Chapter 3. Chemical Reaction Dynamics at Surfaces

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3.1 A New Mechanism for Dissociative Chemisorption on Si: Atom Abstraction

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The classic view of dissociative chemisorption of a molecule incident on a surface involves cleavage of the bond of an incident molecule by formation of two bonds to the surface. The result is two fragments adsorbed on the surface. The dissociation proceeds in this manner because the formation of two bonds is energetically necessary for bond cleavage. This classic mechanism for dissociative chemisorption is operative in many molecule-surface systems. In contrast, one can envision bond cleavage by formation of a single surface-atom bond if the energy released by this bond formation is greater than the bond energy of the incident molecule. Generically, this mechanism, known as abstraction, is a well-documented reaction mechanism between two gas phase molecules.

With JSEP support, we have recently documented the dissociative chemisorption of a molecule on a surface by an abstraction mechanism. Specifically, we demonstrated that a Si(100)2x1 surface abstracts one F atom from an incident F_2 molecule by detecting the complementary F atom scattered back into the gas phase with a triply differentially pumped, rotatable, quadrupole mass spectrometer in a molecular beam-surface scattering UHV apparatus. In addition, we coupled these experiments with He atom diffraction from the resulting fluorinated surface to demonstrate that the Si surface dangling bonds are responsible for the abstraction and are the sites for F adsorption. Because of the experimental complexities in the detection of reactive radicals such as F atoms, this mechanism has not been found in numerous previous studies of the interaction of fluorine and fluorine containing molecules with Si.

Briefly, the triply differentially pumped F_2 beam is formed by expansion of a mixture of 1 percent F_2 in Kr. The velocities of the incident and scattered beam are determined by cross correlation time-of-flight (TOF) methods. The beam is directed at an n-type Si(100) crystal that can be heated resistively and cooled to 150 K. The crystal is etched prior to insertion into the vacuum chamber where it is repetitively sputtered and annealed (850°C for 30 minutes) until Auger spectroscopy reveals carbon as the only contaminant, at a 1 percent or less level. The atom diffraction measurements show the surface to exhibit the well-documented (2x1) reconstruction associated with the formation of Si surface dimers. In real space, the surface exhibits rows of Si-Si dimers, with one dangling bond per Si atom.

Identification of the abstraction mechanism by detection of the scattered F atom is complicated by the fragmentation of the unreactively scattered F_2 in the electron bombardment ionizer of the mass spectrometer to produce both F_2^+ (m/e=38) and F^+ (m/e=19) ions. Therefore, a signal observed at m/e=19 will contain a contribution from scattered F_2 as well as from F atoms, if present. We can distinguish between F^+ arising from F atoms and that produced by the cracking of F_2 on the basis of the different velocities with which they scatter from the surface. Two features are clearly observed in the time of flight spectrum, a narrow one at short times and a broad feature at longer times. The TOF distribution measured at m/e=38, scaled by the F^+/F_2^+ cracking ratio, can be superimposed on the m/e=19 spectrum. The single feature in m/e=38 distribution is observed to occur at the same flight time as the broad one in the m/e=19 distribution and its intensity, scaled to represent the component of the m/e=19 signal attributed to F_2, matches well the intensity of the broad feature in the m/e=19 spectrum. These two observations lead to the conclusion that the broad feature arises from the cracking of the unreactively scattered F_2 while the narrow, short time feature arises from scattered F atoms. A point-by-point subtraction of the two distributions yields the net scattered F atom TOF distribution. From the fits to the distributions, the flux-weighted average velocities of F and F_2 are determined to be 1140±40 m/s and 430±32 m/s, respectively, for a surface temperature of 250K. The incident F_2 velocity is 390 m/s. Measurements of the TOF distributions of F and F_2 scattered from a surface at a temperature of 1000 K show that the velocity of the scattered F is independent of temperature (1181±64 m/s) while the velocity of the scattered F_2 is higher (600±42 m/s). No ions are observed to desorb.

Additional confirmation of the presence of scattered F atoms comes from the F_2 exposure dependence of the scattered signal at m/e=19 and 38. The two signals have a very different dependence on F_2 exposure. While both signals become constant at high exposure, the m/e=19 signal rises significantly more rapidly at very low exposure than the m/e=38 signal. It is clear that the F^+ signal at low exposure arises from a source different from the cracking of F_2 in the ionizer. We assign it to F atoms scattered from the surface. The F atom signal is a maximum at a low but non-zero exposure and then decays to zero with increasing exposure.

