

Monday Morning, November 9, 2009

Surface Science

Room: M - Session SS1-MoM

Vibrational Spectroscopy and Surface Reactions

Moderator: Y. Chabal, University of Texas, Dallas

8:20am **SS1-MoM1 Reaction of Phenylenediamines on Ge(100)-2x1: The Effects of Functional Group Spacing on Reactivity.** *J.S. Kachian, K.H. Squires, S.F. Bent*, Stanford University

While silicon is the current material of choice in the electronics industry, next-generation device requirements make the largely unexplored surface chemistry on germanium, a Group IV homolog with promising electrical properties, an interesting area of study. Multifunctional adsorbates are of particular interest, since they inherently offer a greater degree of tailorability and the potential for subsequent reaction. The adsorption of the *o*-, *m*- and *p*- structural isomers of phenylenediamine on Ge(100)-2x1 at room temperature was investigated to gain a fundamental understanding of how surface bonding of these molecules is affected by the distance between two NH₂ groups attached to a rigid benzene ring. Vibrational spectra of the adsorption products of these three molecules, obtained via multiple internal reflection Fourier transform infrared (MIR-FTIR) spectroscopy in ultrahigh vacuum (UHV), show that all three isomers adsorb via N-H dissociation. The corresponding X-ray Photoelectron Spectroscopy (XPS) results support the MIR-FTIR data and further reveal the bonding configurations of the N-H dissociated adducts at the surface: While there is evidence of both singly and dually N-H dissociated adducts for the ortho isomer, N-H dissociation of only one amino group is observed for the para isomer, while N-H dissociation of both amino groups is observed for the meta adducts. Dative bonding was not observed for reaction of any of the phenylenediamine isomers with the Ge(100)-2x1 surface. The difference in reactivity between isomers likely results from how closely the spacing between NH₂ groups on the benzene ring matches the distance between adjacent surface dimers. The distance is in closest agreement for the meta isomer, which adsorbs exclusively via dual N-H dissociation, and is most mismatched for the para isomer, which adsorbs only via single N-H dissociation. Adsorption of the ortho isomer, which represents an intermediate case geometrically, leads to a mixture of singly and dually N-H dissociated adducts. DFT calculations support the experimental results. The results will be compared to those obtained for reaction of aniline, the monofunctional analog to the phenylenediamine isomers, on Ge(100)-2x1.

8:40am **SS1-MoM2 Electronic and Steric Effects in the Reactions of Isocyanates and Isothiocyanates at the Ge(100)-2x1 Surface.** *P.W. Loscutoff, K.T. Wong, S.F. Bent*, Stanford University

Organic functionalization of semiconductor surfaces has seen increased interest in recent years, due to the ever-decreasing feature sizes of microelectronics, and the advance of organic electronics. Advances in both of these fields require precise interface control at atomic dimensions, and modification of surfaces with organic molecules provides the flexibility necessary for use in a broad spectrum of applications. In this study, we examine the surface products formed by the reactions of various isocyanates and isothiocyanates with the Ge(100)-2x1 surface. Although these two moieties differ only by substitution of an oxygen atom with a sulfur atom, they display markedly different reactivity at the reconstructed germanium surface. Using a combination of infrared spectroscopy, x-ray photoelectron spectroscopy and density functional theory, we examine the reactions of phenyl, *tert*-butyl, and ethyl isocyanate and the corresponding isothiocyanates. Both phenyl isocyanate and phenyl isothiocyanate form multiple adsorption products at the surface. The isocyanate reacts with a Ge surface dimer to form a [2+2] cycloaddition product across the C=N bond to produce a surface-bound carbonyl in addition to other products. In contrast, phenyl isothiocyanate reacts across the C=S bond to form a [2+2] cycloaddition product, in addition to reaction across the C=N bond. When the *tert*-butyl group is substituted for the phenyl ring, the reactivity changes such that dative-bonded products with an intact, surface-bound isocyanate or isothiocyanate group are observed. Upon reaction of ethyl isocyanate and ethyl isothiocyanate at the Ge(100)-2x1 surface, yet another product distribution is observed, which lacks dative-bonded products but demonstrates time-dependence. The wide array of products observed for this set of isocyanate and isothiocyanate molecules demonstrates the influence of the molecular chain on the surface reactivity of these groups, and displays a versatility that could prove useful for tuning reactivity to achieve a desired surface product.

