Chapter 4. Chemical Reaction Dynamics at Surfaces

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4.1 Chemical Reaction Dynamics on Semiconductor Surfaces

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The etching of semiconductor materials in halocarbon plasma environments is a complex chemical process. The plasma is used to produce species that are highly reactive with the semiconductor surface. Because many different reactive species, including radicals, ions, and highly excited neutral molecules are produced in a plasma, the mechanism of the etching reaction is difficult to probe. Our program is aimed at using molecular beam reactive scattering techniques to systematically examine the role of each of these species in the etching process.

The initial goal of this project was to measure the barrier to F_2 dissociative chemisorption on Si(100). Contrary to popular belief, we found essentially no barrier to the dissociation of F_2 on the unfluorinated surface. The dissociative chemisorption of F_2 on Si(100) proceeds with unit probability for translational energies of the incident F_2 molecules as low as 0.5 kcal/mol. However, there is a substantial barrier to dissociation above fluorine coverages of 0.5 monolayer. Higher fluorine coverages sufficient to produce the etch product SiF_4 require a higher translational energy of the F_2 molecule. We have observed efficient etching of Si(100) at 300 K for an incident kinetic energy of F_2 of 15 kcal/mol. The angular and translational energy distributions of the SiF_4 — as measured in our newly constructed scattering apparatus consisting of two beams incident on a surface and a rotatable, triply differentially pumped quadrupole mass spectrometer — indicate that the last step of the reaction is the thermal desorption of the product SiF_4 molecule.

We have established that silicon can be etched without the use of molecules incident with energies of hundreds of electron volts, such as those present in plasma etching environments. Molecular beam techniques utilize molecules with energies only slightly higher than thermal (<1 eV), and therefore do not introduce radiation damage or defects into the Si lattice, which is a typical result of plasma etching. We are continuing our work on this system to understand the lack of F_2 energy dependence on the formation of a second reaction product, SiF_2.

We have also recently observed a new kind of mechanism for dissociative chemisorption. In the limit of zero fluorine coverage, we observed that the Si surface strips one of the fluorine atoms from the incident F_2 molecule, leaving the other fluorine atom to scatter into the gas phase. Although this stripping reaction is analogous to the well-known stripping reactions in gas phase chemical reaction dynamics, this is the first observation of its kind from a surface.

Publications

Ceyer, S.T., D.J. Gladstone, M. McGonigal and M.T. Schulberg, "Molecular Beams: Probes of the Dynamics of Reactions on Surfaces." in *Physical Methods of Chemistry.* 2nd ed. Eds. B.W. Rossiter, J.F. Hamilton amd R.C. Baetzold. New York: Wiley, 1990. In press.

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Gladstone, D.J. *Reaction Dynamics of Fluorine with Silicon (100): Design of a Molecular Beam Surface Reactive Scattering Chamber.* Ph.D. diss. Department of Chemistry, MIT, 1989.

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4.2 Collision Induced Dissociative Chemisorption of CH_4 on Ni(111) by Inert Gas Atoms: The Mechanism for Chemistry with a Hammer

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We observed that the dissociation of CH_4 physisorbed on Ni(111) at 46 K is induced by the impact of incident inert gas atoms. We studied the dynamics and mechanism of this new process — collision induced dissociative chemisorption — using molecular beam techniques coupled with ultrahigh vacuum electron spectroscopies. The absolute cross section for collision induced dissociation is measured over a wide range of kinetic energies (28–109 kcal/mol) and incident angles of Ne, Ar and Kr atom beams. The cross section displays a complex dependence on the energy of the impinging inert gas atom, characteristic of neither total nor normal energy scaling. Quantitative reproduction of the complex dependence of the cross section on the Ar and Ne incident energy by a two-step, dynamical model establishes the mechanism for collision induced dissociation.

Collision induced dissociation occurs by the impulsive transfer of kinetic energy upon collision of Ar or Ne with CH_4, followed by the translationally activated dissociative chemisorption of the CH_4 upon its subsequent collision with the Ni surface. The dependence of the probability of activated dissociation on the resultant CH_4 normal energy, derived from the fit of the model to the experimental cross section, is in excellent agreement with the results of a previous study of the translationally activated dissociative chemisorption of CH_4 on Ni(111). We have shown that collision induced activation and translational activation are consistent mechanisms for providing energy to CH_4, surmounting the barrier to dissociative chemisorption.

