Simulated reaction dynamics of F atoms on partially fluorinated Si(100) surfaces

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Abstract

We have investigated the influence of translational excitation on the reactivity of atomic fluorine with the Si(100) surface via molecular dynamics simulations using a first-principles-derived interaction potential. Surface reactivity is contrasted for both clean and partially fluorinated surfaces with the results of previous simulations of F₂ molecules impinging on Si(100) surfaces, indicating many similarities between the dynamics of F atoms and F₂ molecules. Mechanisms for the reaction are proposed based on reactivity trends and scattered product energy and angular distributions, including evidence for the existence of a precursor-mediated adsorption pathway for low incident energy F atoms on partially fluorinated surfaces.

Keywords: Atom–solid interactions; Fluorine; Low index single crystal surfaces; Models of surface chemical reactions; Molecular dynamics; Silicon; Single crystal surfaces; Solid–gas interfaces; Surface chemical reactions

1. Introduction

Plasma etching of silicon surfaces is the current method of choice for fabrication of microelectronic devices. New plasma etching processes are constantly being developed and tested with the hope of finding a technique to permit controlled etching of ever smaller features on the silicon surface. However, this development occurs largely by trial and error. In spite of the intense scrutiny devoted to the plasma etching environment, the basic mechanisms involved in the etching of silicon are still not fully characterized.

In an effort to reduce the complexity of the problem, experimentalists have attempted to study the etching processes using model systems. A common example is the use of molecular beams to study etching, which allows for characterization of the reactivity of a single reagent with a semiconductor surface. Of particular interest are studies involving beams of atomic or molecular fluorine. Plasmas created using fluorine-containing precursors are commonly used industrially, and F atoms are thought to play an important role in these etching processes. [1] Additionally, beams of atomic fluorine may eventually be employed in neutral beam etching techniques, where translationally activated beams of neutral species are employed as the etchant with the hope of avoiding the surface damage believed to be caused by ionic species in plasma etching. [2–4]

Due to difficulties in generating beams of atomic fluorine, most experimental studies have focused...
on the development of the F atom beam itself rather than its reactivity with the surface. [3,4] Engstrom, Nelson and Engel [5] examined the reactivity of both atomic and molecular fluorine on the Si(100)-(2×1) surface. They reported an adsorption probability for F atoms on the clean Si(100)-(2×1) surface of 0.5 ± 0.3, independent of incident translational energy in the F atom beam up to 0.56 eV. However, further analysis of the data suggests the actual F atom adsorption probability to be unity. [5] However, they did see a reactivity dependence on translational energy for F atoms impinging on surfaces with non-zero fluorine coverage. A more recent study by Giapis et al. [2] investigated the reactivity of hyperthermal atomic fluorine beams with the Si(100)-(2×1) surface. While they did not measure adsorption probabilities for F atoms striking the Si(100)-(2×1) surface, they did characterize the scattered products. Giapis et al. found that the exit angle distribution relative to the surface normal for F atoms scattered from fluorinated Si(100)-(2×1) surfaces was not cosine-like. They also reported that the scattered F atoms had exit energies consistent with inelastic scattering. Using a beam with an average F atom translational energy of 4.8 eV impinging normal to a surface at a temperature of $T = 348 \text{ K}$, they reported that the average escape energy was 0.32 eV for F atoms scattered at 47° from the surface normal. The escape energy increased to 0.38 eV for F atoms scattered at 62° from the surface normal.

The time and length scales involved in etching have also proven intractable for theoretical methods. However, the same type of deconstruction of the etching process can be employed for simulation studies, especially molecular dynamics. Stillinger and Weber have reported on a limited study of this type for F$_2$ interacting with Si(100)-(2×1) in conjunction with their development of an empirical interatomic potential for simulating the interactions between Si and F. [6–8] Schoolcraft and Garrison [9] used this Stillinger–Weber (SW) potential to study consecutive bombardment of a Si(100)-(2×1) surface with 3.0 eV F atoms. This study showed that simulations could be used to predict spontaneous etching of the Si(100)-(2×1) surface by high energy F atoms, providing evidence that molecular dynamics had at least a partial ability to reproduce the known experimental result of spontaneous etching of Si(100)-(2×1) by thermal atomic fluorine. More recently, Stich et al. [10] carried out ab initio molecular dynamics studies of Cl$_2$ molecules impinging on the Si(111)-(1×1) (unreconstructed) surface, where the forces were calculated at each time step via density functional theory using the local density approximation. They predicted that Cl$_2$ chemisorbs dissociatively on the Si(111) surface, with differing initial Cl$_2$ orientations resulting in different dynamic pathways to achieve the same final structure. However, these predictions were based on only five total trajectories due to the expense in cpu time required for this technique.

