

Surface Science Division Room 309 - Session SS2-WeM

Gas-Surface Dynamics

Moderator: B.D. Kay, Pacific Northwest National Laboratory

8:20am **SS2-WeM1 Monte-Carlo Simulation of the Adsorption and Desorption of CF@sub 4@ on Cu/CuO(110), M. Hohage**, University of Wisconsin, Madison; V. Diercks, Forschungszentrum Jülich, Germany; P. Zeppenfeld, Universität Linz, Austria; M.G. Lagally, University of Wisconsin, Madison

The unique adsorption and desorption dynamics of CF@sub 4@ on the Cu/CuO(110) stripe phase is reproduced by a Monte-Carlo simulation to reveal the underlying processes on the molecular scale. As observed by means of thermal energy atom scattering (TEAS), at temperatures above 20K CF@sub 4@ adsorbs preferentially on the CuO stripes. @footnote 1,2@ A comparison of these adsorption measurements with a Monte-Carlo simulation is used to determine the parameters of the CF@sub 4@ diffusion on Cu and on CuO. With the knowledge of these diffusion parameters the more complicated desorption of CF@sub 4@ is analyzed. TEAS and TDS measurements show that annealing the sample with a rate of 1K/s leads to desorption between 55K and 70K@sub 2@. Two well-separated peaks occur. The peak at lower temperature is related to the desorption from the Cu stripes, whereas the peak at higher temperatures is related to the desorption from the CuO stripes. This desorption behavior as well as shifts of the desorption peaks in dependence of the composition of the surface (amount of O on the surface) is reproduced by a Monte-Carlo simulation including the previously determined diffusion parameters as a fixed input. The different features of the desorption spectra, i.e. peak positions, peak shifts, and peak shapes, are assigned to binding energies and diffusion barriers on the molecular scale. This allows the development of a consistent model of the CF@sub 4@ adsorption and desorption dynamics. *Supported by NSF and by the Alexander von Humboldt-Stiftung @FootnoteText@ @Footnote 1@P. Zeppenfeld, V. Diercks, Ch. Tölkes, R. David, and M. A. Krzykowski, Appl. Surf. Sci. (1998) in print. @Footnote 2@V. Diercks, Ph.D. thesis, Bonn 98

8:40am **SS2-WeM2 Adsorption, Absorption, and Abstraction of Hydrogen on Cu(111) Surfaces, Th. Kammler, J. Küppers**, Universität Bayreuth, Germany

The interaction of H(D) with Cu(111) surfaces and the abstraction of D adsorbed on Cu(111) by H was studied with thermal desorption spectroscopy and direct product rate measurements. H atoms were produced in a W tube heated at 2000 K. H atoms directed at clean Cu(111) surfaces at 85 K lead to H adsorption with an initial sticking coefficient of 0.19. After completion of the adsorbed layer with a saturation coverage of 0.25, further H uptake leads to H adsorption. Adsorbed H desorbs as H@sub 2@ via a second order process in the temperature range 250 to 400 K. Adsorbed H desorbs as H@sub 2@ starting at 150 K and peaking around 200 K in a first order process. The interaction of H atoms with a saturated D layer, @THETA@=0.25, at 85 K leads to the formation of gas phase HD and D@sub 2@. The kinetics of HD formation as a function of H atom fluence follows a strict Eley-Rideal-type phenomenology: a HD rate jump at reaction start and a subsequent exponential decay of the HD rate. However, the D@sub 2@ product suggests that the reaction mechanism is not of an Eley-Rideal but of hot atom type. An analysis of the abstraction kinetics in terms of hot-atom mechanisms reveals that on Cu(111) the reaction probability of hot atoms is of the same magnitude as their sticking probability at empty surface sites. About 1% of the adsorbed D appears in the D@sub 2@ reaction channel. The abstraction cross section towards HD is 2.3 Å@sup 2@. The HD yields and rate steps scale with the D coverage at reaction start, the D@sub 2@ yields and rate steps scale with the square of the D coverage. Adsorbed D cannot be abstracted by gas phase H. The kinetics of HD formation is independent of the H flux.

9:00am **SS2-WeM3 A Comparison of State-Resolved Studies of Reaction and Inelastic Scattering for H@sub 2@ with Palladium and Copper Surfaces, E. Watts**, University of Texas, Austin; M. Gostein, Massachusetts Institute of Technology; G.O. Sitz, University of Texas, Austin **INVITED**

We report results of molecular beam experiments of hydrogen scattering from single crystal palladium and copper surfaces. These two materials represent a reactive and unreactive substrate, respectively, for hydrogen dissociation at low (50-70 meV) incident energy. Because the reaction has strong geometrical and dynamical requirements, features of the potential

energy surface are evidenced in the inelastic scattering of those molecules which do not react. This will be demonstrated by comparing scattering distributions for the two surfaces. In addition we have observed efficient loss of initially vibrationally excited H@sub 2@, and have measured the probability that this loss occurs via relaxation into the ground vibrational state for selected final rotation states. For scattering from Pd, an energy balance for the H@sub 2@ degrees-of-freedom indicates that a substantial amount of energy is lost to the surface during the relaxation.