Publications

Beckerle, J.D., A.D. Johnson, Q.Y. Yang and S.T. Ceyer. "Collision Induced Dissociative Chemisorption of CH_4 on Ni(111) by Inert Gas Atoms: The Mechanism for Chemistry with a Hammer." *J. Chem. Phys.* 91: 5756 (1989).

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Ceyer, S.T. "The Mechanism for CH_4 Dissociation and the Synthesis of C_6H_6 from CH_4 on Ni(111)." Paper presented at the Pacifichem '89 Conference, American Chemical Society, Honolulu, Hawaii, December, 1989.

Ceyer, S.T. "Dynamics of Sticky Collisions with a Surface: Splats and Hammers." Paper presented at the National Symposium on Frontiers of Science, National Academy of Science, Irvine, CA March, 1989.

Ceyer, S.T. "Dynamics of Activated Dissociative Chemisorption and Collision Induced Desorption of CH_4 on Ni(111)." Paper presented at the Debye Symposium, American Chemical Society Meeting, Dallas, April, 1989.

Ceyer, S.T. "Dynamics of Sticky Collisions with a Surface: Splats and Hammers." Paper presented at the Ninth International Summer Institute in Surface Science, University of Wisconsin at Milwaukee, August, 1989.

Ceyer, S.T. "Dynamics of Collision Induced Dissociation and Desorption of CH_4 on Ni(111)." American Institute Chem. Eng. Meeting, San Francisco, November, 1989.

4.3 Collision Induced Desorption

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Project Staff

Professor Sylvia T. Ceyer, John D. Beckerle, Andrew D. Johnson, Qingyun Yang

The desorption of CH_4 physisorbed on Ni(111) is observed to be induced by collision with Ar atoms incident with energies less than 2 eV. The absolute cross section for collision induced desorption is measured as a function of the kinetic energy and incident angle of the Ar beam. The mechanism for desorption is shown to involve a direct and impulsive, bimolecular collision between Ar and CH_4. Molecular dynamics simulations show that the energy and incident angle dependence of the desorption cross section are the consequence of two competing dynamical effects.

Publications

Beckerle, J.D., A.D. Johnson and S.T. Ceyer, "Observation and Mechanism of Collision Induced Desorption: CH_4 on Ni(111)," *Phys. Rev. Lett.* 62: 685 (1989).

Ceyer, S.T. "Dynamics of Sticky Collisions with a Surface: Splats and Hammers." Paper presented at the National Symposium on Frontiers of Science, National Academy of Science, Irvine, CA, March, 1989.

Ceyer, S.T. "Dynamics of Activated Dissociative Chemisorption and Collision Induced Desorption of CH_4 on Ni(111)." Paper presented at the Debye Symposium, American Chemical Society Meeting, Dallas, April, 1989.

Ceyer, S.T. "Dynamics of Sticky Collisions with a Surface: Splats and Hammers." Paper presented at the Ninth International Summer Institute in Surface Science, University of Wisconsin at Milwaukee, August, 1989.

Ceyer, S.T. "Dynamics of Collision Induced Dissociation and Desorption of CH_4 on Ni(111)." American Institute Chem. Eng. Meeting, San Francisco, November, 1989.

Ceyer, S.T. "Dynamics of Sticky Collisions with a Surface: Splats and Hammers." Paper presented at Workshop on Dynamics of Surface Reactions, Copenhagen, Denmark, May, 1989.

4.4 Synthesis of Benzene from Methane

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With the knowledge gained from our studies of methane activation about the microscopic origins for the pressure gap, we have been able to develop a scheme for bypassing the high pressure requirement. This scheme involves raising the energy of the incident molecule or collisionally inducing dissociation. In this way, we have been able to perform a high pressure reaction at low pressure: the synthesis of C_6H_6 from CH_4. In addition, because this reaction is carried out at low pressure, we have been able to identify the adsorbed intermediates by high resolution electron energy loss spectroscopy and to determine the mechanism of this reaction.