One possible avenue for improving the predictive quality of MD simulations is to attempt to combine the accuracy of the ab initio MD technique with the speed of an interatomic analytic potential function by directly incorporating ab initio information into the potential fitting process. With this ultimate goal in mind, Wu and Carter [11,12] carried out ab initio calculations on embedded clusters of silicon and fluorine. These clusters were designed to model fluorine atoms interacting with the Si(100)-(2×1) surface, as well as repulsions between fluorine atoms bonded to neighboring silicon atoms. Weakliem, Wu and Carter (WWC) [13] then used data from these ab initio calculations to fit a Stillinger–Weber-style two- and three-body interaction potential for the interaction of silicon and fluorine atoms. (The original SW parameters were used for the pure silicon and pure fluorine interaction terms.) Weakliem and Carter [14] then used this potential to study the interaction of thermal F atoms with both clean and partially fluorinated Si(100)-(2×1) surfaces. We will review their simulations along with the presentation of our new results. We also have used this potential previously to study the interaction of molecular fluorine with Si(100)-(2×1) surfaces having various amounts of fluorine coverage, [15,16] defects, [17] and steps. [18] (A similar study to ours [16] comparing the differences between the SW potential and the WWC potential for the clean Si(100)-(2×1) surface was reported recently by Schoolcraft et al. [19] Herein we
apply the WWC potential to simulation of the reactivity of atomic fluorine with both clean and partially fluorinated Si surfaces as a function of F atom incident energy.

In this work, we will present new results of simulations of F atoms interacting with both clean and partially fluorinated Si(100)-(2 × 1) surfaces, as well as compare and contrast these results with our previous predictions for molecular fluorine interacting with these surfaces. However, this work also represents the culmination of the effort described above to incorporate ab initio data into an interatomic potential for fast, realistic simulation of atomic and molecular fluorine reactivity with the Si(100)-(2 × 1) surface. As a result, we will also review the effectiveness of this technique. Section 2 contains the simulation details for our current F atom study. In Section 3, we present our results as well as a comparison to our previous work with atomic and molecular fluorine on these surfaces. In Section 4 we will broaden our view and discuss the relative success of the effort to incorporate ab initio data into an interaction potential, and discuss possible future applications of this technique for other aspects of the etching process. Section 5 contains our concluding remarks.

2. Simulation details

As mentioned above, we employed an ab-initio-derived two- and three-body potential to describe the interactions between atoms. The pure silicon [6] and pure fluorine [7] interaction potentials are those developed by Stillinger and Weber (SW), who fit these potentials to experimental data and showed their validity for modeling bulk silicon and gaseous fluorine molecules. The terms in the potential involving both Si and F are based on the SW functional form, but fit by Weakliem and Carter to ab initio calculations on embedded clusters of silicon performed by Wu and Carter [11–14]. We previously used this potential to produce excellent qualitative agreement with experiment for simulations of F₂ interacting with the clean Si(100) surface [16].

The details for creation of the silicon surfaces used in these simulations have been described previously elsewhere. [15] All of the simulations below were carried out on Si(100)-(2 × 1) reconstructed surfaces which were either clean or had 0.5 ML or 1.0 ML of pre-adsorbed fluorine on the surface. The Si(100)-(2 × 1) surfaces were modeled using a silicon slab nine layers thick containing 64 atoms per layer, with periodic boundary conditions enforced parallel to the surface to model an infinite structure. Each surface used in the simulations initially exhibited a perfect p(2 × 1) surface reconstruction for the top layer of atoms. The surface was then equilibrated using a Nose–Hoover canonical ensemble algorithm [20,21] to achieve a velocity distribution characteristic of T = 298 K for the upper eight layers of the slab. The bottom layer of atoms was held fixed in ideal bulk positions during this process as well as in all other dynamical simulations in order to prevent reconstruction of the bottom layer.