9:00am **SS1-MoM3 Surface Transamination Reactions for Thin Film Deposition on NH_x-Precovered Silicon.** *A.V. Teplyakov*, University of Delaware **INVITED**

The termination of semiconductor surfaces plays a major role in surface reactivity and in our ability to create a well defined and sharp interface between a semiconductor and a thin film, often required for practical applications. Although hydrogen termination of group IV semiconductors is often a good starting point for deposition chemistry, the reactivity of hydrogen terminated surfaces is often limited. Here we selectively produce a specific NH_x termination of Si(100) surface by exposing it to ammonia and briefly annealing at a predetermined temperature. The reactivity of silicon surfaces prepared in such a way is examined by reacting them with a common organometallic precursor for thin diffusion barrier film growth, tetrakis(dimethylamido)titanium, TDMAT. Experimental observations suggest the occurrence of a surface transamination reaction, where an approaching TDMAT molecule reacts with a surface NH_x site, eliminating dimethylamine and attaching Ti to the surface N atom. Vibrational spectroscopy holds the key to determining this reactivity and surface reaction pathways. Together with temperature programmed desorption and computational DFT investigations, these studies expand the generality of transamination processes to other amines on Si(100). The role of steric and electronic factors is evaluated for improving proposed deposition schemes.

9:40am **SS1-MoM5 Si ALE using Molecular Disilane on Si(100)-(2x1).** *I.S. Chopra, J.-F. Veyan, M.P. Nadesalingam, N. Dao, O. Seitz, W.P. Kirk*, The University of Texas at Dallas, *J. Randall*, Zyvex Labs, *M. Huang, K. Cho, R.M. Wallace, Y. Chabal*, The University of Texas at Dallas

Atomic layer epitaxy (ALE) is a critical step in trying to achieve Atomically Precise Manufacturing (APM) of new devices such as quantum dots, qubits, NEMS oscillators and biomedical devices. Here we report the ALE of Si using molecular disilane on (2x1)-Si(100) surface. The surfaces have been characterized using Fourier transform infrared spectroscopy (FTIR), angle resolved x-ray photoelectron spectroscopy (ARXPS), low energy electron diffraction (LEED) and quadrupole mass spectrometry (QMS).

IR absorption measurements have been performed in transmission mode (70° incidence). Clean Si(100)x(2x1) samples are prepared by controlled thermal desorption of chemically oxidized Si wafers. On clean (2x1) – Si(100) surfaces, saturation doses of the order of 10L are observed, which is considerably lower than data reported earlier (3000L)¹. At saturation coverage absorption bands in the ~2100 cm⁻¹ range (and also ~950 and 650 cm⁻¹) indicate that monohydrides (SiH), dihydrides (SiH₂) and trihydrides are formed, consistent with shifts of the Si2p core level using angle resolved X-ray photoelectron spectroscopy. The relative intensities of these bands have been studied as a function of exposure and substrate temperature, and present differences from earlier room temperature measurements.² The observation of trihydrides indicates that one product from disilane decomposition is the silyl group, although its concentration depends on exposure and temperature. The thermal stability of these resulting surfaces has been examined with infrared absorption, temperature-programmed desorption (TPD) and LEED. We have also examined the effects of He ion surface de-passivation.³

To gain a fundamental understanding on surface reaction mechanisms, we have performed a density functional theory (DFT) study on the reactions of monohydrides (SiH), dihydrides (SiH₂), trihydrides and disilane on both clean and hydrogen passivated Si(100)-(2x1) surfaces. The calculated atomic configurations, electronic structures, and vibration frequencies are compared with the experimental data.

References

- 1 Yoshiyuki Suda, Naoyuki Hosoya and Kazushi Miki, *Appl. Surf. Sci.* 216, 424-430 (2003).
- 2 Masanori Shinohara, Michio Niwano, Yoichiro Neo and Kuniyoshi Yokoo, *Thin. Solid Films* 309, 16-20 (2000).
- 3 This material is based upon work supported by the Defense Advanced Research Project Agency (DARPA) and Space and Naval Warfare Center, San Diego (SPAWARSYSCEN-SD) under contract N66001-08-C-2040. It is also supported by a grant from the Emerging Technology Fund of the State of Texas to the Atomically Precise Manufacturing Consortium.