To probe the site of F adsorption, we have measured He diffraction spectra from the clean and F-covered Si(100)2x1 surface. They are recorded by directing a supersonic He atom beam (E=11 meV, ΔE=4 meV), incident on the 250 K surface at a 20° angle from the surface normal, and then detecting the scattered He in 0.5° increments. The He beam is modulated at 150 Hz for the purpose of background subtraction. The key result is that the half order diffraction beam which is the signature for the presence of the Si-Si dimers, is clearly present in the spectrum from the fluorinated surface, indicating that the adsorption of F does not break the dimer bond. Moreover, the diffraction intensities from the fluorinated surface remain unchanged upon further F_2 exposure, indicating that the surface is saturated and that the F is adsorbed as an ordered overlayer with a (2x1) unit cell. In addition, we have determined, as discussed below, that the coverage of this (2x1) overlayer is 1 ML, which is equivalent to one F for every Si dangling bond. These observations convincingly demonstrate that the reaction of F_2 with Si(100) is occurring at the dangling bond sites of the surface dimers, and that no Si-Si lattice bonds are broken. This structural determination does not suffer from the ambiguity in LEED generated by efficient electron stimulated desorption of F and is consistent with other results that identify SiF as the dominant species.

These results signal the observation of a new mechanism for dissociative chemisorption and we designate it F atom abstraction. As F_2 is incident on this surface, a Si dangling bond abstracts one of the F atoms while the other F atom is scattered away. The cleavage of the F_2 bond by the formation of a single F-Si bond is thermodynamically feasible because the energy released upon adsorption on a single Si dangling bond, which does not require cleavage of a Si lattice bond, is 5-6 eV compared to 1.5 eV for the F_2 bond energy. Some of the exothermicity of this bond formation is converted into translational energy of the scattered F, as evident from the large velocity of the scattered F compared to the incident F_2 and the independence of the velocity on surface temperature. Abstraction has been observed in a simulation of this system.

While the F atom that is not abstracted can scatter back into the gas phase, it does not necessarily do so. It may be caught on its outgoing trajectory by an adjacent dangling bond and adsorb there. It is also possible for both atoms to be simultaneously abstracted each by two adjacent dangling bonds if the F_2 molecular axis is favorably aligned upon its initial collision. We can demonstrate that adsorption of both atoms also occurs by measuring the difference between the total F_2 adsorption probability, P_t, and the probability for single atom adsorption, P_1. P_t is determined from $1-P_u$, where P_u, the probability for unreacted F_2 to be scattered from the surface, is the ratio of the angle integrated F_2 flux to the incident F_2 flux. P_1 is the ratio of the angle integrated F flux to the incident F_2 flux. The difference P_t-P_1 is the probability for adsorption of both F atoms, P_2, and is plotted, along with P_1 and P_t, versus coverage. The coverage is determined by integrating $P_2+0.5P_1$ over F_2 exposure. In the zero coverage limit, P_2 contributes 0.83 and P_1 contributes 0.12 to the total P_t of 0.95, in reasonable agreement with a simulation and with a previous experimental result for P_t. The adsorption probability is observed to decay to zero when the dangling bonds are saturated at 1 ML fluorine coverage.

The maximum in P_1 at a non-zero coverage is also consistent with the presence of a reaction channel in which both F atoms are adsorbed. P_1 is small in the limit of zero coverage because the dangling bonds adjacent to the abstraction site of the first F atom are likely unoccupied and, therefore, have a high probability of trapping the second F. As the coverage increases, the probability of having unoccupied adjacent sites decreases, thereby leading to a higher probability that the second F does not adsorb and scatters back to the gas phase. As the coverage increases beyond 0.6 ML, the effect of the diminishing number of sites for abstraction of the initial F dominates, leading to an overall decay of P_1. In short, the maximum in P_1 arises from the competition between the number of abstraction sites available to the incident F_2, which decreases with coverage, and the number of occupied sites (which cannot trap the second F) adjacent to the abstraction site, which increases with coverage. A simple analytical model which incorporates these physical features well and describes these data is presented in the next section. Note that P_1 is a lower limit to the abstraction probability because its value is based only on those complementary atoms which successfully scatter back to the gas phase.

