I. INTRODUCTION

Fluorine etching of silicon is of great technological interest because of the large number of electronic devices that can be fabricated with etched silicon. Industrial etching of silicon involves plasmas of fluorine-containing molecules, such as CF₄, where atomic fluorine is believed to be the dominant reactive species. Therefore, experimental studies have focused on the simplified systems of silicon surfaces exposed to F, F₂, or XeF₂ (a clean source of atomic F). However, even these simplified systems have defied a clear explanation of the atomic mechanism of etching primarily because of difficulties in experimental characterization. Theoretical studies have only been partially successful because the large number of atoms involved in the etching process precludes detailed high level ab initio calculations. Thus quantum mechanical calculations have been restricted to either lower level calculations that are potentially less accurate, or high level calculations involving very small clusters where the behavior of the larger system must be extrapolated from such results.

The experimental evidence currently available indicates that rapid adsorption of ~1.5 monolayers (ML) of fluorine occurs upon initial exposure of fluorine to silicon. Further exposure involves a slower adsorption of fluorine, which results in the buildup of a fluorosilyl layer (~10 Å thick) with SiF, SiF₂, and SiF₃ present. SiF₃ is thought to exist primarily at the surface, while SiF dominates the fluorosilyl layer–bulk silicon interface. Once this layer has reached a critical thickness and composition, steady state etching begins with production of mostly SiF₄, as well as some Si₂F₆ and Si₃F₈. The fluorosilyl layer is stable once fluorine exposure is terminated, although with increasing temperature, fluorosilyl molecules desorb. For example, when the ~1.5 ML fluorosilyl layer is heated, SiF₄ is the major product desorbed. Recent x-ray photoemission (XPS) and mass spectrometry measurements indicate that large patches on the surface are desorbed rather than species from random positions within the layer. When a thicker fluorosilyl layer is heated, SiF₄ becomes the dominant product.

Few theoretical studies concerning fluorine etching of Si have been reported. Seel and Bagus carried out Hartree–Fock (H–F) calculations investigating, among other things, the diffusion of fluorine into the near surface layers using a cluster model for an unreconstructed Si(111) surface. Fluorine was found to become essentially F⁻ and the barrier to bulk diffusion was predicted to be ~0.7 eV. However, the barrier to breaking Si–Si bonds was found to be quite high. It is well known that H–F calculations, because of the neglect of electron correlation, often incur very large errors (as much as several eVs) in the energetics. Thus these results may be only qualitatively correct. More recently, Wu and Carter have performed extensive ab initio studies, which included electron correlation, on F atom adsorption on Si(100). A mechanism was proposed for the initial fluorine adsorption steps and detailed structural information was predicted that agreed with XPS adsorbate product distributions. Previous isothermal molecular dynamics (MD) simulations using an empirical potential attempted to model larger quantities of F reacting with Si(100), however, these simulations predicted no reaction beyond saturation of the surface dangling bonds, unless the surface was melted, or was exposed to incoming F atoms with large amounts of kinetic energy (E₉ > 3 eV).

We have fit the ab initio results of Wu and Carter to a Stillinger–Weber analytic potential form. We showed previously that MD simulations using this first principles-derived potential exhibits Si–Si bond breaking and a buildup of SiF₈ species upon exposure of Si(100) to room temperature fluorine gas. We have therefore utilized this new potential in additional MD simulations to investigate previously proposed mechanisms for the initial stages of fluorine etching.
etching and present a new mechanism in light of these studies. Comparison of the empirical SW potential to Wu and Carter's \textit{ab initio} data is given in Sec. II. We then describe the method of fitting our new potential using simulated annealing (SA) in Sec. III. Results and implications of MD simulations of adsorption probabilities as a function of fluorine coverage and surface structure are discussed in Sec. IV. Finally, a summary and major conclusions are presented in Sec. V.

