reduced TiO₂(110), clearly revealing their internal structure. High-resolution STM images show extra Ti atoms coordinated in sites of oxygen octahedral channels. In this re-oxidation scheme, these Ti atoms form edge-shared octahedra with five-fold Ti⁴⁺ on surface. The added structure is reminiscent to crystallographic shear planes, in which normally corner-shared octahedra in stoichiometric rutile TiO₂ slip to form face-sharing octahedra to remove the oxygen vacancies. This result provides a new paradigm for the defect chemistry of this surface. The adsorption of O₂ on defects is studied by in-situ STM, illustrating the role of these defects in a surface/gas-phase reaction on TiO₂(110).

10:15 AM *P6.6/R9.6

Seeing Catalysts at Work at High Temperatures and High Pressures, Using STM. J. W. M. Frenken¹, B. L. M. Hendriksen¹, M. D. Ackermann¹, S. Bobaru¹, O. Robach², I. Popa², H. Kim² and S. Ferrer²; ¹Kamerlingh Onnesse Laboratory, Leiden University, Leiden, Netherlands; ²European Synchrotron Radiation Facility (ESRF), Grenoble, France.

This talk discusses experiments performed with two complementary techniques, Scanning Tunneling Microscopy and Surface X-Ray Diffraction, investigating the relation between structure and chemical activity of model catalysts under semi-realistic working conditions. We use the so-called Reⁿactor-STM, a small STM that is integrated with a miniature, high-temperature (500 K), high-pressure (5 bar) reactor cell, inside an ultrahigh vacuum chamber. Reactive gas mixtures at atmospheric pressures flow over the investigated surface, while it is being imaged with the STM. Simultaneously with the imaging, the hot gas mixture, which leaves the reactor, is mass analyzed. Our SXRD experiments are performed in a combined UHV and high-pressure chamber, which can be operated as a batch reactor. Results will be shown for the oxidation of CO on Pt and Pd surfaces, which demonstrate that under high-pressure conditions the mechanism and kinetics for this important reaction are radically different from those in ultrahigh vacuum [1,2]. We resolve various ultrathin oxide structures, which only appear under high partial pressures of oxygen and on which the CO oxidation reaction proceeds via the so-called Mars-van-Krevelen mechanism, i.e. the extraction of oxygen atoms from the oxide. One of the oxide structures is found to be stabilized by the simultaneous presence of both O₂ and CO [3]. Finally, we have observed self-sustained oscillations in the reaction rate and we introduce a simple, new model for these oscillations, which is fully based on our STM and SXRD observations and does not rely on intrinsic non-linearities in the reaction rates. [1] B.L.M. Hendriksen and J.W.M. Frenken, Phys.Rev.Lett. 89 (2002) 046101. [2] B.L.M. Hendriksen, S.C. Bobaru, and J.W.M. Frenken, Surf.Sci. 552 (2004) 229. [3] M.D. Ackermann, O. Robach, B.L.M. Hendriksen, S. Bobaru, I. Popa, H. Kim, J.W.M. Frenken, and S. Ferrer, to be published.

10:45 AM P6.7/R9.7

Heterogeneous Photocatalysis of Oxidation of Acetaldehyde using Titania Nanotubes. Huifang Xu¹, Ganesh Vanamu², Ziming Nie¹, Jonathan Phillips³ and Yifeng Wang³; ¹Department of Geology and Geophysics, University of Wisconsin, Madison, Wisconsin; ²Chemical and Nuclear, University of New Mexico, Albuquerque, New Mexico; ³Engineering Science and Applications Division, Los Alamos National Laboratories, Los Alamos, New Mexico; ⁴Sandia National Laboratories, Albuquerque, New Mexico.

This work show that simple, standard methods of metal addition, without the need for ion implantation or other complex and expensive processes, can dramatically improve the performance of some titania structures for some (i.e. hydrocarbon oxidation) photocatalytic reactions. Titania nanotubes were prepared and incorporated with Au (Au/Nanotube sample) and Pt (Pt/Nanotube sample), and studied the photoactivity of these catalysts. These samples were compared with an industrial standard P25 (Degussa) photocatalyst. The samples were analyzed using a JEOL FEG-2010F field emission gun scanning transmission electron microscopy (STEM) with attached Oxford Instruments, X-ray energy-dispersive spectroscopy (EDS) system and Gatan imaging filtering (GIF) system. Both high-resolution TEM images and high angle dark-field (HAAD) images were recorded for the specimens. Titania nanotubes produced had a consistent structure, and highly dispersed metal catalysts. It was observed that the nanotube consists of low defect density nanotubes all of which have an inner diameter of ~ 6nm. The Au/Nanotube sample contained 1 nm Au nano-particles attached to the nanotube surfaces. The HAAD image did not show visible Pt clusters on the nanotube surfaces. However, X-ray EDS spectra clearly showed the Pt in the nanotubes. It is inferred that Pt ions are distributed evenly on both outer and inner surfaces of the nanotubes. The white Pt/Nanotube sample turned grayish after the photocatalytic reaction. Oxidation of acetaldehyde was used to test the efficiency of the catalysts. Nanotube samples showed better photoactivity than the standard P25. Both the metal identity and the size of the metal particles in the nanotubes affected the photo-activity. Specifically, Pt containing nanotube was a dramatically better catalyst than P-25. The addition of gold had lesser impact compared to the platinum. Au/Nanotube sample showed more than twice the rate of the pure nanotube sample. Pt/Nanotube sample showed the highest rate, more than 10 times the rate of P25. This sample showed 6 times rate of the pure nanotube sample. It suggested that the nanotubes with uniformly distributed Pt (ions) are more photo-reactive than those with Pt nano-particles. Pt nano-particles formed on the nanotube surfaces reduced the reactivity oxidation. It was also found that the reactivity decreased with bigger size particles. The nanotube sample coated with about 2~3 nm (bigger size) Au and Pt nano-particles showed lower photo-reactive rates compared to the Au/nanotube and Pt/nanotube samples.

11:00 AM P6.8/R9.8

Ordered Arrays of Metal Nanoclusters on Oxide Surfaces. Guido Mariotto¹, Nikolai Berdunov¹, Shane Murphy¹, Kannan Balakrishnan¹, Yakob M. Mukovskii² and Igor V. Shvets¹; ¹Physics, Trinity College Dublin, Dublin, Leinster, Ireland; ²MISIS, Moscow, Russian Federation.

The metal-oxide interface is of fundamental importance in many areas such as microelectronics, corrosion and catalysis. Magnetite and iron play 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 $\text{Fe}_3\text{O}_4(111)$ surface exhibits a hexagonal 42 \AA 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 \AA 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 \AA 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 $\text{Fe}_3\text{O}_4(111)$ 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 Al_2O_3 [2]. [1]. N. Berdunov, S. Murphy, G. Mariotto and I.V. Shvets, Phys. Rev. B 70, 085404 (2004). [2]. S. Degen, C. Becker and K. Wandelt, Faraday Discuss. 125, 343 (2004).

11:15 AM P6.9/R9.9

In situ Observation of Electrode Reactions on Solid Electrolytes Probed by Microspectroscopy. Bjoern 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 solid 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. Ladas, 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. 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, Bjoern 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 species in-situ by PEEM. 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 $\text{C} + 2 \text{O}(\text{ad}) \rightarrow \text{CO}_2$ 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 Microspectroscopy of Polarized Pt/YSZ Electrodes, in: Solid State Ionics: The Science and Technology of Ions in Motion, World Scientific, Singapore 2004, pp. 139-149