In summary, we have identified and characterized a new mechanism for dissociative chemisorption, atom abstraction. This mechanism is a consequence of the high exothermicity of the reaction between F_2 and Si and should be observable in other highly exothermic molecule-surface interactions. This mechanism may also be an additional source of radicals that have been previously unaccounted for in models for plasma etching.

3.1.1 Publications

Journal Article

Li, Y.L., D.P. Pullman, J.J. Yang, A.A. Tsekouras, D.B. Gosalvez, K.B. Laughlin, M.T. Schulberg, D.J. Gladstone, M. McGonigal, and S.T. Ceyer. "Observation of a New Mechanism for Dissociative Chemisorption: F Atom Abstraction on Si(100)." Submitted to *Phys. Rev. Lett.*

Chapter in Book

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,* Vol. IXA: *Investigations of Surfaces and Interfaces*, 2nd ed. Eds. B.W. Rossiter and R.C. Baetzold. New York: Wiley and Sons, Inc., 1993.

Meeting Papers

Ceyer, S.T. "A New Mechanism for Dissociative Chemisorption on Si: Atom Abstraction." Paper presented at the American Chemical Society Meeting, Denver, Colorado, March 23, 1993.

Ceyer, S.T. "A New Mechanism for Dissociative Chemisorption on Si: Atom Abstraction." Paper presented at the Gordon Research Conference on Gas-Surface Dynamics, Proctor Academy, Andover, New Hampshire, August 2, 1993.

Theses

Yang, J.J. *Reaction Dynamics of* F_2 *with Si (100): I. A New Mechanism for Dissociative Chemisorption: Atom Abstraction II. Translationally Activated Etching.* Ph.D. diss., Dept. of Chem., MIT, 1993.

3.2 A Model for Atom Abstraction by Surfaces

Sponsor

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Project Staff

Professor Sylvia T. Ceyer, Dr. David P. Pullman, Dr. Athanassios A. Tsekouras, Dr. Zhe Zhang, David B. Gosalvez, Julius J. Yang

The probability for atom abstraction, P_1, exhibits a very non-langmuir dependence on fluorine coverage. Specifically, our abstraction probability first increases, goes through a maximum and then decreases to zero at a coverage of one monolayer of fluorine while a langmuir dependence of an adsorption probability decreases strictly linearly with coverage. We have developed a simple analytical model based on lattice gas kinetics to understand this peculiar dependence on coverage. Consider a F_2 molecule approaching the surface with its molecular axis roughly parallel to the surface. The probability of the first fluorine atom being abstracted depends linearly on the coverage, a $(1-\theta)$ dependence, where θ is the fractional coverage. Once the first F atom is abstracted, the second F atom is propelled away by the exothermicity of the reaction. However, because of the horizontal orientation of the incident F_2 molecule, the second F atom is propelled along the surface. The probability of it showing up in the gas phase where it contributes to our measurement of P_1 is proportional to the occupancy of the adjacent sites which has a θ

dependence. That is, if the fluorine atom is propelled in the direction of a unfilled dangling bond, it will adsorb and will not scatter into the gas phase. But, if it is propelled in the direction of a filled dangling bond, it cannot adsorb and will scatter into the gas phase. Therefore, the $(1 - \theta)$ dependence must be multiplied by a θ dependence resulting in a quantity proportional to P_1 that is zero at zero coverage and that has a maximum at $\theta = 0.5$. Therefore, it is clear that the maximum in the abstraction probability occurs as a result of the competition between the number of unfilled sites for abstraction of the first F atom which decreases with coverage and the number of filled sites to scatter the second F atom into the gas phase which increases with coverage.

However, there is an additional contribution to the abstraction mechanism which shifts the coverage at which the maximum occurs to lower values and which results in a non-zero coverage at zero fluorine coverage. This additional contribution arises from those F_2 molecules that are incident on the silicon surface with their molecular axes perpendicular to the surface. In this case, the probability for abstraction of the first F atom again has a $(1 - \theta)$ dependence, but because of the vertical orientation of the incident F_2, the second F atom is propelled away from the surface. The probability of its appearance in the gas phase is independent of the occupancy of the adjacent sites. Therefore, this $(1 - \theta)$ dependence for the vertically oriented molecules must be added to the $\theta(1 - \theta)$ dependence for the horizontally oriented molecules. The resulting prediction for the abstraction probability P_1 versus coverage agrees reasonably well with the data. The good agreement with this lattice gas model indicates that the mechanism for dissociative chemisorption indeed proceeds as a two step process involving first an abstraction step followed by the adsorption of the second F atom if it is propelled across the surface in the direction of an empty dangling bond. If it is propelled in the direction of a filled site, it scatters into the gas phase away from the surface. Whether the second F atom is propelled across the surface or away from the surface depends on its incident orientation.