10:00am **SS1-MoM6 Adsorption Studies of Molecular Disilane on p-type Ge(100) at Room Temperature.** *M.P. Nadesalingam, N. Dao, I.S. Chopra, J.-F. Veyan, W.P. Kirk*, University of Texas at Dallas, *J. Randall*, Zyvex Labs, *Y. Chabal, R.M. Wallace*, University of Texas at Dallas
ALE (Atomic Layer Epitaxy) is a layer by layer epitaxial thin film growth technique of interest for fabrication of SiGe high speed devices¹ as well as

enabling atomically precise manufacturing (APM) of nanometer scale features. We report on a precision gas dosing technique for Si ALE on Ge(100) p-type using molecular disilane.

The adsorption of molecular disilane on Ge(100) was studied using X-ray photoelectron spectroscopy (XPS), low energy electron diffraction (LEED) and quadrupole mass spectrometry (QMS) and Fourier transform infrared spectroscopy (FTIR). LEED analysis shows that the Ge surface periodicity results in a weak 2x1 pattern upon exposure to molecular disilane. The molecular disilane was delivered to the Ge(100) substrate using micro-capillary array molecular beam doser with an equivalent dose of ~1.2 L, which is a considerably smaller value compared to that reported from previous techniques.² Based on the XPS data, the Si coverage on Ge is nearly half a monolayer.³ The sticking coefficient of molecular disilane on Ge (100) is estimated to be 0.48 with disilane adsorption on Ge(100) that is governed by dissociating Si₂H₆ into two silyl(-SiH₃) groups. IR absorption measurements have been performed in transmission mode (70° incidence) to analyze the adsorption mechanisms as a function of temperature and coverage.⁴

References

1. Y. Suda, H. Koyama, Appl. Phys. Lett. **79**, 2273 (2003).
2. Yoshiyuki Suda, Yasuhiro Misato, Daiju Shiratori, J. of Cryst. Growth **237-239**, 1404 (2002).
3. D. S. Lin, T. Miller and T. C. Chiang, Phys. Rev. **B 47**, 6543 (1992).
4. This material is based upon work supported by the Defense Advanced Research Project Agency (DARPA) and Space and Naval Warfare Center, San Diego (SPAWARSYSCEN-SD) under contract N66001-08-C-2040. It is also supported by a grant from the Emerging Technology Fund of the State of Texas to the Atomically Precise Manufacturing Consortium.

10:40am **SS1-MoM8 High-stability Molecular Interfaces to TiO₂ Surfaces**, *R. Franking, H. Kim, E.C. Landis*, University of Wisconsin, Madison, *S.A. Chambers*, Pacific Northwest National Laboratory, *R.J. Hamers*, University of Wisconsin, Madison

The integration of molecular systems with TiO₂ is of interest in a wide range of emerging applications; however, most methods currently used are not stable under in aqueous media, especially at elevated temperatures or extremes of pH. We demonstrate that well-defined molecular layers can be covalently bound to the surface of nanocrystalline and single-crystal anatase TiO₂ by photochemically grafting organic molecules bearing a terminal vinyl group. Stability tests on nanocrystalline films show the layers have excellent stability in aqueous environments with a wide range of pH for time scales approaching 2 months, and that grafting occurs through the thickness of 10 micron thick porous films. XPS, FTIR, and wavelength-dependent excitation experiments have been performed to help identify the reaction pathway. New methods are being developed using the highly stable chemistry to create highly flexible, modular interfaces with the oxide.

11:00am **SS1-MoM9 HREELS Study on the Doping of ZnO by H and Cu Atoms**, *H. Qiu, Y. Wang, Ch. Wöll*, Ruhr-University Bochum, Germany
Zinc oxide exhibits a number of extraordinary properties and is one of the most technologically important metal oxides [1]. Presently, there is great interest in the doping of ZnO by foreign atoms due to its effects on changing the electrical, optical and catalytic properties of ZnO. In this contribution, the interaction of hydrogen and Copper atoms with ZnO(000-1) was studied by high resolution electron energy loss spectroscopy (HREELS) which recently has been successfully applied to perfect and defective metal oxide surfaces [2].