II. EMPIRICAL VS \textit{AB INITIO} SURFACE Si-F INTERACTIONS

Until our recently developed Si(100)--F potential,\textsuperscript{17} the only potential available for describing the interaction of fluorine and silicon was that of Stillinger and Weber (SW).\textsuperscript{15,18} As mentioned above, room temperature isothermal MD simulations using the SW Si--F potential do not show Si--Si bond breaking and in fact, significant energy had to be introduced into the system to facilitate reaction.\textsuperscript{15,16} This indicates a problem with the SW potential, since F is known to etch Si spontaneously at room temperature.\textsuperscript{1}

The problem with the SW potential arises from the data to which it was originally fit. The homoatomic parts of the potential were fit to experimental data and have been shown to adequately describe bulk Si,\textsuperscript{19} the Si(100) surface,\textsuperscript{20-23} and pure fluorine.\textsuperscript{18} However, since the structures and binding energies of F on Si(100) are currently experimentally inaccessible, the heteroatomic terms in the potential were fit to the only available data for fluorine interactions with Si: gas phase structural and energetic data for SiF\textsubscript{3} (x=1,2,3,4) and Si\textsubscript{2}F\textsubscript{6}. Since these molecules may have quite different properties compared to those for fluorine bonded to a Si(100) surface, Wu and Carter (WC) carried out \textit{ab initio} configuration interaction calculations of fluorine reacting with embedded clusters of silicon constructed to represent pieces of the Si(100) surface.\textsuperscript{13,14}

As a test of the empirical SW potential and the use of gas phase data to describe surface phenomena, we compared WC's \textit{ab initio} data to that predicted by the SW potential. Five types of interactions were investigated with \textit{ab initio} methods. Three of these involved the interaction of a single F atom with a surface dimer: (i) an approach perpendicular to the center of a Si surface dimer bond (a twofold bridging position), (ii) an approach directly toward one of the Si surface dimer dangling bonds, and (iii) a case where a fluorine atom slides from the metastable site above the center of a Si surface dimer to the global minimum where it is attached to the dangling bond. The SW potential predictions of the energetics for these three approaches are compared to the \textit{ab initio} data in Fig. 1. Note that although the overall shapes of the SW curves are correct, the well depths are too small by up to \(\sim 4\) eV, when compared to the quantum mechanical data.

In general then, we found that the bonding interactions are not attractive enough in the SW description. The two other cases investigated involved nonbonded interactions between adsorbed fluorosilyl groups, corresponding to \(\Theta_F > 1\) ML. In the first case, a model for SiF\textsubscript{2} (ad) was brought up next to a model for SiF\textsubscript{2} (ad). This movement approximated the motion that would occur as a fluorinated F--Si--Si--F dimer had a third fluorine atom attack and subsequently break the dimer bond, forming an SiF\textsubscript{2} \(\cdots\) SiF species [as in Figs. 2(a) and 2(b)]. In this case, the distance between the two originally dimerized silicon atoms would increase from \(\sim 2.4\) (the equilibrium dimer bond distance) to \(\sim 3.84\) Å [the equilibrium Si--Si separation on an unreconstructed (100) surface]. In the second case, two models for SiF\textsubscript{2} (ad) are brought up next to one another. An enormous amount of steric repulsion is generated by diffusing every silicon atom on the surface (\(\Theta_F=2\) ML), if the SiF\textsubscript{2} (ad) groups are constrained to retain tetrahedral symmetry around each Si. In this configuration, all F atoms are coplanar, as seen in Fig. 2(c). At \(R_{Si-Si}=3.84\) Å and \(\Theta_F=2\) ML, the corresponding nonbonded F--F distance is 1.24 Å, which is even shorter than the equilibrium bonding F--F distance in F\textsubscript{2} (1.44 Å). At \(R_{Si-Si}=3.84\) Å, the terribly short F--F nonbonded distance leads to pairwise SiF\textsubscript{2} (ad)--SiF\textsubscript{2} (ad) repulsions of \(\sim 17\) eV. The SW potential is compared to the \textit{ab initio} data in Fig. 3 for the latter two cases, where we see that it is too repulsive compared to the \textit{ab initio} data points for nonbonded interactions.

