

Surface Science

Room 213B - Session SS3-ThM

Halogen and Oxygen Surface Reactions and Etching

Moderator: J.J. Boland, Trinity College Dublin, Ireland

8:20am SS3-ThM1 Ultra-Low Coverage Spontaneous Etching and Hyperthermal Desorption of Aluminum Chlorides from Cl₂/Al(111), A.C. Kummel, T.J. Grassman, G.C. Poon, University of California, San Diego

INVITED

Non-resonant multiphoton ionization and time-of-flight mass spectrometry have been used to monitor the desorption of aluminum chloride (Al_xCl_y) etch products from the Al(111) surface at 100 K and 500 K during low-coverage (< 5% monolayer) monoenergetic Cl₂ (0.11 eV to 0.65 eV) dosing. The desorption products in this low-coverage range show predominantly hyperthermal exit velocities under all dosing conditions. For example, with 0.27 eV incident Cl₂, the etch product was found to have a most-probable velocity of 517 Å ± 22 m/s at an Al(111) surface temperature of 100 K. This corresponds to 22 times the expected thermal desorption translational energy for AlCl₃. Sticking probability measurements and Al_xCl_y etch rate measurements show etching even at Cl₂ coverages of less than 5% monolayer at surface temperatures between 100 K and 500 K. These experimental results are consistent with a combination of fast-time-scale surface agglomeration of the adsorbed chlorine to form aluminum chlorides and the presence of activated aluminum chloride chemisorption states having potential energies above the vacuum level. Density functional theory calculations yield results that are consistent with both our experimental findings and mechanistic descriptions.

9:00am SS3-ThM3 Real-time and In-situ Surface Stress and STM Measurements and their Application to Halogen Etching of Silicon Surfaces, T. Narushima, N. Kinahan, J.J. Boland, Trinity College Dublin, Ireland

All reactions between surfaces and other species induce strain at the interface to compensate for size differences, electronegativity differences, morphology changes etc. These days, to understand detailed reaction mechanism, contribution of the strain is an important factor which cannot be ignored. The resolution of SPM, however, is poor for this purpose because it does not have absolute but relative resolution. This makes strain determination via this visual method unreliable. In this presentation, we will demonstrate how this induced strain can be determined more accurately through simultaneous surface stress measurements and STM observations as a function of time. To realise this, we have designed a special monitoring system. Surface stress can be readily measured via a capacitance method. The bending of a simple cantilever was measured as a change of capacitance between sample itself and reference electrode. Change from an initial capacitance value corresponds to sample bending which indicates the surface stress change. For surface structure observation, we used conventional STM. In this configuration, conventional direct current heating of the cantilever Si sample is not possible. To heat and prepare samples we used an infrared heating source. This method allowed us to heat sample via a non-contact and static means, which is preferable for STM observation as it induces no noise effects during imaging. At high temperature, surface stress measurements become quite difficult, because high temperature induces thermal stress at interface between heterogeneous materials of sample holder. To avoid this affect, we chose a good combination of quartz and super invar that both have low thermal expansion coefficients and almost equivalent values. We will describe the application of this system to the study of halogen etching of Si surfaces.

9:20am SS3-ThM4 Chemically Assisted Ion Beam Etching of GaAs by Argon and Chlorine Gases: Experimental and Simulation Investigations, A. Rhallabi, University of Nantes, France; M. Gaillard, Veeco, France; L. Elmonser, IMN-LPCM, France; G. Marcos, LPCM-IMN, France; A. Talneau, LPN-CNRS, France; F. Pommereau, OPTO+, France; P. Pagnod, University of Nantes, France; J.P. Landesman, LPCM-IMN, France; N. Bouadma, France Telecom

It is now evident that the improvement of the optical and electrical performances of the III-V components depends on the optimization of the critical process steps such as the dry etch processes especially for the submicron and nanometer devices. The Chemically Assisted Ion Beam Etching (CAIBE) is one of dry etch processes where etching rate and etched surface profile are controlled by the synergy between the reactive neutral