At this point fluorine atoms were added to the surfaces when initial fluorine coverage was desired. Surfaces with \( \Theta_F = 0.5 \) ML were generated by randomly choosing one Si atom from each dimer pair and placing a fluorine atom 2.0 Å above it. For \( \Theta_F = 1 \) ML, a fluorine atom was placed above every Si atom in the top layer. The surface was then re-equilibrated via the same Nose–Hoover scheme to permit the fluorine atoms to move and form Si–F bonds, as well as to subsequently generate a velocity distribution characteristic of 298 K for all moving atoms. Note that for both the \( \Theta_F = 0.5 \) and 1 ML ordered surfaces, no Si–Si dimer bonds were broken during this procedure.

Alternate \( \Theta_F = 1 \) ML surfaces which did not retain the underlying 2 × 1 structure of the Si surface dimers were also created. These “disordered” surfaces were inspired by the observations of Weakliem et al. [13,14] that disordered surfaces are created during etching. Thus we created such surfaces efficiently using a scheme involving consecutive bombardment of the Si(100)-(2 × 1) surface with 1.5 eV translationally excited F atoms. A full description of the process for creating these disordered surfaces can be found elsewhere [15]. Note that the surfaces created by this method are only modestly disordered. Later we will provide characterization that this disorder increases the number of reactive sites on the surface by roughly 10%.
Each trajectory started by placing a single F atom at a randomly chosen location above one of the previously equilibrated surfaces beyond the interaction range of any atoms on the surface. The initial configuration of the silicon surface was identical for all simulations involving a particular value of \( \Theta_F \). The fluorine atom was given a selected initial translational energy, and the velocity of the F atom was always directed normal to the surface.

All of our simulations were carried out in the microcanonical (constant number of particles, \( N \), constant volume, \( V \), and constant energy, \( E \)) ensemble, so that the trajectories represent true classical dynamics. The majority of the trajectories were propagated forward in time using a simple Verlet [22] algorithm with an integration time step of 3.065 \( \times 10^{-18} \) s. (For incident energies \( >2.5 \) eV, the time step was reduced to 2.500 \( \times 10^{-16} \) s.) The simulations were propagated until the trajectory of the F atom could be classified as belonging to some reaction pathway (see below for pathway descriptions) and until any species ejected from the surface were beyond the interaction range of the surface. Typically, this involved about 1 ps of simulation time, although some trajectories required up to 6 ps for full characterization.

For each selected initial energy 200 trajectories were performed. Two different methods were used to calculate error bars during data analysis. For averaged quantities, such as the average exit energy of scattered F atoms, the error bars represent one standard deviation for the data. For the probability of a given reaction outcome, such as the percentage occurrence of dissociative chemisorption, the error bar was computed as \( \sigma = \sqrt{p(1-p)/n} \), where \( p \) is the probability and \( n \) is the number of trajectories [23].

We have used three basic styles of graphs to display and analyze the data generated by our simulations. The first type of graph displays the partitioning between reaction channels as a function of incident F atom translational energy for a given surface. In these graphs, the percentage occurrence of each reaction channel is plotted for each incident energy, in order to elucidate reactivity trends and relationships between the reaction pathways. A second kind of graph shows the energy of F atoms which are non-reactively scattered from the surface. The final type of plot also assists in characterizing scattered species by depicting the angular distribution of scattered F atoms for a particular \( \Theta_F \) and F atom incident energy. When displaying the angular distribution relative to the surface normal, we summed over all angles in the plane of the surface (azimuthal angles). This is justified, since we have found that the F atom azimuthal angular distributions are isotropic, similar to the behavior found for F\(_2\) molecules non-reactively scattered from Si(100) surfaces. [15] The data were then grouped into 5° bins and displayed in a polar plot.

3. Results

We characterized the results of all of our trajectories as belonging to one of three reaction pathways: (a) chemisorption, where the F atom forms an Si–F bond on the surface, (b) non-reactive scattering, where the F atom leaves the interaction range of the surface without forming an Si–F bond, and (c) precursor formation, where the incident F atom forms a metastable Si–F–F complex with an existing Si–F group on the surface (an extrinsic precursor state). Although these precursor states should eventually fall apart to yield one of the former two trajectories, the lifetime of these complexes is longer than the picosecond time-scales of our simulations.

