

Initial Stages of Etching of the Si{100}(2×1) Surface by 3.0-eV Normal Incident Fluorine Atoms: A Molecular Dynamics Study

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Abstract: Etching of the dimer reconstructed silicon surface with an initial coverage of a monolayer of fluorine by 3.0-eV fluorine atoms at normal incidence has been examined with molecular dynamics. In the simulation, fluorine adsorption and product etching occur at the top of two atomic layers of silicon, which are exposed to the vacuum. We have identified mechanisms responsible for the gas-phase products SiF₄ and Si₂F_x, where $x = 5$ and 6. In addition, we have simulated a near-steady-state etched surface where the majority of the adspecies are monofluorinated species with a significant amount of difluorinated and trifluorinated species. Observed fluorosilyl towerlike structures are found to be important to the etching of the Si₂F_x species, and they also provide insight as to the possible structure of the adlayer formed on silicon samples after long time exposure to XeF₂.

Introduction

The fundamental reaction mechanisms involved in the adsorption of atomic fluorine to silicon and the subsequent etching are poorly understood despite intensive experimental¹⁻¹¹ and theoretical¹²⁻¹⁶ investigations. One can easily imagine that the fluorine atoms would react with the dangling bonds on the silicon surface because the Si-F bond strengths are quite strong at 5.0-7.0 eV. After this step, it is unclear as to how and which silicon bonds will be broken in order to produce the gas-phase products, predominantly SiF₄ with small amounts of other species including Si₂F₆. Experimentally, it is found that, during the initial exposure, the fluorine atoms adsorb to the surface, forming the reaction intermediates SiF_x ($x = 1, 3$).¹ As the fluorine exposure is increased, the intermediates form a fluorosilyl adlayer 10-20 Å thick. The SiF and SiF₂ species are thought to be located deeper in the adlayer near the silicon substrate, with the SiF₃ species terminating the surface.² The absolute amounts of the intermediates are still unresolved, and the atomic structure of the adlayer has not yet been determined.

Of the experiments that have been performed within the past decade, the soft X-ray photoelectron spectroscopy (SXPS) studies by McFeely,^{1,10,11} Yarmoff² and co-workers have provided the most complete picture of the fluorosilyl layer. They found that upon low XeF₂ exposure the surface geometry determines the relative amounts of the adspecies whereas the surface geometry is irrelevant after very large XeF₂ exposures. For example, on the Si{100}(2×1)

surface, the majority of the adspecies after exposure to 50 L (1 L = 1×10^{-6} Torr-s) of XeF₂ are monofluorinated silicon atoms.¹ Significant quantities of difluorinated and trifluorinated silicon adspecies are also observed but are attributed to the presence of steps or defects. There is, however, an almost equal distribution of all three fluorinated adspecies when the Si{111}(7×7) surface is exposed to 50 L of XeF₂. Regardless of the initial silicon surface geometry, crystals that are exposed to XeF₂ for approximately 1 h display similar SXPS spectra, suggesting that the initial surface structure is not important to the formation of the fluorosilyl layer.¹⁰ Recently, Yarmoff and co-workers examined the evolution of the reaction intermediates in the adlayer on the Si{111}(7×7) surface versus increased XeF₂ exposure.² They used SXPS, which probes the entire adlayer, and photon-stimulated desorption (PSD) spectra, which is sensitive to the very surface of the adlayer, to determine the relative amounts and vertical positions of the reaction intermediates. By comparing these two different spectra, the researchers determined how the adlayer evolves. As the exposure is increased, the concentration of SiF₃ species at the surface increases and subsequently buries a relatively constant concentration of SiF₂ and SiF species that are found nearer to the pure silicon substrate. The reaction layer ceases to grow thicker after exposure to 100 kL of XeF₂ as evidenced by the nearly constant SXPS spectra intensities versus increased exposure; thus, the adlayer had reached a steady state. The fact that the amount of SiF₃ increases during exposure while the concentrations of the other intermediates remain constant also indicates that the conversion of SiF₃ to the product SiF₄ is the rate-limiting step of this reaction.

Theoretical calculations using ab initio techniques have been performed in order to elucidate how fluorine atoms penetrate the silicon crystal and how the major gas-phase product SiF₄ is formed.¹²⁻¹⁴ Two studies have investigated the manner in which fluorine atoms penetrate the crystal in order to form the reaction layer. The first study, performed by Bagus, found that the fluorine atoms have almost a full negative charge above and below the 3-fold hollow site of the Si{111} surface.¹² When the ionic interaction was taken into account, there was no barrier for the negatively charged fluorine to penetrate the crystal. Although these calculations indicate that fluorine can exist as an interstitial in the crystal, there is no positive SXPS experimental evidence for this state.¹¹ However, this only acknowledges that the concentration of interstitial fluorine atoms or their lifetimes may not be sufficient to be experimentally observed. The second study by Van de Walle and co-workers¹³ also found that the fluorine atoms penetrate the crystal when negatively charged. They observed that the fluoride ion is stable in the tetrahedral interstitial; however, they feel that the fluoride ion is unlikely to disrupt the

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lattice by forming a bond since the ion's electron must be placed in the conduction band at a cost of ~ 1.2 eV, or a hole must be present to annihilate the negative charge. Because of this, the researchers propose that the disruption of the lattice occurs when a neutral fluorine atom inserts into a Si-Si bond center. When the surrounding silicon atoms are allowed to relax, the fluorine atom is found symmetrically between the two silicon atoms with a Si-F bond distance of 1.9 Å. This configuration was found to be more stable than the fluoride ion in the tetrahedral interstitial.

In addition to these penetration studies, Garrison and Goddard have performed calculations on the formation of the product SiF₄.¹⁴ They suggested that a SiF₃ adspecies reacts with an incoming fluorine atom by an S_N2-like reaction. Their initial reaction configuration resembles an adsorbed trifluorinated silicon atom with the adsorbed fluorine atoms extending into the vacuum and the approaching fluorine atom aimed at the trifluorinated silicon atom. The adsorbed fluorine atoms invert toward the surface upon reaction of the silicon atom with the incoming fluorine atom, forming the tetrahedral molecule SiF₄. This umbrella-type motion typifies the S_N2 reaction. At the transition state, electron transfer occurs from the Si-Si bond to the Si-F bond that is being formed. These ab initio calculations provide valuable insight as to how the fluorine atoms penetrate the silicon lattice and what type of mechanism is responsible for the formation of SiF₄. However, due to the computational time required for performing ab initio calculations, an investigation using this technique is not practical for searching for mechanisms involved in the evolution of the defect free silicon surface to the disordered fluorosilyl adlayer.