species and ion bombardment. This technique uses inert ion bombardment in a reactive gas environment to achieve a separate control between sputtering and chemical etching components. A direct injection of a reactive gas close to the surface avoids the development of chemical reactions in gas phase and allows to have a better control of the transfer of the slopes in the case of mesa structure etching and the anisotropy in the case of trench etching. Experimental investigations of the chlorine and argon CAIBE process for the fabrication of vertical, ultrahigh quality facets in GaAs are reported. The effects of CAIBE process parameters as ion current and energy, chlorine flow rate and substrate temperature on the etching rate and etched GaAs topography evolution have been analyzed. To complete the experimental study, two types of 2D CAIBE model have been developed to predict the etching rate evolution and the etching GaAs profiles through the mask. The first one is an analytical model based on the concept of adsorbed surface fraction by chlorine and the second is based on the Monte-Carlo technique to study the etched surface kinetic. For both models, the simulation and the experiment results agree well with the experiment. Finally, in order to assess the compliance of Cl₂/Ar+ CAIBE etching with device applications, 980 nm Ridge lasers have been processed and their electro-optic characteristics have been compared to regular wet-chemical etched ridge stripe.

9:40am SS3-ThM5 Semiconductor Surface Chemical Functionalization for Microelectronics Applications: Gas Phase Chlorination of H-Passivated Silicon Surfaces, S. Rivillon, F. Amy, Y.J. Chabal, Rutgers University; M.M. Frank, IBM

Controlling the surface chemistry of semiconductor surfaces is critical and particularly important for the growth of alternative dielectrics (i.e. other than SiO₂) on silicon surfaces. For high-k dielectrics growth using atomic layer deposition, for instance, the chemical nature of the surface determines the abruptness of the resulting interface. Chlorination of H-terminated surfaces is a powerful way to grow high-k dielectrics with minimum interfacial SiO₂ and needs to be studied. We used several different processes to chlorinate the surfaces: chlorine Cl₂ gas phase, wet chemistry and photochlorination, and investigated the resulting surfaces by infrared absorption spectroscopy looking directly at the Si-Cl modes. The surface termination is independent of the chlorination method: 1) H-terminated Si(111) surfaces are fully covered by chlorine and remain atomically flat meaning that chlorination processes do not change the surface morphology; 2) only partial chlorination of the Si(100) surface is achieved, with a high degree of disorder. The stability of both chlorinated surface has been studied under nitrogen (N₂) and in ambient atmosphere.

10:00am SS3-ThM6 Charge-Carrier-Stimulated Halogen Desorption from Si(100)-(2x1), B.R. Trenhaile, G.J. Xu, A. Agrawal, A.W. Signor, K.S. Nakayama, J.H. Weaver, University of Illinois at Urbana-Champaign

Scanning tunneling microscopy was used to investigate spontaneous Br atom desorption from Br-terminated Si(100)-(2x1) as a function of temperature for 620 Å < T < 775 K. Significantly, analysis demonstrates that the activation energy and pre-exponential factor for the desorption depend on both the doping type and concentration. Moreover, the kinetic parameters are observed to follow the compensation (Meyer-Neldel) rule, and analysis yields a characteristic energy in good agreement with the phonon Debye energy for silicon. The activation energies correspond to the antibonding Si-Br levels, and we propose that thermally-excited charge carriers produce intermediate electronic states that lead to a novel form of electron-stimulated desorption. The desorption of other halogens from Si(100) will also be discussed.

10:20am SS3-ThM7 Morphological Evolution during Competitive Etching and Oxidation of Vicinal Si(100) Surfaces, M.A. Albao, D.-J. Liu, J.W. Evans, Iowa State University

Exposure of a vicinal Si(100) surface to oxygen at ~600C produces etching-mediated step recession. This process is impacted by the formation oxide islands which act as pinning centers for the receding steps, as observed in STM studies by Pelz et al. We develop an atomistic model for this process which accounts for the interplay between oxygen surface chemistry (adsorption, diffusion, oxide formation, and etching via SiO desorption) and the Si surface and step dynamics (anisotropic diffusion and aggregation of vacancies formed by etching with each other or with steps, and attachment-detachment dynamics at steps incorporating anisotropic energetics). Kinetic Monte Carlo simulation of this model produces etch morphologies where receding steps retain qualitative features of their equilibrium morphology (alternating rough SB steps and smooth SA steps), although pinning greatly distorts equilibrium structure (as seen in STM

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studies). Even without pinning, step evolution is a driven far-from-equilibrium process (as is step flow during MBE) which is impacted by the details of the etching process (e.g., anisotropic vacancy diffusion can lead to an alternation between etch pit nucleation and step flow on adjacent terraces). Simulations used to characterize the dependence of the complex etch morphologies for this model on temperature and oxygen pressure.

superstructures whose physical properties are further characterized by ex-situ electron and ion spectroscopies.