3.1. Clean Si(100)-(2 × 1) surface

Although previous simulations with the WWC potential exhibited adsorption probabilities less than unity for F\(_2\) molecules impinging on the clean Si(100)-(2 × 1) surface, [15,16] they did show that at least one F atom in each F\(_2\) molecule formed a Si–F bond, suggesting an adsorption probability of unity for individual F atoms striking the surface. Weakliem and Carter [14] also observed a unit sticking probability in their simulations of thermal (300 K) F atoms impinging on the clean Si(100)-(2 × 1) surface. Our simulations of atomic fluorine impinging on the Si(100) surface confirm these predictions, yielding an adsorption probability of exactly unity regardless of incident energy in the approaching F atoms. This is in excellent
agreement with the revised analysis of the adsorption probability data of Engstrom et al. [5]. In our simulations, the reaction has no barrier and takes place without passing through an intermediate precursor state. The complete reaction of all incident F atoms with the Si(100) surface, independent of the incident energy shows that the chemisorption of atomic fluorine on the surface is a direct process, as has been proposed experimentally by Behringer et al. [24]. This also makes sense from the point of view of the electronic structure of both F atoms and the Si(100)-(2 × 1) surface. Since both the F atom and each surface Si atom have one unpaired radical electron (or dangling bond), we should expect and do observe reactivity similar to gas phase radical recombination reactions, which typically are barrierless and have unit reaction probability.

3.2. Θ_F ≠ 0 ML surfaces

The introduction of pre-adsorbed fluorine on the surface produces dramatic changes in reactivity. Fig. 1a shows that both non-reactive scattering and extrinsic precursor formation occur in the presence of surface Si–F groups on the Θ_F = 0.5 ML surface. This result is similar to our previous results for reactive scattering of F_2 from Si(100)–(2 × 1) surfaces [15], where we also found that non-reactive scattering occurred only with the introduction of pre-adsorbed fluorine. Obviously, with some adsites now blocked by preadsorbed F atoms, F atoms impinging near such sites can either be repulsively scattered or caught in a weak physisorption well corresponding to the extrinsic precursor state. As we discussed in previous work [15,16], this metastable state has a lifetime longer than the picosecond time-scale accessible in our simulations. Further evidence for its metastable nature comes from its disappearance with increasing F atom incident energy. The precursor channel is completely absent for F atoms with translational energies above 2.5 eV.

In addition to lower overall amounts of adsorption, due to the introduction of other reaction pathways, Fig. 1a shows a dependence on incident energy for the adsorption pathway. The percentage of adsorption events stays near 70% for most incident energies, but near 1 eV the adsorption probability dips down to 0.6 and then rises back to 0.7 at 1.5 eV. We believe that this drop in adsorption for intermediate amounts of translational excitation of the impinging F atoms is due to a change in adsorption mechanism on the Θ_F = 0.5 ML surface from a precursor-mediated adsorption mechanism, present at the lowest incident energies, to a direct mechanism at higher energies, such as the one observed on the clean surface. A precursor must be involved at lower energies in order to account for the higher adsorption probability than that expected from Langmuir-type kinetics. We observe such a precursor explicitly in representative trajectories. Experimental evidence for a precursor-mediated adsorption mechanism has already been reported by Engstrom et al. [5], for the interaction of F_2 with a partially fluorinated Si(100) surface.

