

Chapter 3. Chemical Reaction Dynamics at Surfaces

Academic and Research Staff

Professor Sylvia T. Ceyer, Dr. Yulin Li, Dr. David P. Pullman, Dr. Arthur L. Utz

Graduate Students

Sean P. Daley, Theodore R. Trautman, Julius J. Yang

Undergraduate Students

Gerald R. Cain

Technical and Support Staff

Anne Stollerman

3.1 Dynamics of the Reaction of F₂ with Si(100)

Sponsor

Joint Services Electronics Program
Contract DAAL03-89-C-0001
Contract DAAL03-92-C-0001

Project Staff

Professor Sylvia T. Ceyer, Dr. Yulin Li, Dr. David P. Pullman, Julius J. Yang, Gerald R. Cain

As we have shown previously, F₂ reacts with Si(100) with very close to unity probability (~ 0.95) up to one monolayer of coverage, contrary to popular belief. We have now also shown that the sites for fluorine adsorption under these conditions are the dangling bonds and that the adsorbed fluorine does not lift the reconstruction. This was accomplished using a new technique of He atom diffraction that we have recently implemented in our molecular beam-ultrahigh vacuum surface scattering apparatus. The experiment is carried out by directing a well-characterized, monoenergetic beam of He atoms at the surface and monitoring the angular distribution of the diffracted atoms. This arrangement adds a powerful new structural probe to our experimental capabilities. While the binding of fluorine to the dangling bonds along with the maintenance of the surface dimer bond is not surprising, our results show the first experimental evidence for it. No experimental information about this system had been available previously because the common structural probes, electron diffraction techniques, are not sensitive to halogens.

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, and R.C. Baetzold. New York: Wiley, 1991. Forthcoming.

3.2 Dynamics of the Reaction of F₂ with Fluorinated Si(100)

Sponsor

Joint Services Electronics Program
Contract DAAL03-89-C-0001
Contract DAAL03-92-C-0001

Project Staff

Professor Sylvia T. Ceyer, Dr. Yulin Li, Dr. David P. Pullman, Julius J. Yang, Gerald R. Cain

We have previously shown that the reaction probability of F₂ with a clean Si(100) surface decays from near unity to zero as the fluorine coverage increases to one monolayer. This lack of reactivity with the fluorinated Si surface is the source of the misconception that F₂ does not react with Si. The lack of reactivity with the fluorinated surface precludes the build up of a sufficient layer of fluorine to produce the volatile etch product, SiF₄. However, we have also previously shown that if the kinetic energy of the incident F₂ molecule is increased above a threshold value of 6 kcal/mol (~ 0.25 eV), the dissociation probability of F₂ with a fluorinated Si surface increases linearly with the normal component of kinetic energy. This is a result of a barrier to dissociation that is overcome by translational energy of the incident molecule.

The enhancement in the dissociation probability allows enough fluorine to be deposited to form the etch product, SiF_4 . This result establishes that Si can be etched with low energies using molecular beam techniques and without the use of plasmas. The low energies afforded by molecular beam techniques prevent the introduction of radiation damage or defects into the Si lattice, which are typical results of plasma etching.

We have begun a new project aimed at determining the origin of the barrier to dissociation of F_2 on the fluorinated surface. The hypothesis is that the barrier to F_2 dissociation is largely associated with breaking the Si surface dimer bond. To test this hypothesis, we are using He atom diffraction as a probe of the surface structure after exposure to the energetic F_2 . Preliminary measurements indicate that the disappearance of the dimer bond, as measured by the half order diffraction feature, correlates well with the increase in the dissociation probability as a function of the F_2 incident translational energy in the normal direction. This result may be the first determination of the physical origin of a reaction barrier in any semiconductor system.