Exposing the fully hydroxylated ZnO(000-1) surface to atomic hydrogen leads to a significant broadening of the quasi-elastic peak in HREELS, which corresponds to the existence of free charge carriers at ZnO surface region [3]. These free charge carriers result from the thermal excitation of electrons at the donor level into the conduction band. The shallow donor states are created via diffusion of H atoms into the bulk. The analysis of the temperature dependence yields a shallow donor ionization energy of 25 ± 5 meV [4].

Cu deposition on O-ZnO leads to the formation of well-defined islands with the Cu(111) facets. For the small clusters the partial oxidation of Cu⁰ into Cu⁺ was clearly identified by the characteristic C-O stretching frequencies. Upon heating the Cu atoms undergo, instead of desorption, diffusion into the bulk. The doping of ZnO by Cu leads also to the formation of shallow donor states, in which the electrons can be thermally excited into the conduction band and, as a result, giving rise to the plasmon-induced broadening of the quasielastic peak in HREELS. From the observed temperature dependence, the donor level ionization energy was determined. This unexpected doping effect of ZnO by Cu has important consequences

for its chemical activity, as confirmed by the detailed studies on CO₂ adsorption.

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- [2] Y. Wang, Z. Phys. Chem. 222 (2008) 927.
- [3] Y. Wang, B. Meyer, X. Yin, M. Kunat, D. Langenberg, F. Traeger, A. Birkner, Ch. Wöll, Phys. Rev. Lett. 95 (2005) 266104.
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11:20am **SS1-MoM10 Reactions of NO₂ with BaO and Ba(OH)₂ on Pt(111)**, *K. Mudiyansele*, Pacific Northwest National Laboratory, *C.W. Yi*, Sungshin Women's University, Korea, *J. Szanyi*, Pacific Northwest National Laboratory

Reactions of NO₂ (in the pressure range of 1.0 × 10⁻⁹ - 1.0 × 10⁻⁴ Torr) with BaO(> 20 MLE), amorphous-Ba(OH)₂ and crystalline-Ba(OH)₂ supported on Pt(111) were studied using infrared reflection absorption spectroscopy (IRAS), temperature programmed desorption (TPD) and X-ray photoelectron spectroscopy (XPS). The amorphous and crystalline Ba(OH)₂ layers were prepared by adsorbing H₂O on BaO(> 20 MLE)/Pt(111) at 300 and 425 K, respectively. The amorphous-Ba(OH)₂ layer partially converts to Ba(NO_x)₂ (nitrites and nitrates) following exposure to elevated NO₂ pressure (~1.0 × 10⁻⁴ Torr) at 300 K. The exposure of the crystalline-Ba(OH)₂/Pt(111) system to NO₂ at 425 K leads to the desorption of H₂O and the complete conversion of the crystalline-Ba(OH)₂ layer to Ba(NO_x)₂, which consists of mainly crystalline nitrates and a small amount of nitrites. Adsorption of NO₂ on BaO(> 20 MLE)/Pt(111) at 425 K also forms crystalline nitrates. The amounts of NO_x uptaken by BaO(> 20 MLE)/Pt(111) and crystalline-Ba(OH)₂/Pt(111) systems at 425 K are very similar as determined by the NO TPD peak areas.

11:40am **SS1-MoM11 In-situ Spectroscopy Studies of Surface Species on Pd Surfaces during CO Oxidation**, *M.S. Chen, X. Wang, H.L. Wan*, Xiamen University, China

Previous we had found that CO oxidation on Pd-group metals at temperatures between 450 and 600 K and pressures between 1 and 300 Torr increases markedly with an increase in the O₂/CO ratio above 0.5. [Surf. Sci. 2007,601, 5326.] The catalytic surfaces, formed at discrete O₂/CO ratios > 0.5, exhibit rates 2 to 3 orders of magnitude greater than those rates observed for stoichiometric reaction conditions and similar reactant pressures or previously in ultrahigh vacuum studies at any reactant conditions and extrapolate to the collision limit of CO in the absence of mass transfer limitations. Here we used HREELS to address the relative activities of surface CO and oxygen species. The surface oxygen species can be removed by CO at room temperature and low pressure, 10⁻⁸ Torr. While a much higher oxygen pressure or above room temperature is required to remove surface adsorbed CO species. Furthermore, *in-situ* RAIRS and Raman spectroscopy were used to characterize this highly active surface formed at higher O₂/CO ratios on Pd.

Keywords: CO oxidation, Pt-group metal, Oxygen covered surface

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