In this paper, we discuss results of a molecular dynamics simulation of the etching of the Si{100}(2×1) surface by normal incidence 3.0-eV fluorine atoms. We have chosen fluorine atoms as the reactants because they are generally accepted to be the dominant reactive species responsible for the etching of silicon wafers that are exposed to fluorine-containing plasmas.³⁻⁵ We have examined our results in terms of the possible structure of the fluorosilyl adlayer and the atomic mechanisms responsible for the etched products. Our simulation is the first to examine the atomic details of the etching of silicon upon exposure to energized fluorine atoms, producing the products SiF₄ and Si₂F_x, where $x = 5$ and 6. Stillinger and Weber, who developed the potential energy functions that we are using, have studied the reaction between F₂ molecules and the Si{100}(2×1) surface.^{15,16}

Description of the Simulation

We are interested in elucidating the atomic mechanisms responsible for the formation of the gas-phase products observed during the etching of silicon by fluorine atoms and in examining the structure of the surface during etching. In order to accomplish these objectives, we have chosen to use molecular dynamics since, by using this simulation technique, the atomic coordinates can be viewed for structural information and the motions of the atoms can be observed for mechanistic information. Molecular dynamics treats a group of atoms as individual classical particles where the interaction between the atoms is described by a potential energy function. From this function, the forces on the atoms are calculated, which in turn gives the new positions and velocities by integrating Newton's equations of motion. We have used the Stillinger and Weber potential energy function that describes the interaction between silicon and fluorine atoms.¹⁵ This potential is the only potential developed thus far for this heteroatomic system. For the purpose of simulating the initial stages of fluorine adsorption on the Si{100} surface, a microcrystallite of 10 layers of silicon atoms with 32 atoms per layer is used. Periodic boundary conditions are applied perpendicular to the surface plane in order to mimic an infinite crystal. The surface atoms are arranged into the dimer reconstructed surface, which is the accepted reconstruction for the Si{100} surface.¹⁷ Our initial surface is defect

free. To prevent reconstruction of the bottom layers of the crystal, the bottom-layer atoms are held rigid in their bulk terminated positions.

The surface dimer atoms each have a dangling bond where attachment of a fluorine atom is anticipated. In a previous molecular dynamics study, we found that the adsorption of near-thermal fluorine on the Si{100}(2×1) surface follows Langmuir adsorption where the adsorption probability is proportional to the number of dangling bond sites.¹⁸ Therefore, we have adsorbed one monolayer of fluorine atoms to the dangling bonds as an initial condition since this is the extent of fluorination that would be simulated by using thermal fluorine atoms. In order to induce fluorination past this coverage, we previously found¹⁸ that the kinetic energy of the atoms must be at least 1.0 eV. Experimentally, for etching by F atoms in CF₄ plasmas, Sommerer and Kushner¹⁹ have calculated the kinetic energies of fluorine atoms that reach the substrate. They find a range of energies between thermal and 8 eV. Hence, we have chosen to use normal incidence, randomly aimed 3.0-eV fluorine atoms both as a reasonable approximation to the kinetic energy in the plasma and also to achieve reasonable sticking and reacting probabilities.

Since the reaction between silicon and fluorine is very exothermic, we have employed a heat source/sink in order to dissipate the heat evolved from fluorination, which prevents the crystal from eventually melting. To maintain a temperature of 300 K, we have divided the crystal into two regions. The first region, the reaction region, consists of the top five layers. Since the reactions of interest will occur in this region, the forces on the atoms in these layers are not modified from those derived from the Stillinger and Weber potential energy function.¹⁵ It is in this region where two silicon layers are added once fluorination begins to occur to the third layer; thus in effect, there are seven layers in the reaction region, giving a total of twelve silicon layers during the simulation. This addition is performed to keep a buffer of at least two layers between the reaction region and the heat bath. The next four layers comprise the stochastic region. This part of the crystal acts as the heat source/sink. A frictional force is used to add or subtract heat from the crystal. The frictional force is calculated by using the Berendsen scheme.²⁰

In addition to having a heat source/sink, we regulate the introduction of fluorine atoms to ensure that the generation of heat does not occur more rapidly than the stochastic region can dissipate it. To accomplish this task, we have defined the possible results of a fluorine atom trajectory and the consequences. The first possible result is for the fluorine atom to be repelled from the surface. Since no reaction occurs, very little heat is generated. Once the fluorine atom has no potential energy with the surface, the repelled fluorine atom is removed from the simulation and then a new randomly aimed fluorine atom is introduced. The second possible outcome, which is rarely observed, is for the fluorine atom to become weakly attracted to the surface. This result has been documented previously in two papers^{16,18} and is thought to be an artifact of the potential energy function.¹⁸ Like the previous case, this weakly attracted fluorine atom does not react and hence does not generate much heat. Atoms observed in this state are treated the same as if they have been repelled. Upon removal of these atoms, no change is observed in the bonding at the surface, and therefore we assume no negative effect is caused by removing them. The final possible result is for the fluorine atom to adsorb. Upon adsorption, the temperature of the crystal rises to approximately 400 K. We consequently equilibrate the crystal for 3300 time steps (~ 1 ps) in order to return the temperature of the crystal to 300 K.