9:40am **SS2-WeM5 Energy Dependent Al(111) Oxidation Kinetics, H. Ternow, I. Zori@aa c@, M. Zäch, B. Kasemo**, Chalmers University of Technology, Sweden

We have investigated the oxidation kinetics of the Al(111) surface at different O@sub 2@ kinetic energies, using molecular beam technique, Auger electron spectroscopy, AES, and surface plasmon spectroscopy. The central issue we concentrate in this report is how the oxide growth kinetics depends on kinetic energy of the impinging O@sub 2@ molecules. A series of oxygen uptake experiments, a la King and Wells, were performed for two oxygen beam energies yielding low (0.8) initial dissociative sticking probabilities. The total coverage (chemisorbed plus oxidic oxygen) was increased in steps of 0.1 ML until the surface was saturated with oxygen. Between each step the surface was analyzed by AES and surface plasmon measurements. Al(LVV) transitions influenced by oxygen chemisorption and oxide formation were measured as a function of the total amount of oxygen on (in) the sample for different oxygen beam energies. We find the appearance of oxide in a submonolayer regime at a threshold coverage which depends on oxygen beam energy. Furthermore, the growth kinetics of the oxidic phase is also energy dependent. We attribute the latter to energy and coverage dependent dissociation dynamics, resulting in an energy dependent distribution of oxygen atoms among available adsorption sites. Surface plasmon spectroscopy (plasmon energy and lifetime dependence on total oxygen coverage) also reflects the existence of the well defined threshold for oxide appearance as well as heterogeneous distribution of chemisorbed and oxidic phases on the surface. A simple kinetic model which accounts for these observations is presented.

10:00am **SS2-WeM6 Initial Stages of Al(111) Oxidation by Oxygen - Temperature and Surface Morphology Effects, V. Zhukov, I. Popova, J.T. Yates, Jr.**, University of Pittsburgh

The mechanism of oxygen chemisorption and the oxidation of aluminum is again of interest in the light of recent STM studies on Al(111).@footnote 1,2@ We have used X-Ray Photoelectron Spectroscopy (XPS) and High Resolution Electron Energy Loss Spectroscopy (HREELS) to carefully examine the temperature dependence of the Al(111) oxidation kinetics in the range 95-773 K. The onset of oxide formation was detected near 473 K at the low oxygen coverages investigated here. Both activated and non-activated adsorption channels have been found depending on surface temperature and the degree of oxide formation, causing nonmonotonic behavior of the sticking coefficient versus temperature. These results are discussed in terms of a one-dimensional potential energy diagram. Surface defects along with the presence of the oxide structures have been found to influence the kinetics of O@sub 2@ adsorption. The importance of careful surface preparation and smooth surface morphology for the reproducible adsorption measurements are demonstrated in this work. Coverage sensitive HREELS measurements are highly dependent upon surface conditions, and these results may rationalize contradictions present in the literature. Work supported by AFOSR. @FootnoteText@ @footnote 1@H. Brune, J. Wintterlin, J. Trost, G. Ertl, J. Wiechers, R.J. Behm, J. Chem. Phys., 99 (1993) 2128. @footnote 2@J. Trost, H. Brune, J. Wintterlin, R.J. Behm, G. Ertl, J. Chem. Phys., 108 (1998)1740.

10:40am **SS2-WeM8 Comparison of Chemical Selectivity and Kinetic Energy Release in Si@sub (s)@ + ICl@sub (g)@ and H@sub (g)@ + ICl@sub (g)@, K.A. Pettus, T. Ahmadi, E. Lanzendorf, A.C. Kummel**, University of California, San Diego

The chemisorption of ICl on the Si(111)-7x7 surface is comparable to the gas reaction of ICl and hydrogen. ICl chemisorbs onto Si(111)-7x7 by two mechanisms: dissociative chemisorption and abstractive chemisorption. Abstractive chemisorption, in which one halogen atom of ICl bonds to the silicon surface while the other is ejected into the gas phase, is the dominant chemisorption mechanism for ICl/Si(111)-7x7. Multiphoton ionization (205 nm MPI) spectroscopy and time-of-flight (TOF) mass spectrometry were used to determine that the ratio of iodine-selective abstraction to chlorine-selective abstraction is at least 34 +/- 4 :1. Furthermore, the chemical selectivity of ICl + Si(111)-7x7 is greater than the

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chemical selectivity of the gas phase reaction of $\text{H} + \text{ICl}$ where the ratio of formation of HI to HCl is 4:1.¹ In both reactions, the iodine atom of ICl molecules is more reactive than the chlorine atom because the π antibonding orbital (the orbital that reacts with any other species) consists primarily of atomic iodine orbitals.² The difference in the chemical selectivities of the silicon surface and gaseous hydrogen reactions with ICl is due to the ability of the silicon surface to rotationally steer ICl molecules and the inability of silicon to migrate between the iodine and chlorine atoms in ICl . The median translational energies of the abstracted halogen atoms were determined to be 0.18 ± 0.04 eV for chlorine atoms and 0.53 ± 0.27 eV for iodine atoms which are a small fraction (14% for ejected iodine atoms and 9% for ejected chlorine atoms) of the total reaction exothermicities. The low translational energy of ejected atoms is due to the fact that the iodine-chlorine bond of ICl lengthens as the Si-I bond contracts and there is little repulsion energy attributed to the Si-I-Cl transition state.¹ J.C. Polanyi, *Chemica Scripta*, 27, 229 (1986) ²J.D. McDonald, P.R. LeBreton, Y.T. Lee, and D.R. Herschbach, *J. Chem. Phys.*, 56, 769 (1972)