The synthesis is effected by exposing a monolayer of CH_4 physisorbed on Ni(111) at 47 K to a beam of Kr atoms. The collision of the incident Kr with the physisorbed CH_4 distorts the CH_4 from its tetrahedral configuration, thereby lowering the barrier to dissociation into an adsorbed methyl radical and an adsorbed hydrogen atom. As the surface temperature is raised to 230 K, all the adsorbed CH_3 dissociates to CH and the CH recombines to form adsorbed C_2H_2. Some of the C_2H_2 trimerizes to adsorbed C_6H_6 and at 410 K and 425 K, respectively, the atomically adsorbed hydrogen desorbs as H_2 and some of the chemisorbed C_6H_6 desorbs. The gas phase benzene is detected mass spectrometrically in a thermal desorption experiment. Although the maximum thermal desorption yield for benzene is 1.5 percent at a crystal heating rate of 17 K/S, the gas phase hydrocarbon selectivity of this synthesis for benzene production is 100 percent. This is the first observation of a reaction of CH_4 to form a gas phase, higher hydrocarbon over a metallic catalyst at the low pressures commensurate with a UHV environment.

Publications

Ceyer, S.T. "Bridging the Gap Between Surface Science and High Pressure Processes." Langmuir Award Lecture presented at the American Chemical Society, Miami, Florida, September, 1989.

Maynard, K.J., Q.Y. Yang, A.D. Johnson and S.T. Ceyer, "The Synthesis of C_6H_6 from CH_4." Paper presented at the American Vacuum Society, Boston, October, 1989.

Yang, Q.Y., A.D. Johnson, K.J. Maynard and S.T. Ceyer. "Synthesis of Benzene from Methane over a Ni(111) Catalyst." *J. Am. Chem. Soc.* 111: 8748 (1989).

4.5 The Structure and Chemistry of CH_3 and CH Radicals and Isotopic Variants Adsorbed on Ni(111)

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Project Staff

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We present a detailed analysis of the vibrational spectra of CH_3 , CH_2D and CD_3 adsorbed on Ni(111) and of the products of its reactions. Molecular beam techniques effect the synthesis of adsorbed methyl radicals from CH_4 , CH_3D or CD_4. Because we can measure these spectra at both higher resolution (30 cm^{-1}) and higher sensitivity (5×10^6 counts/sec), we have been able to observe both new features and also to carry out a symmetry analysis. The CH_3 radical is shown to be adsorbed with C_{3v} symmetry on a threefold hollow site. The symmetric C-H stretch mode of CH_3 and the overtone of the asymmetric deformation mode are shown to be in Fermi resonance. At temperatures above 150 K, CH_3 dissociates to form adsorbed CH.

Confirmation for the assignment of the spectrum to a CH species is found in the spectrum measured after thermal decomposition of CH_2D. This species decomposes to a mixture of adsorbed CH and CD. The frequencies of the C-H and C-D stretch modes are identical to the frequencies of these species produced from the decomposition of CH_3 and CD_3. The adsorption site of the CH species is determined to be a threefold hollow site and the geometry of the Ni_3-C-H is determined to be pyramidal. At temperatures above 230 K, carbon-carbon bond formation between the CH species is observed to yield C_2H_2. Low coverages of C_2H_2 are shown conclusively to dissociate to C_2H and C_2 species at 400 K in contrast to a literature report of C_2H_2 dissociation to adsorbed CH. At temperatures above 380 K, high coverages of C_2H_2 result in trimerization to adsorbed benzene. The relative stabilities of the C_1 species on Ni(111) are determined to be $CH_2 < CH_3 < CH$.

Publications

Yang, Q.Y. *The Chemistry of CH4 on Ni(111).* Ph.D. diss. Dept. of Chemistry, MIT, 1989.

4.6 High Resolution Electron Energy Loss Spectroscopy of H on Ni(111)

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A high resolution electron energy loss spectrum of half of a monolayer of H(D) adsorbed on Ni(111) has been measured with sufficient intensity and resolution to allow seven vibrational loss features to be observed: $\nu_{asy} = 745$, 790 cm^{-1}; $\nu_{sym} = 1085$, 1105 cm^{-1}; $2\nu_{asy} = 1260$, 1400 cm^{-1}; $2\nu_{sym} = 2180$ cm^{-1}. The assignments of the fundamentals are based on the measured anharmonicity and angular distributions of the vibrational loss features.

The splitting of the ν_{asy} and ν_{sym} modes is explained by the local potential difference of H adsorbed on the fcc and hcp threefold sites. The absence of dispersion of these modes, as evidenced by measurements of the spectra at Σ of the Brillouin zone, indicate that dynamical coupling between the hydrogen atoms on neighboring sites is not operative to within the resolution of this experiment.