Along with removing any fluorine atoms that have repelled or are weakly attracted to the surface, we remove any etched products from the simulation. A product is considered etched when all of its atoms have passed a plane at a height of ~ 14.5 Å above the

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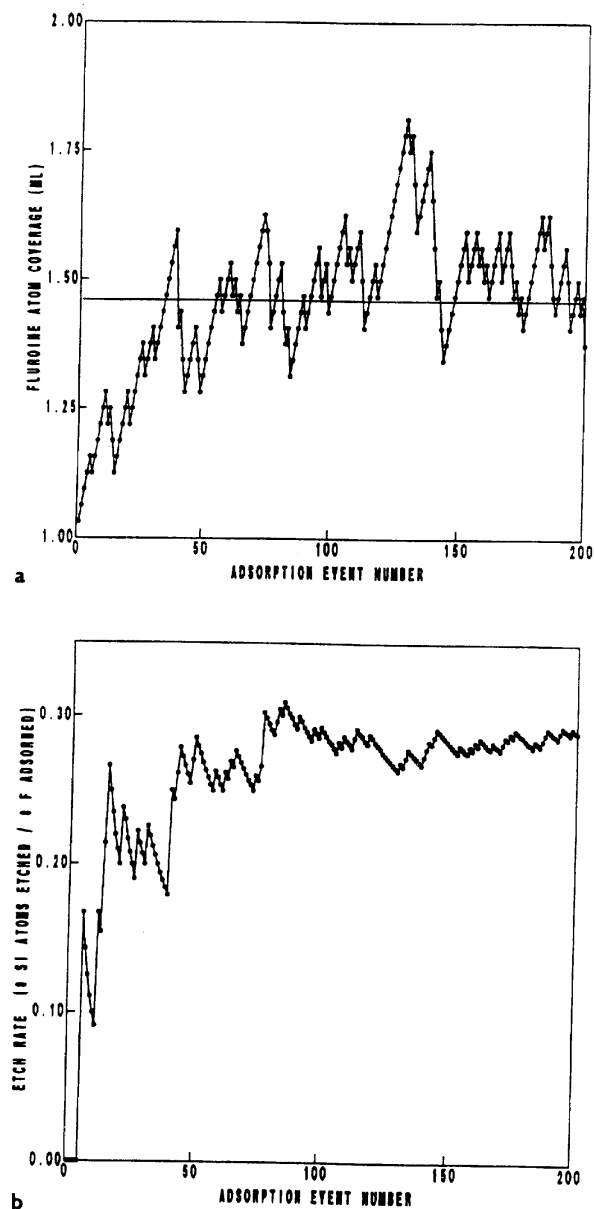


Figure 1. (a) Fluorine atom coverage expressed in monolayers, where one monolayer equals 32 fluorine atoms, plotted versus the adsorption event number. The horizontal line indicates the average fluorine coverage for the 200 adsorption events. (b) The etch rate expressed as the total number of silicon atoms etched divided by the total number of fluorine atoms adsorbed plotted versus the adsorption event number.

surface. At this height, there is no doubt that the etched product has ceased to have any potential energy with the surface. The types and numbers of atoms present in the moiety are analyzed to identify the removed product.

During the simulation, we have monitored the fluorine coverage and the rate of etching to determine a termination point. Figure 1a shows a plot of the fluorine atom coverage versus the adsorption event number. We define an adsorption event as a successful fluorine atom trajectory. In order to obtain the 200 adsorption events, 891 fluorine atom trajectories are performed, thus giving an adsorption probability of 22%. The plot of fluorine coverage versus adsorption event number increases from the initial coverage of one monolayer (1 ML, 32 fluorine atoms), one for each surface atom, and then fluctuates around an average of 1.47 ML (47 fluorine atoms). The rate of etching is shown in Figure 1b where we define the etch rate as the total number of silicon atoms etched divided by the total number of fluorine atoms adsorbed thus far. Both of these rates are approaching convergence. On the basis of the near convergence of these plots and the fact that no new mechanisms are being observed, the simulation is terminated after

the 200th adsorption event. Thus, this paper reports the first molecular dynamics calculation in which a near-steady-state reaction condition of an observed macroscopic process has been simulated.

Results and Discussion

This section is divided into a quantitative description of the fluorine adsorption and a qualitative description of the reaction mechanisms. The quantitative description includes the analysis of the relative concentrations of the different silicon adspecies, the depth of the adsorbed fluorine atoms in the crystal, and the structure of the fluorinated surface. The reaction mechanisms responsible for the formation of SiF_4 and Si_2F_x , $x = 5, 6$, are described subsequently.

The relative amounts of the different silicon adspecies have been monitored during the simulation in order to compare our simulated results to SXPS data. The numbers of monolayers of SiF , SiF_2 , and SiF_3 adspecies are displayed versus the adsorption event number in Figure 2a. For all the adspecies, the silicon atom of the adspecies is bonded to the surface through at least one other silicon atom. The monolayers of SiF adspecies is initially 1 ML (32 SiF adspecies), which is one fluorine atom per silicon atom on the dimerized surface. Upon dimerization, the number of monolayers of SiF adspecies decreases from 1 ML and subsequently fluctuates around an average of 0.75 ML (24 SiF adspecies). Since no SiF_2 and SiF_3 adspecies are present on the initial surface, their concentrations rise from zero to averages of 0.28 ML (9 SiF_2 adspecies) and 0.06 ML (2 SiF_3 adspecies). Qualitatively, our data agree with the SXPS data collected by McFeely et al. for a $\text{Si}\{100\}(2\times 1)$ surface that was exposed to 50 L of XeF_2 .¹ These researchers observed that the SiF adspecies dominate the spectra with the SiF_2 and the SiF_3 adspecies in significant but lesser amounts. The presence of the SiF_2 and SiF_3 species was attributed to defects or steps on the surface. Our initial crystal is defect free; yet upon fluorination, we eventually observe SiF_2 and SiF_3 adspecies. In effect, we are creating defects for the formation of SiF_2 and SiF_3 adspecies by using a fluorine atom whose kinetic energy is comparable to the Si-Si bond energy. In contrast to the low-dose experiments, the relative amounts of the silicon adspecies changed from predominantly SiF to predominantly SiF_3 as the XeF_2 exposure was increased from 50 L to 700 kL during SXPS experiments.²

We have further analyzed the data from the simulations by plotting several other quantities. One quantity that we monitor is the monolayers of fluorinated silicon atoms. We find that, on average, only 1.06 ML of silicon atoms (34 silicon atoms) are fluorinated at any one time. Since the initial amount of fluorinated silicon is 1.0 ML and the number of monolayers of fluorinated silicon does not increase significantly above 1 ML, it therefore seems likely that only the surface atoms are fluorinated along with a small number of atoms in other layers. In order to determine which silicon layers are fluorinated, we plot the original silicon layer number to which the incoming fluorine atom adsorbed versus the adsorption event number in Figure 2b. Only the silicon atoms in the first and second layers are fluorinated until the 76th adsorption event. The silicon atoms in the second and third layers are predominantly fluorinated after this adsorption event. The only manner in which a third-layer silicon atom can be fluorinated is if the first-layer atom or second-layer atom or both have been etched or have been displaced from their original lateral position. Figure 2c displays the monolayers of silicon atoms that remain in each of the top four layers versus the adsorption event number. By the 76th adsorption event, more than half of the first-layer atoms have been etched, placing some third-layer atoms nearer to the vacuum and thus making them more available for fluorination. It is possible that the amount of simulated fluorinated silicon is a function of the number of surface atoms, i.e., the size of the crystal in the simulation, and the degree of roughness of the surface. Our crystal is not sufficiently large to allow for large defects and strains to be accommodated.