While precursor-mediated chemisorption is occurring at low F atom energies, clearly some amount of direct chemisorption takes place on the Θ_F = 0.5 ML surface. The F atoms impinge along the surface normal, so any F atoms which approach the surface above an unoccupied dangling bond site will be able to directly react, as they would on the clean surface. The precursor is important only for those trajectories where the F atom approaches the surface above an occupied dangling bond site (i.e. an Si–F group). In these trajectories, if the relatively weak van der Waals attractions of the surface fluorine atoms are able to hold the impinging F atom close to the surface, the unbonded fluorine atom will have additional time to explore the surface, possibly allowing it to find an unoccupied dangling bond site. Further evidence for this comes from the length of simulation time required for definitively assigning an outcome to a trajectory. At energies greater than 0.906 eV, all trajectories can be classified as non-reactive scattering, formation of a long-lived precursor or F atom adsorption at the end of 1.2 ps. In these trajectories, almost no surface diffusion takes place. When an F atom approaches the surface above an Si–F group, the incident F atom either promptly scatters off of the Si–F group, deflecting to an adjacent unoccupied dangling bond site or bouncing away from the surface, or immediately forms an Si–F–F
Fig. 1. Reaction channel partitioning for F atoms impinging on the (a) $\theta_F = 0.5$ ML surface; (b) 1.0 ML "disordered" surface; and (c) $\theta_F = 1.0$ ML ordered surface. The percentage occurrence of each channel is shown as a function of incident translational kinetic energy of the F atom.

precursor. Conversely, at the lowest incident energy of 0.078 eV, some trajectories required up to three times as much simulation time for definitive classification. When the impinging F atom approaches the surface above an Si–F group, the F atom generally becomes accommodated by the surface. In these trajectories, often requiring additional simulation time, the F atom drifts above Si–F groups until it either diffuses to an available dangling bond, forms a long-lived precursor or escapes the interaction range of the surface.

Using this same potential, Weakliem and Carter [14] reported an adsorption probability of 0.6 for F atoms with velocities chosen from a $T=300$ K distribution on the $\theta_F = 0.5$ ML surface, which corresponds to an average incident energy of $\approx 0.04$ eV. While this is similar to our predicted value of 0.7 for the $\theta_F = 0.5$ ML surface, it is not in complete agreement. The most notable difference is that Weakliem and Carter allowed their impinging F atoms to have initial velocities with components parallel to the surface, rather than using normal incident F atoms [14]. Since their velocities were chosen randomly from a 300 K distribution, the F atoms could have velocity components parallel to the surface which were relatively large when compared to the normal component. At grazing incident angles, F atoms initially encountering surface Si–F groups might skim along the surface, instead of inelastically transferring their incident energy as would occur for normal incidence. Thus these F atoms might never equilibrate
with the surface, and would scatter away without finding an available dangling bond site.

Ideally, these same trends should be visible in Fig. 1b, which shows the reaction channel partitioning for the $\Theta_F = 1.0$ ML “disordered” surface. At 1.0 ML of coverage, an ordered surface would have no available dangling bonds, as one F atom would be adsorbed at each dangling bond site. Introducing disorder into the surface exposes additional dangling bonds, thus increasing the number of dangling bond sites available for reaction at a given coverage. We mentioned previously that our “disordered” surface is really a lower bound for a true disordered surface. On our surface, only six dangling bonds, or an additional 10%, are available due to the presence of disorder. Even this minimal disorder is created by disrupting the dimer rows and exposing atoms in the lower layers of the lattice. Rather than having a well defined layer of Si atoms each with one Si–F bond, the disordered surface has Si atoms with Si–F bonds distributed through a thickness of $\approx 4$ Å. Although the dimer row nature of the surface is no longer visible, the majority of the surface is still unreactive. In their simulations, Weakliem and Carter [14] observed that F atoms from a $T = 300$ K distribution were unable to form new Si–F bonds with surfaces which had no available dangling bonds for reaction. This contributed to their prediction that local-heating-induced disorder was important in etching processes, in order to generate additional dangling bonds for reaction.

Although the total number of available dangling bonds is lower on the $\Theta_F = 1$ ML surface compared to the $\Theta_F = 0.5$ ML surface, the presence of a precursor state should enhance the reactivity of the F atoms with the surface at low incident energies and thus show a minimum in reactivity at an intermediate energy, where the precursor disappears but where the direct adsorption mechanism has yet to turn on fully. Unfortunately, if this effect is present, it is hidden by the $\approx 40\%$ probability for precursor formation observed for incident energies $< 0.906$ eV. While these trajectories suggest that a long-lived precursor is important in the reaction mechanism, the long-lived nature of these complexes relative to the time-scale of our simulations prevents us from classifying these trajectories as either reactive or non-reactive, eliminating the possibility of observing a similar minimum in reactivity at intermediate incident energies. Fig. 1b also differs from the $\Theta_F = 0.5$ ML surface at higher energies, where increasing incident energy leads to a noticeable rise in reactivity. The only similarity is that as before, increasing the incident kinetic energy in the impinging F atom eventually leads to elimination of the precursor state for energies above 3.5 eV. The precursor state is observed at higher energies on this surface compared to the $\Theta_F = 0.5$ ML surface because of the higher fluorine coverage.