III. FITTING THE \textit{AB INITIO}-DERIVED SURFACE Si-F POTENTIAL

Figures 1 and 3 illustrate that although the potential appears to be too repulsive, its qualitative character seems to be satisfactory. Therefore, we made only a minor change in the functional form and refit the potential to 42 \textit{ab initio} data points and the experimental gas phase SiF\textsubscript{2} data.\textsuperscript{24} The potentials for the homoatomic and heteroatomic interactions all share a similar form of a polynomial that is modulated by an exponential function that goes smoothly to zero at a cutoff. The total potential is a combination of both two-body (over all pairs of atoms) and three-body (over all triplets) terms, where all of the units are reduced. The two-body Si--F term is

\begin{equation}
\psi_{SiF} = A_{SiF}(B_{SiF}r^{-2} - r^{-2})\exp[\gamma_{SiF}(r-a)^{-1}] (0 < r < a),
\end{equation}

which becomes zero beyond the cutoff, \(a\), which is set equal to 3.76 Å. The three-body term for a triplet of atoms, \(i,j,k\), is a combination of three terms, \(h\) onc for each atom in the triplet. Each of these terms is a function of the vectors connecting the central atom to the other two members of the triplet. In this way, the most general potential function for a single triplet is

\begin{equation}
U(r_{ij}r_{ik}r_{jk}) = h(r_{ij}R_{jk}\theta) + h(r_{ip}r_{jk}\theta) + h(r_{ik}r_{jk}\theta),
\end{equation}

where the \(h\) terms will vanish if either of the vector lengths is greater than the cutoff \(a\). There are four types of triplet functions corresponding to the different combinations and permutations of the atoms in the triplet. These functions, \(h\), where \(\theta\) is the angle and \(r\) and \(s\) are the lengths of the vectors, have the form.
FIG. 1. Potential energy (eV) as a function of distance (Å) for the different approaches of a single fluorine atom towards a Si(100) surface dimer: (a) the perpendicular approach (R$_d$) to the center of the dimer bond; (b) the approach (R$_{db}$) along the dangling bond direction (θ = 113°); and (c) where the F atom moves parallel to the dimmer bond (R$_f$) from the center of the dimer (R=0) toward the dangling bond at a constant height of $R_f = 1.6$ Å. The dashed line is the empirical SW potential, the circles are the ab initio configuration interaction data, and the solid line is our current potential.

The $h_{\text{SiSiF}}$ term differs from the SW form of the potential because of the added factor $c_{\text{SiSiF}}$. Also note the placement of the brackets in Eq. (6); one was misplaced in the previous paper.\cite{17}

Once the functional form was defined, the next step involved fitting the 13 parameters of the function. In a general fitting procedure, one is trying to minimize the “cost” of a least squares formula

$$\text{cost} = \sum_i (E_{\text{potential}}(i) - E_{\text{actual}}(i))^2 \omega_i.$$
where the sum in this case is over the number of theoretical or experimental data points. $E_{\text{actual}}(i)$ is the experimental or quantum mechanical energy difference, $E_{\text{potential}}(i)$ is the energy difference from the potential function with the current parameters, and $w_i$ is a weighting factor, which is used to define the relative importance of each data point. For our purposes, a point at the bottom of the well should be fit closely, but a point far up the repulsive wall can be fit less accurately. Conventional minimization of the cost, such as by conjugate gradients or steepest descent, will likely take the function to a local minimum.

To avoid biases due to the choice of the initial conditions and to instead approach the global minimum, we used the method of simulated annealing (SA). In this method, one changes the parameters in the potential randomly and accepts this new set of parameters with a Metropolis Monte Carlo probability. SA therefore has an "effective temperature" which governs the probability of acceptance. As this "temperature" is lowered, the system can explore less and less of its parameter space and if the system is cooled slowly enough, then the global minimum is reached in the limit of zero temperature. There has been considerable debate as to the optimal cooling schedule to use, however, our fits yielded a family of parameters with similar costs so that it was not necessary to obtain the exact global minimum (which depends on the arbitrary weights anyway), but only to obtain members of this closely related set of minima. We therefore used an exponential cooling schedule, i.e., $T_{\text{new}} = \alpha T_{\text{old}}$, where $\alpha$ is a constant, and briefly investigated the effects of different values of $\alpha$. In general, if $\alpha$ was greater than approximately $\frac{3}{4}$, then minima of similar costs were obtained. Interestingly, even with values of $\alpha$ close to unity, the system occasionally did get trapped into a very high cost state as the temperature decreased, indicating that the parameter space was not smoothly varying. Thus, slow cooling did not always result in a good final parameter set. By plotting the average cost at each temperature, a "cooling curve" is obtained that helps indicate the temperature region in which annealing should be done more slowly. From the representative cooling curves shown in Fig. 4, we see that the annealing should be concentrated in the area of the steepest slope. At higher temperatures, the system is moving around on high cost areas of the surface, so that it is rarely probing the low cost regions. After the temperature has been lowered suf-
efficiently so that the system is caught in a minimum, additional annealing will do nothing and steepest descent should be performed to find the exact position of the minimum.