10:40am **SS3-ThM8 Atomic Oxygen Etching of Phosphorous-containing Polymer Surfaces**, *H. Fairbrother, G. Wolfe, J. Torres*, Johns Hopkins University

The aerospace industry has recently developed phosphorous-containing polymers that can resist the severely oxidizing environment encountered by vehicles traveling in Low Earth Orbit (LEO). Post-flight analysis shows that upon exposure to atomic oxygen (AO) present in LEO, these polymers form a self-passivating phosphate like ($\text{P}_{\text{sub } x}\text{O}_{\text{sub } y}$) overlayer that hinders etching of the underlying bulk. The protective capabilities of these phosphorous-containing polymers, whose synthesis is complex and expensive, derive solely from the chemical characteristics of the near surface region rather than the bulk. In an attempt to develop a more cost-effective and generally applicable method of creating polymer surfaces with the ability to resist etching by AO, we have initiated studies on polyethylene (PE) ion-implanted with trimethylphosphine. X-ray photoelectron spectroscopy reveals that under ambient conditions the P-implanted PE readily oxidizes to form phosphate-containing bonds at the surface. The thickness of the phosphate layer increases with a logarithmic dependence on air exposure, indicating that the growing phosphate structure limits diffusion of oxygen species through the near-surface region. Subsequent exposure of these films to AO leads to carbon etching from the surface, leaving behind a phosphorous-rich overlayer. Related studies of thin films used to simulate the P-implanted PE surface show that these phosphate structures remain thermally stable under vacuum conditions up until ~ 650 K. Results from atomic force microscopy studies will also be presented to illustrate the morphological changes in the polymer surface that accompany air oxidation and AO exposure.

11:00am **SS3-ThM9 Structural Damage of Self-Assembled Monolayers Induced by 5-eV O^+ Bombardment**, *T.D. Tzvetkov, X. Qin, D.C. Jacobs*, University of Notre Dame

Self-Assembled Monolayers (SAM) of decanethiol/Au(111) are bombarded with 5-eV O^+ ions in UHV. XPS reveals that the carbon content of the SAM decreases, while the oxygen content increases with O^+ dose. STM images of ion-exposed and unexposed regions of the SAM are compared. The SAM layer exhibits greater disorder after only modest doses of 5-eV O^+ ions. Initially, ion-induced damage occurs predominantly near domain boundaries, surface steps, and vacancies. In contrast, large defect-free surface domains show considerable stability against 5-eV O^+ bombardment. A mechanism for degradation of the SAM by low-energy O^+ ions is proposed.

11:20am **SS3-ThM10 In-situ STM-studies of Solid/Liquid Interfaces: Growth of Ultrathin Compound Films**, *A. Spaenig, S. Huemann, J. Hommrich, P. Broekmann, K. Wandelt*, University of Bonn, Germany

Electrochemical Atomic Layer Epitaxy (ECALE) is quite an interesting alternative route for the synthesis of ultrathin layers, instead of vacuum based chemical vapour deposition techniques. This technique is based on alternating reductive and oxidative underpotential deposition (UPD) processes, e.g. of metal cations and halide or chalcogenide anions. In this contribution the growth of ultrathin semiconducting cadmium sulfide and insulating cadmium chloride films on Cu(111) and Cu(100) single crystal electrodes has been studied in-situ using an ElectroChemical Scanning Tunnelling Microscope (ECSTM). Atomically resolved ECSTM images are presented and discussed for the binary systems of either sulfide or chloride on Cu(111) and Cu(100) as well as for the ternary systems of cadmium sulfide and cadmium chloride on both surfaces. Chloride forms a ($\sqrt{3} \times \sqrt{3}$)R30° and c(2x2) adsorbate structures on Cu(111) and Cu(100), respectively, and has only a restructuring influence on the morphology of surface steps. In turn, sulfide forms several structures of low and high commensurability on both Cu surfaces, namely a c(2x6) on Cu(100) and a ($\sqrt{7} \times \sqrt{7}$)R19.1° and ($2\sqrt{7} \times 2\sqrt{7}$)R19.1° on Cu(111). Moreover at very positive electrode potentials sulfide induces severe reconstructions of both Cu surfaces with a checker-board like superstructure on Cu(100) and a hexagonal Moire like superstructure on Cu(111). Post-deposition of cadmium onto the chloride or sulfide pre-covered Cu surfaces leads to the formation of cadmium chloride or cadmium sulfide compound layers with interest periodic nanoscale

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