We have also examined all of the surface configurations during the simulation in order to elucidate the possible structure of the

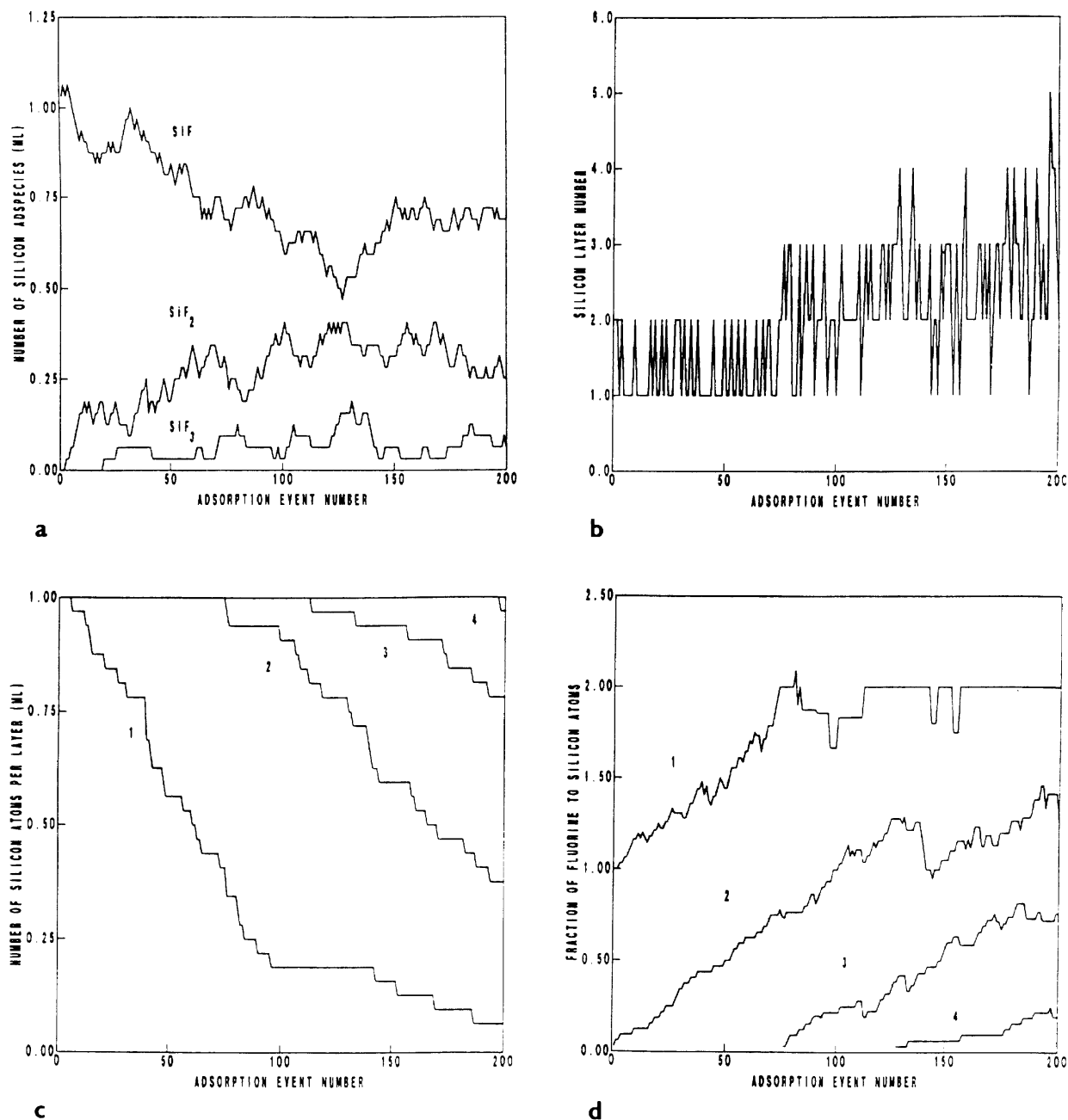


Figure 2. (a) The monolayers of fluorinated silicon adspecies plotted versus the adsorption event number. The top curve displays the monolayers of monofluorinated silicon atoms, the middle curve displays the monolayers of difluorinated silicon atoms, and the bottom curve displays the monolayers of trifluorinated silicon atoms. (b) The silicon layer to which the fluorine atoms adsorbed plotted versus the adsorption event number. Layer number one is the first layer, and higher numbers indicate deeper layers in the crystal. (c) The monolayers of silicon atoms remaining in the crystal per original layer plotted versus the adsorption event number. The curve labeled as 1 represents the first layer, the curve labeled as 2 represents the second layer, the curve labeled as 3 represents the third layer, and the curve labeled as 4 represents the fourth layer of the crystal. (d) The fraction of fluorine atoms to silicon atoms per original layer of silicon plotted versus the adsorption event number. The labeling scheme is the same as described in (c).