We performed many fits with different weighting factors until we found an optimal set of weighting factors. Changes in the factors had a large effect on the quality of the fit and thus many sets of weighting factors had to be investigated. We found that unless the experimental bond dissociation energies for SiF$_2$ and SiF$_1$ had weightings $\approx 0$ the accuracy of the fit for the surface interactions was decreased. This decrease in Si–F bond energies going from SiF$_2$ to SiF$_1$ is a quantum mechanical effect, which arises as a result of a decoupling of the Si 3s pair to form the third SiF bond, which subsequently weakens that bond. To properly model this trend, the potential would require the addition of higher order terms in the many body expansion.

While this phenomenon would be important in gas phase reactions, it is not expected to be significant in the reaction of fluorine with solid silicon.

After an appropriate set of weightings were obtained, sample cooling curves were calculated to determine the area in which to concentrate the annealing. By using SA, with 5000 steps at each “temperature” and 15–20 cooling stages for each curve, we obtained approximately 50 candidate sets of parameters. The energetics and structures predicted using these sets then were compared to both the first principles quantum mechanical data and the available gas phase experimental data for the SiF$_x$ molecules. The potential curves were also examined to look for unphysical behavior for each set. As a pathological example, if the function went exactly through the data points that were being fit, the cost would be zero, regardless of the behavior of the function between the points. This would often lead to unphysical barriers occurring between the points. The set of parameters that best fit the ab initio and experimental data is presented in Table I. It was ultimately found that the parameter $\gamma_{\text{SiFF}}$ had to be held fixed at a value of unity to more easily obtain an adequate fit. The new potential is compared to the ab initio data in Figs. 1 and 3 (solid line), where we see this potential provides a significant improvement over the old potential’s description. Additionally, the SiF$_x$ experimental data are also fit adequately, as seen in Table II. Unfortunately, the experimental decrease in the SiF$_x$–F bond energy is a quantum mechanical effect, as mentioned above, that can not be modeled in the current functional form of the potential. Again, this phenomenon is only important for reactions involving gaseous SiF$_x$, a reaction type with which we are not primarily concerned.

IV. SIMULATIONS OF COVERAGE-DEPENDENT REACTION PROBABILITIES

Using our new potential, we calculated the adsorption probabilities and investigated reaction mechanisms for a single fluorine atom impinging on a surface of varying fluorine coverages, whose structures were based both on those suggested previously by ab initio calculations and those derived from our “long time” (~95 ps) etching simulations.

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**TABLE I. Parameters for heteroatomic terms.**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>SW value</th>
<th>Our value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{\text{SiF}}$</td>
<td>21.234 141 38</td>
<td>21.199 221</td>
</tr>
<tr>
<td>$B_{\text{SiF}}$</td>
<td>0.569 547 643 3</td>
<td>0.546 418</td>
</tr>
<tr>
<td>$\gamma_{\text{SiF}}$</td>
<td>1.3</td>
<td>1.339 450</td>
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<tr>
<td>$A_{\text{SiF}}$</td>
<td>15.0</td>
<td>3.624 533</td>
</tr>
<tr>
<td>$\gamma_{\text{SiF}}$</td>
<td>0.0</td>
<td>0.218 615</td>
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<tr>
<td>$\gamma_{\text{SiF}}$</td>
<td>1.0</td>
<td>0.463 088</td>
</tr>
<tr>
<td>$A_{\text{SiF}}$</td>
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</tr>
<tr>
<td>$\gamma_{\text{SiF}}$</td>
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<tr>
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<td>2.792 073</td>
</tr>
<tr>
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<td>1.0</td>
</tr>
<tr>
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</tr>
<tr>
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<td>2.068 601</td>
</tr>
<tr>
<td>$\gamma_{\text{SiF}}$</td>
<td>1.0</td>
<td>0.890 132</td>
</tr>
</tbody>
</table>