We have also carried out a Monte Carlo simulation of the abstraction probability versus coverage. The results of this simulation show that steric hindrance between the incident F_2 and the filled dangling bond sites at intermediate coverages plays a large role in the rapid drop of the adsorption probability of F_2 with coverage. That is, even though the first abstraction step requires only a single empty dangling bond site, it is difficult for an incident F_2 molecule to access this site if it is surrounded by sites on which F atoms are already adsorbed.

3.2.1 Publication

Pullman, D.P., Y. Li, J.J. Yang, A.A. Tsekouras, D.B. Gosalvez and S.T. Ceyer. "Analytical and Monte Carlo Models for Atom Abstraction by Surfaces." Submitted to *J. Chem. Phys.*

3.3 Atom Abstraction and its Relationship to Thin Film Growth

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Project Staff

Professor Sylvia T. Ceyer, Dr. David P. Pullman

We have recently demonstrated by Monte Carlo simulation, that our newly discovered mechanism, atom abstraction, provides a suitable physical explanation for non-statistical island growth. Specifically, Brune et. al. employed scanning tunneling microscopy to show that the spatial distribution of O atoms on Al(111) after adsorption of O_2 at low exposures was essentially random. This is a surprising result because within a conventional view of dissociative chemisorption, the adsorbing atoms are expected to reside on neighboring sites. The resulting spatial distribution is therefore non-random and is manifested in a pair correlation function that peaks at the first nearest-neighbor shell. They explained these observations by a hot adatom model in which the reaction exothermicity is channelled into adatom translational motion parallel to the surface plane. If the transfer of energy into translation is large, the mean flight path of adatoms on the surface will likewise be large and the pair correlation function will be structureless.

We have shown however, that the structureless pair correlation function at low coverage and the non-statistical island growth at high coverage are also consistent with abstraction of one of the O atoms from the incident O_2 molecule while the unabstracted atom is either propelled into the gas phase or propelled along the surface. The trajectory of this latter atom may be halted if it collides with an island next to which there is an empty site but if not, it will scatter into the gas phase. As we have pointed out, the abstraction of an O atom from O_2 by Al is thermodynamically feasible as it is in the interaction of F_2 with Si(100). Our analysis demonstrates the generality of the atom abstraction mechanism and the importance of this mechanism to thin film growth.

3.3.1 Publication

Pullman, D.P., and S.T. Ceyer. "New Mechanisms of Dissociative Chemisorption on Surfaces: Analysis of the O_2/Al(111) and F_2/Si(100). Reactions." Submitted to *J. Chem. Phys.*