11:00am SS2-WeM9 Hydrogen Atom Induced Decomposition of Water Adsorbed on Si(100), L.M. Struck, National Institute of Standards and Technology, US; S.A. Buntin, National Institute of Standards and Technology
The reaction of incident atomic hydrogen with water adsorbed on Si(100) is investigated using multiple internal reflection infrared (IR) spectroscopy. The clean Si(100) surface is exposed to water forming a half monolayer of both SiH and SiOH surface species. Atomic hydrogen is generated by hot filament decomposition of molecular hydrogen. The evolution of the adlayer is probed with IR spectroscopy by following the silicon hydride and hydroxyl stretch features as a function of atomic hydrogen exposure for different isotopic reaction combinations (e.g., incident D atoms on adsorbed H_2O). The results show a concomitant decrease in the Si-H and O-H stretch features with increasing D atom exposure, indicating the involvement of both the surface hydride and hydroxyl species in the initial adlayer decomposition. The implications of these results with regard to the reaction mechanism will be discussed.

11:20am SS2-WeM10 Nonthermal Effects of Photon Illumination on Surface Diffusion, E.G. Seebauer, D. Llera-Rodriguez, University of Illinois, Urbana

The presence of an energy bandgap in semiconductors together with their ability to support significant separations in charge offer the potential to observe surface phenomena not seen on metals. For example, several years ago this laboratory predicted the possibility of photon-influenced surface diffusion on semiconductors by nonthermal mechanisms. The present work reports the first experimental confirmation of this prediction for Ge, In, and Sb diffusion on Si(111), using second harmonic microscopy as the measurement probe. At modest illumination intensities of 2 W/cm^2 or less, we have observed substantial changes in diffusional activation energy E_{diff} and prefactor D_0 . For all the adsorbates on p-type Si, illumination increases E_{diff} by about 0.3 eV (out of 2.4) and increases D_0 by nearly two orders of magnitude. However, use of n-type substrates causes decreases of the same magnitude. All effects remain independent of illumination wavelength as long as the photon energy remains higher than the substrate bandgap energy. We can explain most of these effects by extending our adatom-vacancy model for surface diffusion at the experimental temperatures (400 to 1000 C) to incorporate charging of the surface vacancies, in direct analogy with vacancy behavior in bulk semiconductors. Charging of the vacancies requires electron transfer to or from surface quasi-fermi levels, whose positions are modified by illumination as in surface photovoltage spectroscopy. Our results have significant implications for semiconductor manufacturing steps performed by the lamp illumination of rapid thermal processing.

11:40am SS2-WeM11 The Role of Surface Reconstruction in the Photofragmentation Dynamics of Oriented Methyl Bromide Adsorbed on GaAs, K.A. Khan, N. Camillone III, R.M. Osgood Jr., Columbia University; J.A. Yarmoff, University of California, Riverside

Our previous work has detailed the UV-initiated dissociation of CH_3Br physisorbed on GaAs(110), both by numerous experimental techniques and theoretical calculations. The substrate-electron-mediated dissociation yields energetic (1.4eV) methyl fragments whose dynamics are governed by surface-alignment forces acting on the adsorbate. The anisotropic angular distribution of the methyl fragments reflects the surface corrugation of the 1×1 reconstruction of GaAs(110). In this paper

we demonstrate that significant changes are observed in the fragment dynamics upon modifying the surface reconstruction via well-controlled surface preparation protocols. Specifically, to further explore and understand the role played by the surface morphology in fragmentation dynamics, we have compared the photodissociation of methyl bromide on two different surface reconstructions of the (100) face of GaAs. In contrast to the (110) surface, mass and angle-resolved time-of-flight measurements show the ejection of methyl fragments from the (100) surface to be symmetrical about the surface normal. Photoinduced fragmentation of monolayers of methyl bromide on $c(8 \times 2)$ -reconstructed Ga-rich and $c(2 \times 8)$ -reconstructed As-rich GaAs(100) surfaces also reveals a striking difference between these two surface structures. On the Ga-terminated surface we observe desorption of intact CH_3Br as well as methyl fragments formed by photoinduced dissociation. Only methyl fragments are detected leaving the (110) surface and the As-terminated (100) surface. As in the (110) case, the mechanism for C-Br bond cleavage in the (100) cases is photo-initiated electron attachment from the surface to the molecule. However, the energetics of the methyl fragments are quite different on the three surfaces suggesting site-specific dissociation. Therefore, the energetics of the methyl fragments will be discussed in terms of the surface texture and stoichiometry of the three surfaces.

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