---

**TABLE II. Bond dissociation energies for SiF$_x$ gas phase molecules.**

<table>
<thead>
<tr>
<th>Species</th>
<th>Exper.</th>
<th>SW</th>
<th>Current</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiF</td>
<td>5.72</td>
<td>5.72</td>
<td>6.10</td>
</tr>
<tr>
<td>SiF$_2$</td>
<td>6.72</td>
<td>5.84</td>
<td>6.23</td>
</tr>
<tr>
<td>SiF$_3$</td>
<td>5.33</td>
<td>6.18</td>
<td>6.31</td>
</tr>
<tr>
<td>SiF$_4$</td>
<td>6.93</td>
<td>6.46</td>
<td>6.33</td>
</tr>
</tbody>
</table>

*From Ref. 24.*
The Si(100) crystal was modeled by a periodically replicated (in the surface plane) five layer slab with 32 atoms per layer. The top two layers were propagated via Newton’s equations of motion by the Verlet algorithm (constant total energy, and therefore the microcanonical ensemble, constant NVE). The lower two layers followed Nosé’s equations of motion that recreate the canonical ensemble (constant NVT) distribution. This was done so that the excess heat generated by the exothermic Si–F reaction would be carried from the upper layers, to the lower layers, and out of the system, thus maintaining a constant temperature. This method has been used successfully before in isothermal MD simulations of the reconstruction of Si and Ge. Both the NVE and the NVT integrators used a time step of 0.25 fs. As in earlier studies of the Si(100) surface, the bottom layer was held fixed to represent the infinite bulk lattice. The surface atoms were initially displaced to form the familiar $p(2\times1)$ rows of Si dimers, followed by thermal equilibration at 300 K for typically 1.25 ps, which was sufficient to ensure a constant average potential energy. Fluorine atoms were then introduced randomly between 6 and 8 Å above the surface with random velocities corresponding to a temperature of 300 K. One hundred 5 ps trajectories were run for each type of surface, described below.

### A. Submonolayer adsorption probabilities

We first examined the initial (zero coverage) adsorption probability. In agreement with Schoolcraft and Garrison (SG), who used the original SW potential with its empirically fit parameters to calculate the adsorption probability for clean Si(100)–$2\times1$, we also found three possible outcomes for a trajectory. The first was the formation of an Si–F bond (assumed to occur when the system’s potential energy dropped by at least 5 eV, since the Si–F bond energy is approximately 6 eV). The second was scattering of the F atom, which was defined to be when the atom passed a plane 8 Å above the surface, since at this distance the F atom and the surface no longer interact. The third was when the F atom was physically adsorbed but had not yet reacted. In this case, the atom was either trapped in a metastable state or was diffusing. SG only considered the first case to be a sticking event. By using the same criterion, examination of each 5 ps trajectory yielded an adsorption probability on a clean surface of $S_0=1.0$, in agreement with the calculations by SG who found $S_0=0.95$. The agreement is good because the F atom is simply adding to the high density of dangling bonds available on the surface, a reaction that both potentials predict to be energetically favorable [the ab initio value is 6.4 eV (Refs. 13, 14) compared to a value of 5.4 eV for SW]. Molecular beam studies determined $S_0=0.5\pm0.3$, in reasonable agreement with the theoretical results. The measured value could be lower for several reasons, including the fact that the incident energy of their beam was a bit higher than ours, which could lead to more scattering. In addition, the experimental value was obtained using a mixed F/F$_2$ beam where the adsorption probability of molecular fluorine had to be subtracted out and the effect of F$_2$ on F atom adsorption is unknown.

The adsorption probability for a surface at room temperature with $\Theta_F=0.5$ ML was calculated in the same manner. The adsorbed F atoms comprising the half monolayer randomly occupied Si dimer dangling bonds. The adsorption probability was found to be 0.6, with 10% of the trajectories resulting in physisorbed atoms that had neither desorbed nor reacted with the surface at the end of the 5 ps trajectory. The remaining 30% of the trajectories were events where the incoming F atom left the surface without reacting. This type of event would happen when the incoming F atom would impinge on an area where several F atoms were already adsorbed. Thus these results suggest primarily Langmuirian kinetics, where the adsorption probability is proportional to $1-\Theta_F$, however, a slight precursor effect produces $S>1-\Theta_F$. Thus all the dangling bonds that remain on a surface at $\Theta_F=0.5$ ML are available for reaction with incoming fluorine atoms.