3.4 Etching of Si(100) by Energetic Fluorine

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Project Staff

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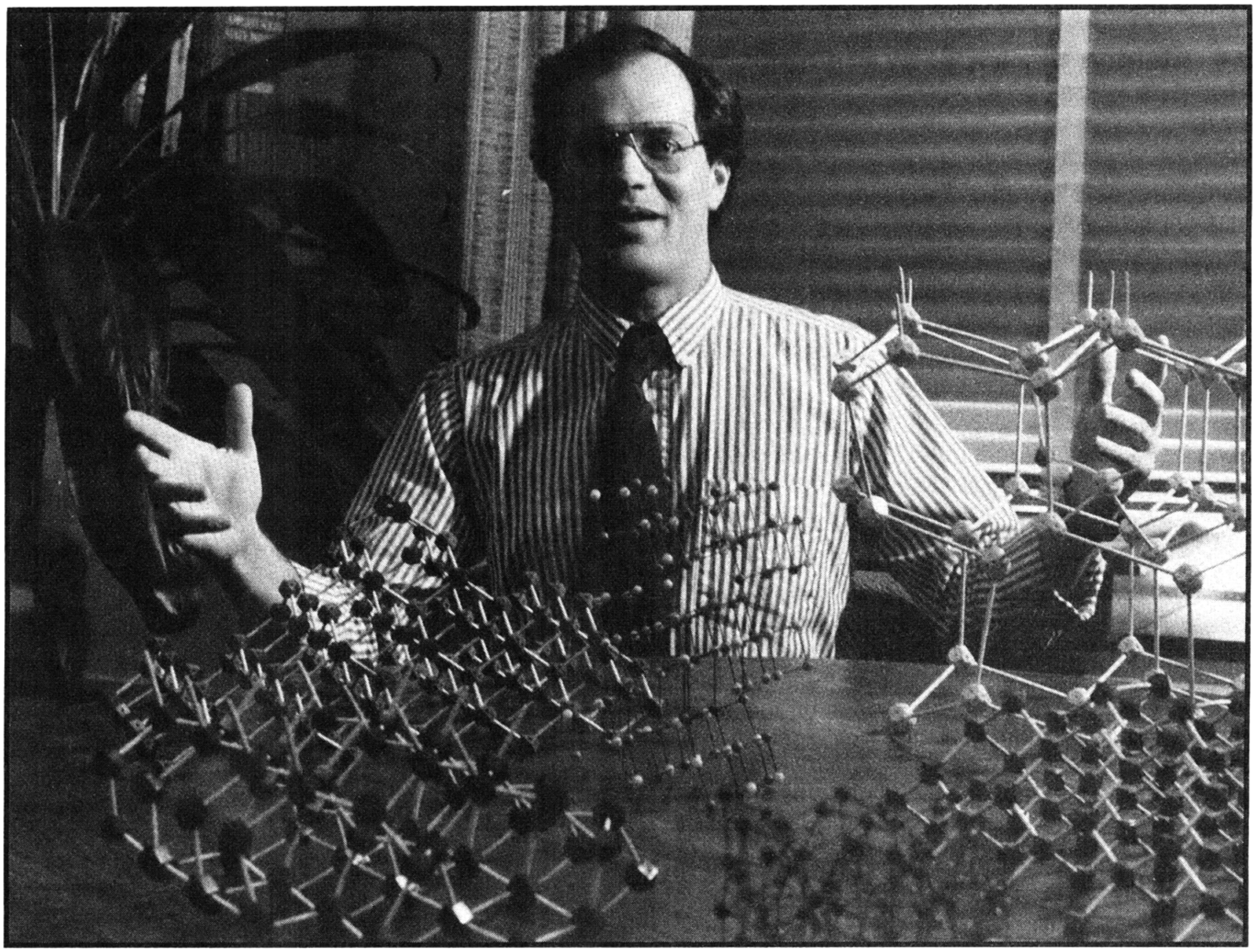
The reaction of F_2 with Si(100) ceases after the dangling bonds are saturated at one monolayer of coverage. This lack of additional reactivity precludes the build up of a sufficient layer of fluorine to produce the volatile etch product SiF_4, and therefore the use of F_2 as an etchant of Si. However, we have shown that if the kinetic energy of the incident F_2 molecule is increased above a threshold value of 4-5 kcal mol^{-1} (0.2 eV), the dissociation probability of F_2 on a fluorinated surface increases linearly with the normal component of the kinetic energy. This additional reactivity at higher translational energies, which results in fluorine coverages greater than one monolayer, is the result of surmounting barrier to dissociation on the fluorinated surface. During this funding period we coupled our measurements of the reactivity of F_2 as a function of energy with a structural technique, He atom diffraction. The goal was to identify the sites for the reaction of the translationally activated F_2 with the fluorinated surface. Our measurements of the He atom diffraction spectra as a function of the incident F kinetic energy indicate that the barrier is associated with dissociative chemisorption on the second layer of Si atoms as well as on Si dimer atoms. These conclusions are based on the identical rate of linear decay for all diffraction features with increasing F_2 normal energy above the threshold. There is no preferential cleavage of the Si dimer atoms. These observations may represent the first experimental correlation of the barrier for dissociation with the sites for dissociation.

These results also provide conclusive evidence that Si can be etched with low energies, two orders of magnitude below the energies used in plasmas, using molecular beam techniques, and without the use of plasmas. The low energies afforded by molecular beam techniques preclude the introduction of radiation damage or defects into the Si lattice, which is a typical consequence of plasma etching.

3.4.1 Publication

Li, Y., D.P. Pullman, J.J. Yang, and S.T. Ceyer. "Structure and Reactivity of Fluorinated Si(100)." Submitted to *J. Chem. Phys.*



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