experimentally observed fluorosilyl layer. In Figure 3a–f, we display the surface configuration produced by the last fluorine adsorption event, at which time approximately 1.8 ML of silicon had been etched. Only the top five layers of the crystal are depicted. Upon examination of this surface, there are many scattered vacant regions that are created by the etching of silicon atoms. The vacancies are scattered inhomogeneously across the surface due to the random nature of the etching process. Moreover, the surface configuration has evolved such that it is difficult to locate the position of the dimer rows of the initial defect free surface. Some interlayer mixing is also observed. More information regarding the typical surface structure is revealed when the surface configuration is examined for local structure. For instance, some pairs of adspecies dimerize while others retain approximately the bulk geometry of the silicon lattice. In addition to the bonding between pairs of adspecies, there are two groups

of three adspecies where the bonding direction among the three adspecies is nearly perpendicular to the surface plane, forming a towerlike structure. These structures are still in the solid and are attached to the solid through the SiF and SiF₂ moieties. The first tower, whose composition is SiF–SiF–SiF₃ (green–green–red spheres), is best observed in Figure 3f on the left side of the crystal. The second tower, SiF–SiF–SiF₂ (green–green–pink spheres), is best seen in Figure 3b in the middle of the crystal, near the top. We also observe towers that are not in the solid but that protrude into the vacuum, as shown in Figure 4f. We refer to these towers as free-standing towers. For all the tower structures, the SiF and SiF₂ are adspecies that lengthen the tower whereas the SiF₃ are adspecies that terminate the tower at the vacuum/surface interface. This observation would suggest that a type of layering occurs while the surface is being fluorinated. In Figure 2d, we have plotted the fraction of fluorine atoms to silicon atoms for

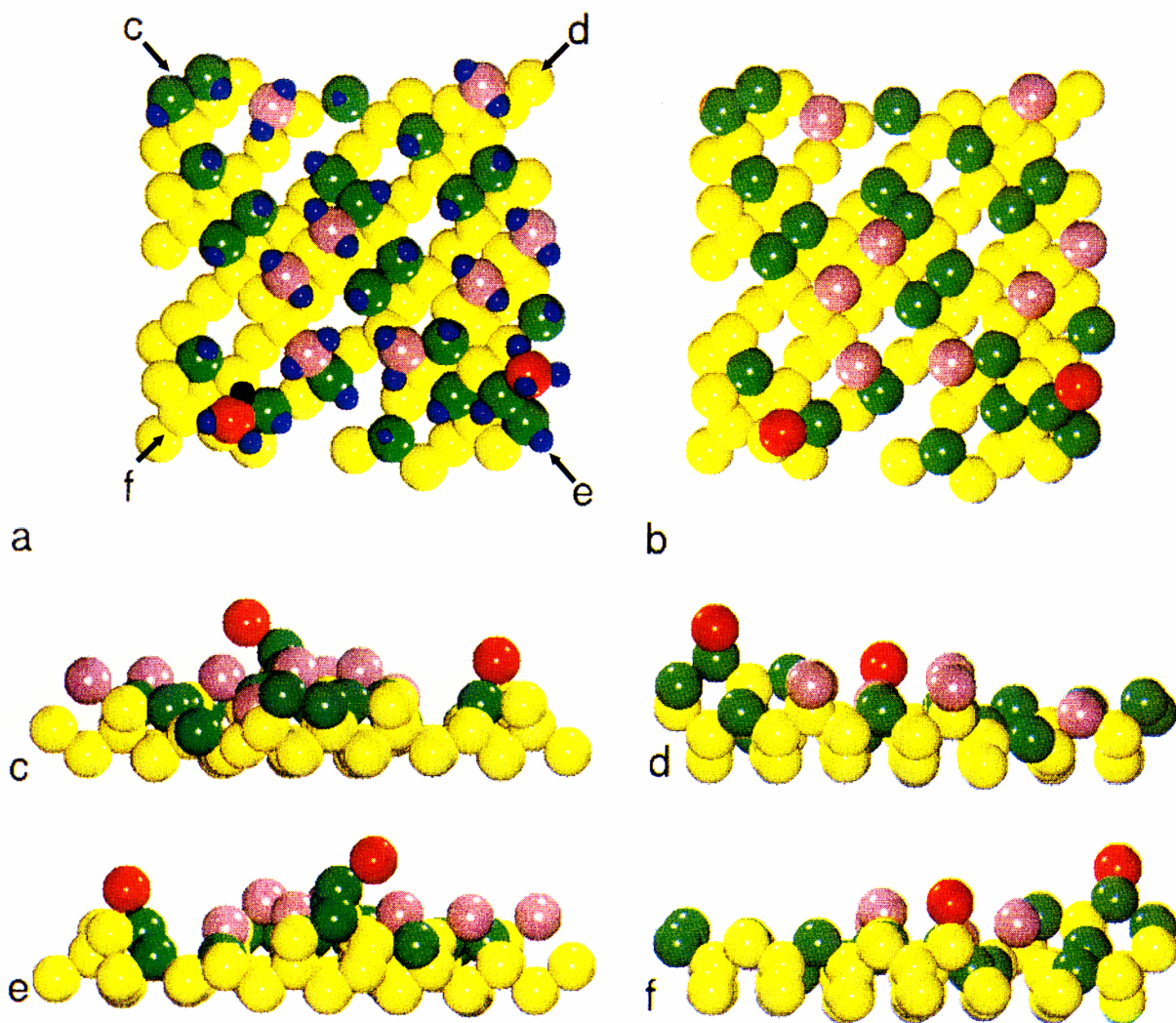


Figure 3. The top five layers of the crystal at the end of the simulation depicted from different views. Yellow spheres represent nonfluorinated silicon atoms, green spheres represent monofluorinated silicon atoms, orchid spheres represent difluorinated silicon atoms, and red spheres represent trifluorinated silicon atoms. Small blue spheres represent the adsorbed fluorine atoms. (a) Top view of the surface configuration is shown. The arrows indicate the direction of the side views (c–f). (b) Top view of the surface configuration is shown except that the fluorine atoms are removed to emphasize the positions of the fluorinated silicon atoms with respect to each other. (c) The side view of the crystal is shown except from the [110] direction as indicated in (a). (d) The side view of the crystal is depicted from the [110] direction. (e) The same direction as in (c) is shown except from the other side of the crystal. (f) The same direction as in (d) is shown except from the other side of the crystal.

each of the original silicon layers. The fraction of fluorine in the different layers at the end of the simulation suggests that the first-layer silicon atoms are mainly SiF_2 adspecies and the second-layer silicon atoms are mainly SiF adspecies while the third and fourth layers are beginning to be fluorinated. Thus, a sequential fluorination appears to be occurring to the crystal, starting with the first layer and progressing deeper into the crystal. This observation agrees with conclusions drawn by Yarmoff and co-workers.² They compared SXPS and PSD spectra of the adlayer and found that the SiF_3 species are located at the surface of the adlayer while the SiF and SiF_2 species are located closer to the silicon substrate.