### B. Adsorption probabilities on ordered fluorine overlayers

For a surface with $\Theta_F=1$ ML, equilibrated at room temperature; and where the fluorine atoms saturated all of the silicon dimer dangling bonds on the surface forming an ordered $p(2\times1)$ overlayer, the adsorption probability was found to be zero. The incoming F atoms would either bounce off of the surface or physisorb above the adsorbed monolayer of fluorine. Once physisorbed, the F atom could diffuse across the surface, but never showed any tendency to either replace one of the adsorbed F atoms or penetrate through the adsorbed layer and attack the silicon substrate. As discussed later, this negative result has important implications for the etching mechanism.

The experimentally observed rapid initial adsorption of fluorine could be due to an orderly saturation of only surface dimer dangling bonds. The next step in the mechanism might therefore involve breaking the Si–Si dimer bonds on the surface. Although we see no evidence for this in the adsorption probability simulations of the ordered 1 ML structure discussed above, we have investigated the surface where the fluorine coverage is greater than 1 ML and the additional fluorine atoms are taken up in situs resulting from the unreconstruction of the surface, i.e., the breaking of the dimer bonds. Three different coverages were examined, $\Theta_F=1.25$, 1.5, and 2.0 ML. The ordered structures investigated for these coverages are shown in Fig. 2.

The $\Theta_F=1.25$ ML surface was found to be stable after room temperature equilibration. At this coverage, the adsorbed fluorine atoms were still separated enough so that steric repulsions did not cause any significant rearrangement of the surface. Although dangling bonds were available on the surface [see Fig. 2(a)], no incoming F atoms were observed to react with these dangling bonds. Approximately 30% of the incoming F atoms physisorbed above the adsorbed F atoms, however there was no reaction of these physisorbed atoms with the dangling bonds on the...
tetrahedral geometry. Steric repulsions on the surface force the SiF to high eF. The SiF group originally is sp\(^2\) hybridized so that it has a limit of S=O.3 at C&=1.25 ML. The high coverage of the half-filled rehybridize to sp' so that the geometry of the group is now planar, with the half-filled p orbital perpendicular to the plane containing the atoms.

time scale of these trajectories (5 ps), placing an upper limit of S=0.3 at ΘF=1.25 ML. The high coverage of fluorine apparently provides a barrier to this reaction that is above thermal kinetic energies. This apparent barrier is also consistent with the dropoff in adsorption rate observed experimentally, although we observe this to occur at a lower coverage (ΘF≈1.1 ML vs ΘF≥1.5 ML).

The initial structure for the 1.5 ML surface, taken from the ab initio predictions of the structure preferred at 0 K, was quite unstable at 300 K. Steepest descent quenching was probably not representative of the actual ΘF=2 ML surface, but instead opting for a planar structure with the F atom sticking straight up out of the surface. Electronically, silicon atom to an sp\(^2\) hybridization, such that a half-filled p orbital perpendicular to the plane containing the atoms.

FIG. 5. Change in structure of surface SiF group with a dangling bond at high ΘF. The SiF group originally is sp\(^2\) hybridized so that it has a tetrahedral geometry. Steric repulsions on the surface force the SiF to rehybridize to sp\(^2\) so that the geometry of the group is now planar, with the half-filled p orbital perpendicular to the plane containing the atoms.

predicted huge pairwise repulsions between SiF\(_2\) (ad) groups (~17 eV) because of the overlap of the neighboring fluorine atoms. Thus it was concluded that this structure could not exist, with the possible exception of a structure obtained by concerted twisting all of the SiF\(_2\) groups by approximately 30°, which minimized the pairwise repulsions to about 1.8 eV. Our simulations show the same behavior. Even after extensive quenching, the untwisted 2 ML surface was unstable and would desorb fluorine when the system was allowed to evolve at room temperature. For the case where the SiF\(_2\) groups were twisted, taken to a local minimum by steepest descent, and subsequently allowed to evolve in a room temperature simulation, fluorine atoms would again desorb from the surface. If the system was periodically quenched during this simulation, a stable surface could be obtained, however rearrangement occurred to form SiF\(_3\) as well as surface and subsurface SiF species, in addition to SiF\(_2\) groups. These results agree with the proposal from the ab initio calculations, which suggested that adsorption of more than 1.5 ML of fluorine will result in formation of SiF\(_3\) and SiF\(_4\), instead of orderly formation of an SiF\(_2\) covered surface. Thus etching must begin to occur above ΘF=1.5 ML because further addition of F atoms to the surface silicon atoms is energetically unfavorable.