The splitting of the overtone of the asymmetric Ni-H stretch mode is due to a transition of each of the two different hydrogen atoms to the second vibrationally excited state. The observation of two distinct vibrational frequencies corresponding to the hydrogen atoms adsorbed on two threefold sites, whose structures differ only in the presence of a Ni atom in the second layer, confirms the previously proposed structure for the (2x2)2H overlayer. Since this is the first observation of any experimentally determined distinction in the physical properties of hcp and fcc threefold sites on any metal surface, these results provide a critical test of theory.

Publications

Yang, Q.Y., A.D. Johnson and S.T. Ceyer, "High Resolution Electron Energy Loss Spectroscopy of H on Ni(111)." Paper presented at American Vacuum Society, Boston, October, 1989.

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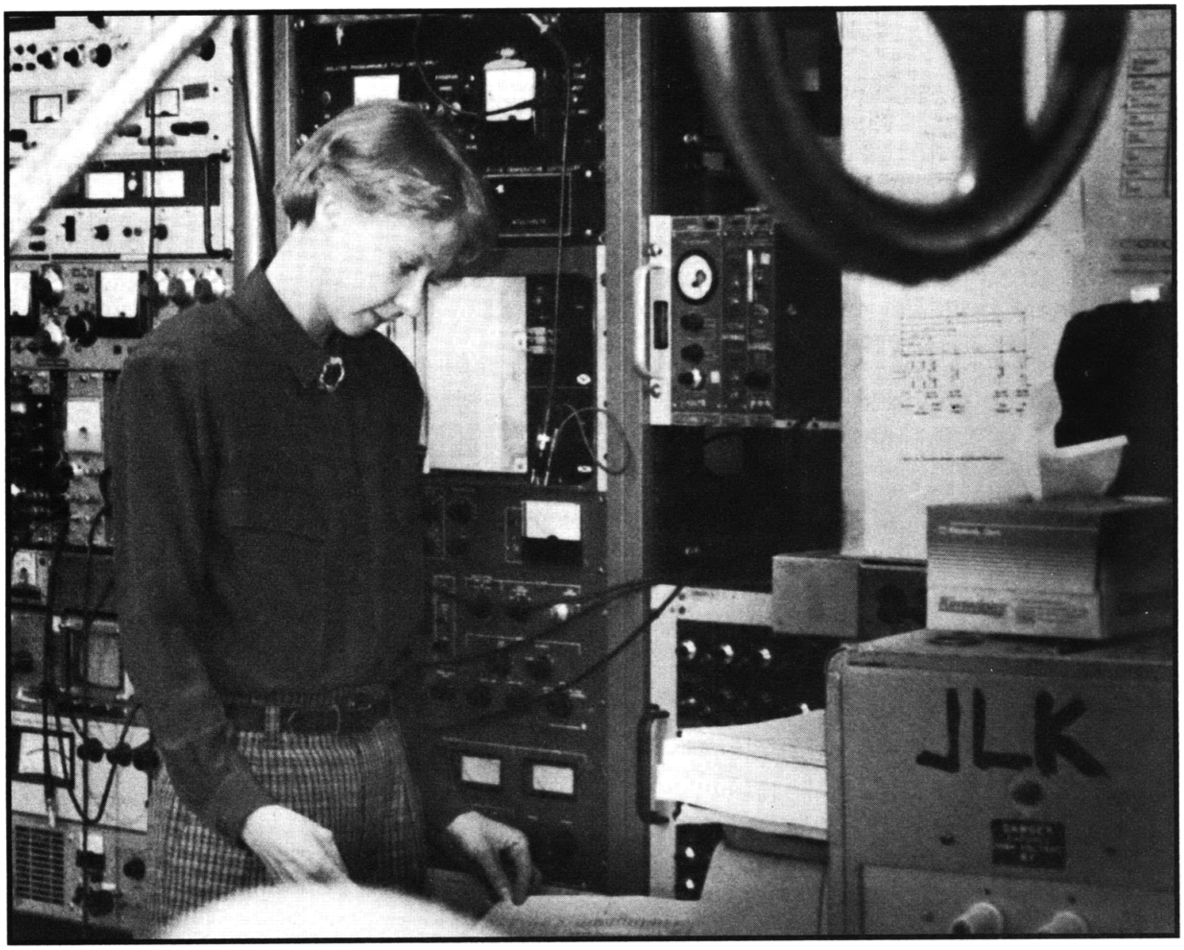

Professor Sylvia T. Ceyer with the molecular beam surface scattering apparatus.