Along with examining the fluorination process in terms of the quantitative description of the fluorine adsorption events and the adspecies configurations, we have also determined the mechanisms for the formation of two free-standing towers during the simulation. Since the mechanisms for the formation of the two are similar, we will only examine the formation of one tower in detail as shown in Figure 4a–f. The starting configuration is a pyramid-like arrangement of three fluorinated adspecies where at least two of the adspecies are difluorinated. This pyramid structure

forms when two bonded difluorinated silicon adspecies join to a monofluorinated silicon adspecies when the surface rearranges to reduce strain. Before the rearrangement, several silicon atoms near these fluorinated adspecies are 3-fold or 5-fold coordinated. The Stillinger and Weber potential favors 4-fold coordinated silicon atoms by penalizing deviations from the tetrahedral geometry. Once the surface rearranges, the number of 3-fold and 5-fold coordinated silicon atoms decreases; thus, the pyramid structure forms to reduce strain in the surface. The tower forms from the pyramid structure when the incoming fluorine atom approaches the monofluorinated silicon adspecies at one end of the pyramid structure, Figure 4b. Upon fluorination of the monofluorinated adspecies to form a difluorinated adspecies, Figure 4d, the two Si–Si bonds between the difluorinated adspecies and the surface break, Figure 4e. These Si–Si bonds are sufficiently weak and the exothermicity is sufficiently great that both Si–Si bonds to the surface break as opposed to the more common occurrence of only one Si–Si bond breaking during fluorine atom adsorption. This recently fluorinated silicon atom then rolls on top of its neighboring SiF_2 adspecies to form the resulting free-standing tower structure, Figure 4f. The tower in Figure 4f is capped with

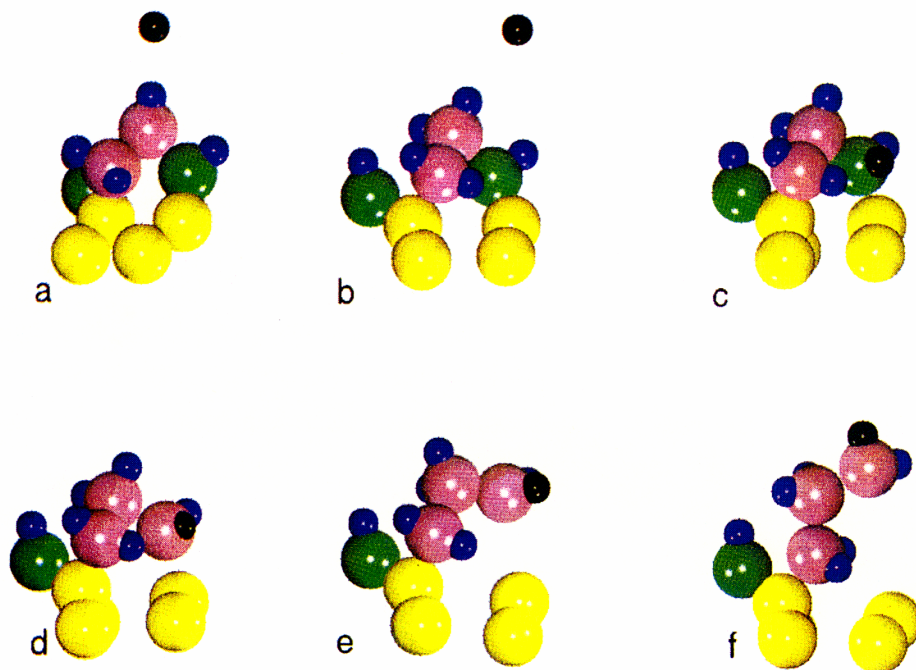


Figure 4. Side view of the mechanism responsible for the formation of the first fluorinated tower from a fluorinated pyramid structure. The same color scheme is used as in Figure 3. The small black sphere represents the incoming fluorine atom. (a) The incoming fluorine atom approaches the initial configuration of the pyramid. (b) The same view as in (a) is shown except rotated 90°. (c) The fluorine atom begins to adsorb to the monofluorinated silicon atom. (d) The two Si-Si bonds to the crystal start to lengthen. (e) The tower moves to a final configuration. (f) The tower reaches its final structure.

a SiF_2 adspecies and therefore possesses a dangling bond. This dangling bond can easily be fluorinated, thus producing a tower of the type $\text{SiF}_2\text{SiF}_2\text{SiF}_3$, which is the composition of the other free-standing tower observed in our simulation.

During the simulation, we have observed that the free-standing tower in Figure 4f is a good starting configuration for the production of the gas-phase product Si_2F_5 . The mechanism of this reaction is depicted in Figure 5a-f. The incoming fluorine atom approaches the middle SiF_2 adspecies in the tower, resulting in an adsorbed SiF_3 species, Figure 5b-d. Once the fluorine adsorbs, the top SiF_2 adspecies desorbs due to the energetically unfavorable configuration that forms between the top two silicon adspecies. Meanwhile, the Si-Si bond between the bottom SiF_2 and the surface lengthens to the breaking point, Figure 5c-f, thus allowing the desorption of the Si_2F_5 species. The other free-standing tower in the simulation is etched from the top silicon atom down to the bottom silicon atom, and therefore no Si_2F_x species result. Hence, in order for the etching of a Si_2F_x species to occur from a free-standing tower, it is important for the incoming fluorine atom to adsorb to any silicon in the tower *except* the top silicon atom.

By extrapolation of the above mechanism, we propose two mechanisms for the formation of the experimentally observed product Si_2F_6 . The first mechanism is similar to the above mechanism except that the starting configuration would be a tower that is capped with a SiF_3 adspecies. The incoming fluorine atom would approach the middle SiF_2 adspecies, and its direction would be parallel to the surface or away from the surface, which would occur with a grazing or reflected fluorine atom. The direction of the fluorine atom would increase the probability that the breaking Si-Si bond would be between the bottom silicon atom and the middle silicon atom of the tower, thus producing Si_2F_6 with the top and middle silicon atoms of the tower. The second mechanism does not require a tower for a starting configuration but a pair of silicon atoms, one difluorinated and the other trifluorinated, SiF_2SiF_3 . The incoming fluorine atom could be aimed at the difluorinated species of the structure, thus forming Si_2F_6 , which would then desorb. We are currently performing molecular

dynamics simulations in order to examine these proposed mechanisms.