Since this ΘF=2 ML surface that we obtained via periodic quenches is probably not representative of the actual ΘF=2 ML surface, we did not perform adsorption probability simulations for it. However, these results suggested that we should examine adsorption probabilities for disordered overlayers.

C. Adsorption probabilities for disordered overlayers

A "long time" simulation of 95 ps had been performed previously with a larger crystal that contained 72 atoms per layer and a gas of 160 fluorine atoms above the surface. During the simulation, the system was probed for adsorbed fluorosilyl groups. These species would be identified by groups of atoms where the separation between Si and F atoms was less than 1/3 of the equilibrium bond distance, in order to account for vibrational excitation. It was found that fluorine atoms did not adsorb exclusively on the dangling bonds on the surface. Rapid adsorption of ~1.1 ML of fluorine occurred, producing a variety of fluorosilyl species on the surface and leaving a number of unreacted dangling bonds (~9% of the original dangling bonds remained unreacted). A single SiF\(_3\), three SiF\(_2\), and 65 SiF species formed, where three of the SiF species originated from second layer silicon atoms. Thus, disordered rather than ordered overlayers appear to dominate the structure of the initial fluorosilyl layer.

To alleviate concerns regarding whether our model realistically reproduces the chemical dynamics of a semi-infinite crystal with appropriate heat transfer to the bulk crystal, we repeated this simulation with a silicon slab that was nine (rather than five) layers thick, with the bottom layer again held fixed. The top four layers were propagated with NVE dynamics while the lower four unconstrained layers were propagated by NVT dynamics. The reaction
was essentially the same as that observed with the five layer slab, with Si dimer bond breaking, attack of second layer Si atoms, and rapid adsorption of $\sim 1.1$ ML of fluorine observed. Thus these results appear to be independent of the thickness of the slab and the location of the heat bath, suggesting that we are appropriately modeling a semi-infinite slab of silicon.

The mechanism of the buildup of the fluorosilyl layer seen in these long simulations is not consistent with the idea of an orderly sequential adsorption of F atoms forming first F-Si-Si followed exclusively by F-Si-Si-F. In the 0 K \textit{ab initio} calculations, saturation of the Si dimer dangling bonds to form F-Si-Si-F prior to further reaction was predicted to be preferred. At finite temperature, the MD simulations predicted that saturation of the Si dimer bonds was not a prerequisite for further reaction. Indeed, the adsorption probability study at $\theta_F = 1$ ML showed that full saturation of these dangling bonds inhibits rather than enhances further reaction. Thus ordered fluorosilyl layers appear to poison the surface toward further etching.

To examine the effect of disorder in the fluorosilyl surface further, we performed adsorption probability studies on the disordered 1.0 ML surface produced by the long time etching simulation. After the gas phase fluorine atoms initially present in this simulation were removed, the system was allowed to equilibrate and then the adsorption probability was calculated in the same manner as described above. It was found to be approximately 0.15. The incoming F atom reacted only with exposed surface dimer dangling bonds and never with subsurface Si atoms. Occasionally, the F atom became bound in a metastable site above the adsorbed F atoms. This physisorbed atom would sometimes desorb from this site, but was never seen to penetrate into the bulk. The trajectories of the physisorbed F atoms were not followed beyond 5 ps, so the possibility of future reaction can not be ruled out. The key conclusion though is that an ordered monolayer of F$_{\text{bulk}}$ yields $S=0$, while the disordered $\theta_F = 1$ ML structure formed in an etching simulation has a nonzero adsorption probability, with $S>0.15$.