3.3 New Mechanisms for Surface Processes

Sponsor

National Science Foundation
Grant CHE 90-20623

Project Staff

Professor Sylvia T. Ceyer, Dr. Arthur L. Utz, Andrew D. Johnson, Sean P. Daley, Theodore R. Trautman

We report the first detection and identification of vibrational modes of buried species by high resolution electron energy loss spectroscopy (HREELS) and the observation of a new mechanism for absorption of adsorbates, collision-induced absorption, as applied to the interaction of hydrogen with Ni(111).

Subsurface or bulk sites of a Ni single crystal are populated with atomic hydrogen by exposure of the (111) face of the Ni crystal at 130 K to atomic hydrogen. Atomic hydrogen is generated by thermal dissociation of H_2 over a hot tungsten filament positioned 0.25 inches from the crystal surface. This results in a flux of both atomic and molecular hydrogen to the front surface of the crystal. The H^+ ions and electrons generated by the

filament are shown to play no role in the following observations. Both atomic H and H_2 result in population of the threefold hollow surface sites up to a surface saturation coverage of 1 ML. The HREEL spectrum at 1 ML is characterized by the Ni-H asymmetric stretch at 955 cm^{-1} and the Ni-H symmetric stretch at 1170 cm^{-1} , and the thermal desorption spectrum exhibits two maxima at 340 and 380 K. Further exposure to atomic H results in the appearance of a new feature in the HREEL spectrum at 800 cm^{-1} and in the thermal desorption spectrum at 180-220 K. The loss feature at 800 cm^{-1} , for which an impact scattering mechanism is operable, is identified as a Ni-H vibration of bulk H by the similarity of the dependence of its intensity on electron impact energy to the dependence of the electron inelastic mean free path on electron energy. At 3 eV impact energy, the intensity of the 800 cm^{-1} loss feature is large but decreases monotonically to almost zero as the impact energy is increased beyond 15 eV. This kind of dependence of the intensity of a loss feature associated with a bulk vibrational mode is expected because the inelastic mean free path of an electron, which is 80 \AA at 3 eV, rapidly drops to 1 \AA as the energy is increased above the plasmon frequency of the metal (15 eV), where plasmon creation is the predominant energy loss mechanism which shortens the mean free path. In contrast, the intensity of the two loss features associated with surface chemisorbed H exhibits almost no dependence on electron energy with the exception of a resonance at 7 eV. As much as an equivalent of 8 monolayers of hydrogen have been absorbed into the bulk.

Subsurface or bulk sites of Ni can also be populated via a newly observed mechanism, collision-induced absorption. A beam of monoenergetic Kr or Xe atoms, produced by the supersonic expansion of Kr or Xe seeded in He, is directed at a monolayer of atomic hydrogen chemisorbed on Ni(111). The impacts of the incident inert gas atoms are observed to induce the absorption of the chemisorbed hydrogen. The hydrogen thus absorbed is identified by the appearance of (1) a loss feature at 800 cm^{-1} and (2) a feature at 180-220 K in the thermal desorption spectrum, consistent with the study of atomic hydrogen absorption. The absorption probability scales linearly with the energy of the incident Xe atom above a threshold energy of 2.5 eV. Collision-induced absorption may play a significant role in the mechanism for hydrogen absorption in the high pressure environments of a hydrogen storage cell where the hydrogen saturated surface is continually subject to bombardment by a large flux of energetic particles.

Publications

Johnson, A.D. *Dynamics of Hydrogen Absorption into the Ni(111) Bulk: Spectroscopic Identification and Chemistry of Subsurface Hydrogen*. Ph.D. diss., Dept. of Chem., MIT, 1991.

Johnson, A.D., K.J. Maynard, S.P. Daley, Q.Y. Yang and S.T. Ceyer. "Hydrogen Embedded in

Ni: Production by Incident Atomic Hydrogen and Detection by High Resolution Electron Energy Loss." *Phys. Rev. Lett.* 67: 927 (1991).

Maynard, K.J., A.D. Johnson, S.P. Daley and S.T. Ceyer. "A New Mechanism for Absorption: Collision Induced Absorption." *J. Chem. Soc., Faraday Discussion* (1991). Forthcoming.



Professor John D. Joannopoulos