We have also elucidated the mechanism responsible for the major gas-phase product SiF_4 . We find predominantly one mechanism, which is shown in Figure 6. The initial configuration is a SiF_3 adspecies with its Si-F bonds directed into the vacuum. As the fluorine atom approaches the silicon atom, the Si-F bonds invert from extending into the vacuum (Figure 6b) to being planar with the silicon atom (Figure 6c) to being directed toward the surface (Figure 6d). During the reaction, the Si-Si bond lengthens and breaks. This umbrella-type motion of the Si-F bonds typifies the $\text{S}_{\text{N}}2$ reaction. Garrison and Goddard have also concluded a similar mechanism for the production of SiF_4 by using *ab initio* electronic structures calculations.¹⁴ We would like to note that the Stillinger and Weber potential energy functions were fit to spectroscopic data and not to any particular reaction path.

The gas-phase product distribution from our simulation is as follows: 54% SiF_3 , 35% SiF_4 , 7% SiF_2 , and 4% other. Etching experiments observe SiF_4 as the major gas-phase product with some $\text{Si}_2\text{F}_6 + \text{Si}_3\text{F}_8$.⁶⁻⁹ SiF_2 and SiF_3 are thought to be minor products.⁹ This disagreement between the simulated and experimental gas-phase product distributions is probably due to two factors. The first factor is that, during the simulation, the fluorine atom coverage may not always be at its maximum value. Dangling bonds are formed during the simulation that do not always become saturated by the 3.0-eV normal incident fluorine atoms. In contrast, any dangling bonds that occur during an experiment would be saturated by the lower energy fluorine atoms, thus keeping the surface saturated with fluorine and shifting the product distribution toward SiF_4 . The second factor that could be responsible for the overabundance of SiF_3 product in the simulation is a deficiency in the potential energy function. The Stillinger and Weber Si/F potential energy function overestimates the amount of energy gained by a SiF_2 species when a fluorine atom reacts with it. The F-SiF₂ bond energy calculated by using the potential energy function is ~6.6 eV whereas this bond energy is found by experiments to be ~5.1 eV²¹ and calculated by ab

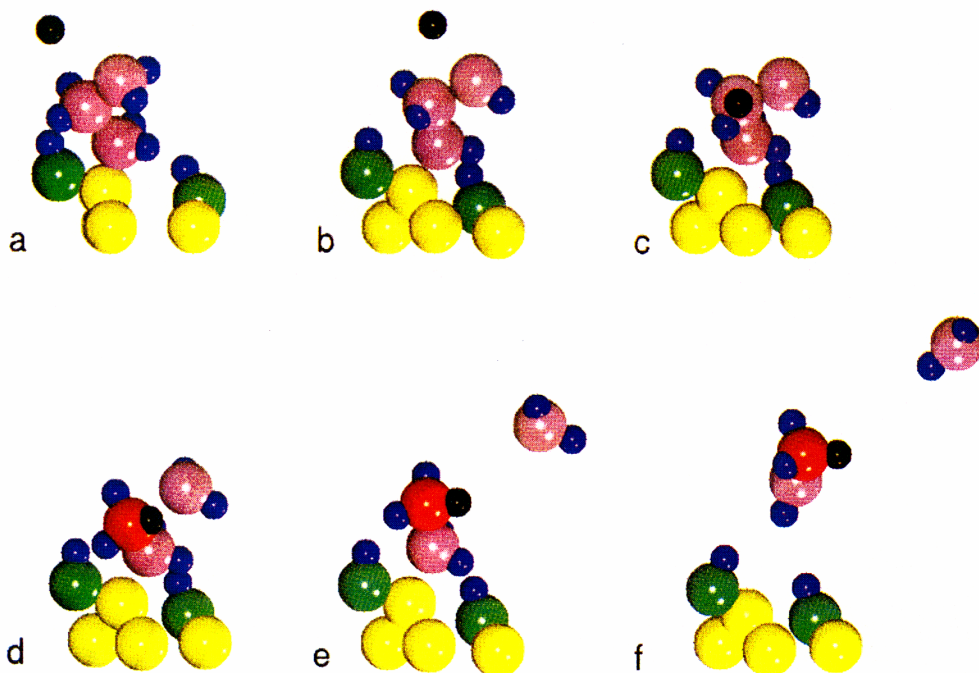


Figure 5. Side view of the mechanism responsible for the formation of the Si_2F_5 gas-phase molecule formed from the tower in Figure 4. The color scheme is the same as previously described. (a) The incoming fluorine atom approaches the tower. (b) The same view as in (a) is displayed except rotated to a view which shows that the fluorine atom approaches the middle silicon adspecies in the tower. (c) The incoming fluorine atom begins to bond to the middle silicon in the tower, and the Si-Si bond to the crystal lengthens. (d) The middle silicon is now trifluorinated. The top SiF_2 species desorbs due to the formation of the SiF_3 species below it. (e) The pentafluorodisilane adspecies rearranges. The Si-Si bond to the crystal lengthens. (f) The Si_2F_5 species desorbs into the gas phase.