From the results above, it is clear that disorder in the fluorosilyl layer is an important part of the mechanism of the buildup of the layer. The long time trajectory was examined for microscopic mechanisms leading to this disorder. The most obvious aspect involved the reaction of gas phase F$_2$ molecules with the surface. F$_2$ was observed to simultaneously attack both the dangling bond and the dimer bond of a single surface silicon atom. The resultant formation of two SiF bonds released $\sim 12$ eV of energy, more than enough to break the two remaining subsurface Si bonds to the surface silicon atom ($\sim 2$ eV/bond). This allowed the resulting SiF$_2$ to diffuse across the surface to a neighboring silicon dimer, where it attached to a dangling bond. The exposed SiF$_2$ group rapidly formed an SiF$_3$ species. This local release of energy was a common mechanism for accelerating other bond breaking. For example, it was easier for an incoming F atom to break a dimer bond that was vibrationally excited. Recent measurements of vibrational relaxation times of the Si-H bonds on hydrogen terminated silicon indicate that the relaxation times are on the order of $\sim 100$ ps, lending credence to the argument that the heat generated during the surface reaction is dissipated slowly into the silicon substrate and that local heating can affect subsequent reactive events.

Another mechanism that we observed, which produces the disorder necessary for further reaction, involved the attack of second layer silicon atoms by fluorine. Typical F atoms that were able to accomplish this had hyperthermal translational energies. This excess energy was usually gained through collision with surface atoms that were vibrationally excited via the highly exothermic formation of Si-F bonds. However, translational energies on the order of only 0.1 eV appeared to be high enough for attack of second layer Si atoms. The incoming fluorine usually entered the trench between the dimer rows. If it was too close to the dimer on either side of it, then it either reacted with the closest dangling bond or it was repelled if a fluorine atom already occupied that dangling bond. The fluorine atom then attacked a second layer silicon atom, pulling it part way out into the trench, thereby causing subsurface distortion that is likely to be important for further reaction.

This disorder mechanism can be examined in the context of a proposal by Engstrom \textit{et al.},\textsuperscript{2} who examined the decomposition and subsequent reformation of the fluorosilyl layer. They state that their results suggest the existence of preferential sites for adsorption at surface steps and defects that are formed during anisotropic decomposition of the SiF$_n$ layer upon heating. On the real surface, steps and defects could provide extra sites for the incorporation of fluorine that would subsequently increase the bulk distortion in this region, making the area more susceptible to continued reaction. Thus this is consistent with our results indicating that the disorder, or defects in the fluorosilyl layer, are necessary for continued incorporation of fluorine into the layer.

V. SUMMARY

In conclusion, we see that the mechanism for etching can not be simply modeled by an organized progression of ordered structures. Many different paths of reaction are competing at once, e.g., fluorination of the dangling bonds, breaking of dimer bonds, and attack of subsurface Si atoms. This leads to the concurrent formation of adsorbed SiF, SiF$_2$, and SiF$_3$. The large exothermicity of the reaction due to the tremendous strength of the Si-F bonds results in a local heating effect that introduces disorder in the lattice, weakening existing bonds and exposing new dangling bonds. The ordered surfaces with coverages of one monolayer of fluorine or more are not reactive due to the formation of an impenetrable layer of F atoms at the surface. The 1.5 ML ordered surface contains planar F-Si-Si$_{\text{subsurface}}$ species (Fig. 5) which have been pushed down below the surface so that their singly occupied $p$ orbitals are out of range of incoming fluorine atoms. The creation of new dangling bonds that are accessible to incoming F atoms is clearly key to steady-state etching. The ordered 2.0 ML structure formed by saturation of the dangling bonds on the unreconstructed surface is unstable and desorbs fluorine atoms at room temperature. The preferred structure at
$Q_r - 2.0$ ML is highly disordered and contains SiF, SiF$_2$, and SiF$_3$ species. Thus there is both a thermodynamic and kinetic influence suggesting that disorder is necessary for continued reaction. Indeed, we find nonzero adsorption probabilities for a disordered overlayer at the same coverage where an ordered overlayer produced an adsorption probability of zero.

Our etching simulations show that rapid adsorption of slightly more than a single monolayer of fluorine occurs, the structure of which is highly disordered. Extensive investigation of this disordered surface is key to understanding the next phase of reaction, which involves the considerably slower fluorine adsorption that builds up the fluorosilyl layer. Since further incorporation of fluorine is a rare event, as seen by the slower adsorption of F after the first 10 ps of the long time simulation,$^{17}$ alternative simulation methods will have to be developed in order to investigate this etching reaction further.

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