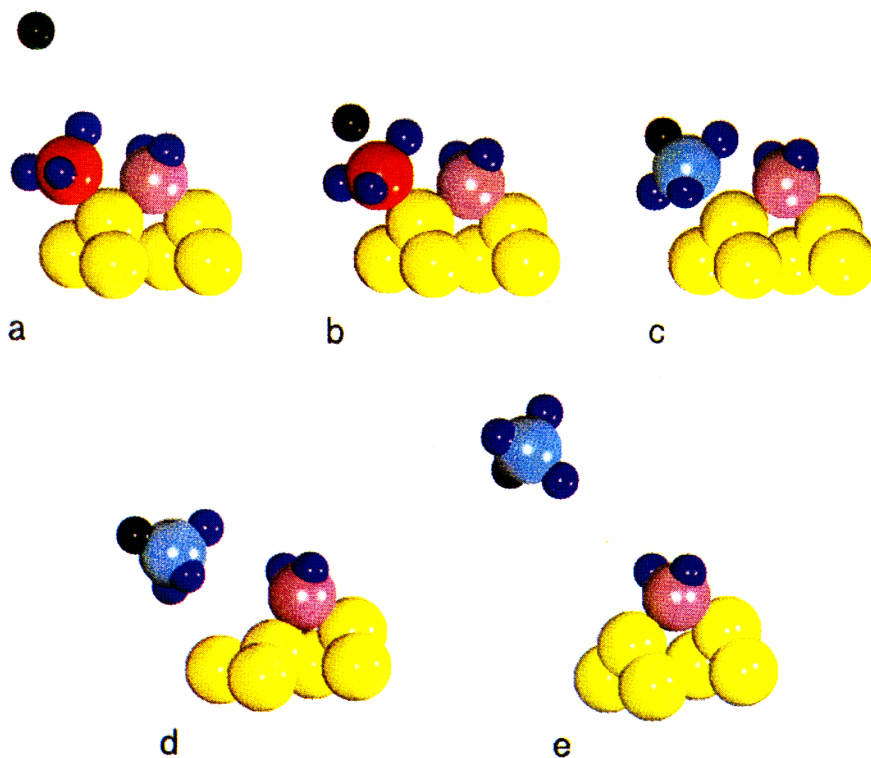


Figure 6. Formation of SiF_4 from the reaction between the incoming fluorine atom with an SiF_3 adspecies is depicted. In addition to the previous color scheme, the turquoise sphere represents a tetrafluorinated silicon atom. The mechanism is $\text{S}_{\text{N}}2$ -like.

initio methods to be ~ 4.6 eV.²² Therefore, during some F + SiF_2 trajectories, the strain placed on the SiF_2 adspecies to form

another Si-F bond can be large enough to cause the forming SiF_3 species to etch. If one assumes that the etched SiF_3 species would

have remained on the surface until they could have been etched as SiF_4 , then the gas-phase distribution would have been 89% SiF_4 , which is in reasonable agreement with experimental findings of approximately 85%. A detailed account of the SiF_3 and SiF_2 etching trajectories will be published later.

Conclusions

We have examined the initial stages of adsorption and etching of the $\text{Si}\{100\}(2\times 1)$ surface upon low exposure to 3.0-eV normally incident fluorine atoms. The results of our molecular dynamics simulation indicate that fluorination occurs to the top two exposed silicon layers where the amount of fluorinated silicon averages around one monolayer. The majority of fluorinated silicon is monofluorinated with significant amounts of difluorinated and trifluorinated silicon. McFeely et al. also observe this trend for a $\text{Si}\{100\}(2\times 1)$ surface that has been exposed to 50 L of XeF_2 by using SXPS.¹ In order to gain some insight as to the structure of the fluorosilyl adlayer, we have examined the bonding between the different fluorinated silicon atoms. Some pairs of adspecies are found to dimerize, and other pairs are found to retain the geometry of the silicon lattice. We also observe towerlike structures that we define as three neighboring adspecies whose bonding direction is nearly perpendicular to the surface plane. A few towers are found within the crystal and two free-standing towers are found that protrude into the vacuum. In all the towers, we find that SiF and SiF_2 adspecies are responsible for lengthening the towers whereas SiF_3 adspecies terminate the tower at the vacuum/surface interface. Additional support of this locally observed adspecies layering is found by examining the fraction of fluorine atoms to silicon atoms per the original silicon layer. This ratio increases for each layer. When the fraction of fluorine to silicon in each layer is compared, a hierarchy of fluorination

is observed that suggests a layering process. That is, by the end of the simulation, the first layer has an average appearance of an SiF_2 adlayer and the second layer has an average appearance of an SiF adlayer, while the deeper layers are just beginning to fluorinate. Similar layering in the fluorosilyl adlayer has been observed by Yarmoff and co-workers.² Upon comparison of PSD to SXPS spectra, these researchers conclude that SiF_3 species are found at the surface of the adlayer and the SiF and SiF_2 species are found deeper in the adlayer, near the silicon substrate. Besides providing insight into the structure of the adlayer, we propose the free-standing towers to be important for the etching of Si_2F_x ($x = 5, 6$). When an incoming fluorine atom reacts with the middle silicon in a free-standing tower, a Si_2F_5 species is etched. The mechanism of this reaction is extrapolated in order to elucidate a mechanism responsible for the etching of Si_2F_6 . We also observe a mechanism for the formation of SiF_4 . Upon reaction with the incoming fluorine atom, the Si-F bonds on a SiF_3 adspecies invert from extending into the vacuum to directing toward the surface while the Si-Si bond between the forming SiF_4 and surface lengthens. A similar mechanism has been proposed by Garrison and Goddard for the formation of SiF_4 based on ab initio calculations.¹⁴

These molecular dynamics calculations are the first simulations to simulate a near-steady-state reaction condition of a macroscopic process. These results open the door for the study of other chemical reactions such as the etching of silicon by chlorine or hydrogen and diamond film growth. Since molecular dynamics is capable of reaching a near-steady-state condition, which is usually a regime explored via Monte Carlo techniques, then the detailed atomic mechanisms and structures of other heteroatomic reactions can be investigated.

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Registry No. SiF_4 , 7783-61-1; Si_2F_5 , 19091-17-9; Si_2F_6 , 13830-68-7; Si, 7440-21-3; atomic fluorine, 14762-94-8.

(21) Calculated from $\Delta H_f^\circ(\text{SiF}_3) = -239 \pm 5$ kcal/mol determined by Doncaster, A. M.; Walsh, R. *Int. J. Chem. Kinet.* **1978**, *10*, 101-110 and from $\Delta H_f^\circ(\text{SiF}_2) = -140 \pm 2$ kcal/mol determined by Farber, M.; Srivastava, R. D. *J. Chem. Soc., Faraday Trans. 1* **1978**, *74*, 1089-1095 and from $D_e(\text{F}_2) = -1.659$ eV reported by Huber, K. P.; Herzberg, G. *Molecular Spectra and Molecular Structure IV: Constants of Diatomic Molecules*; Van Nostrand Reinhold: New York, 1978; pp 214-215.

(22) Calculated from $\Delta H_f^\circ(\text{SiF}_3) = -240.7$ kcal/mol and $\Delta H_f^\circ(\text{SiF}_2) = -153.0$ kcal/mol determined by Ignacio, E. W.; Schlegel, H. B. *J. Chem. Phys.* **1990**, *92*, 5404-5416.