Fig. 1c shows that the $\Theta_F = 1.0$ ML ordered surface exhibits only minimal reactivity, but otherwise follows the general trends of the $\Theta_F = 1.0$ ML “disordered” surface. The absence of data points below 1.5 eV is due to a barrier to reactivity of 1.0–1.1 eV predicted by our simulations. This is once again consistent with the simulations of Weakliem and Carter [14], who observed no reaction for thermal F atoms impinging on $\Theta_F = 1.0$ ML ordered surfaces. This also mirrors the results of our studies for F$_2$, where we similarly found a high barrier to reaction of F$_2$ with the $\Theta_F = 1.0$ ML ordered surface. Once above the barrier, increasing incident energy leads to increasing reactivity, as for the $\Theta_F = 1.0$ ML “disordered” surface. However, only at our highest incident energy of 3.5 eV did we see a substantial amount of reactivity. Again, this demonstrates the importance of disorder for etching processes. Introduction of disorder into the surface creates additional dangling bonds for a given coverage, allowing for reaction well beyond one monolayer.

3.3. Scattered products

As in our previous work, we also characterized those F atoms which non-reactively scattered away from the Si(100) surface in our trajectories. Fig. 2 shows the average escape energy of F atoms scattered away from the $\Theta_F = 0.5$ ML, 1.0 ML “disordered” and 1.0 ML ordered surfaces, respectively. In all three cases, the average escape energies indicate that most F atoms undergo highly inelastic scattering. The majority of the F atom incident energy is transferred to the surface, since, for
example, the average escape energy is still below 1.4 eV for F atoms incident on any of the three surfaces with 3.5 eV of energy. However, there is a moderate dependence on the incident energy of the atomic fluorine, indicating some memory of its initial conditions. In fact, this is remarkably similar to the scattering observed for F$_2$ molecules. Fig. 3 shows the average exit energy of F$_2$ molecules scattered from the $\Theta_F=0.5$ ML surface for many of the same incident energies used for atomic fluorine, taken from our previous work [15]. This plot for scattered F$_2$ molecules is nearly identical to Fig. 2 for non-reactively scattered F atoms, and is certainly the same to within the limits of our error bars. As for comparison to experimental values, our predictions agree qualitatively with Giapis et al.’s observation of inelastic scattering for F atoms ejected from fluorinated Si(100) surfaces [2]. However, quantitatively, we predict a much higher scattered F atom translational energy than the measured values of Giapis et al. Even considering the fact that their measurement was performed on a beam having a range of incident energies (4.8 eV average, with a 3.0 eV full-width half-maximum), their measurement of $<$0.4 eV for the scattered F atom energy is what we predict only for the lowest incident energy species in their distribution, although the rather large uncertainties in our predicted values somewhat compensate for this. We also note that the F atom beam in Giapis et al.’s experiment is not pristine; SF$_x$ by-products (from SF$_6$ – the beam precursor) were present and may complicate interpretation of the data [2].

We have also characterized the angular distributions of scattered F atoms in our simulations. Fig. 4a–c depict the angular distribution relative to the surface normal for F atoms scattered away from the $\Theta_F=0.5$ ML surface for incident kinetic energies of 0.078, 0.906 and 2.5 eV, respectively. Fig. 4a is somewhat different from Fig. 4b and c, as it has as much character along the surface normal as for any other exit direction. Fig. 4b and c, however, show a maximum of scattering intensity for angles increasingly farther from the surface normal. The latter two figures are similar to the distributions found for non-reactively scattered F$_2$ molecules in our previous work. These latter distributions are not cosine-like, indicating that the scattered F atoms do not equilibrate with the surface before leaving its interaction range. Giapis et al. [2] also reported non-cosine distributions for F atoms undergoing non-reactive scattering. The maximum intensity is also not along the surface normal, as would be expected for perfect elastic scattering given that the F atoms are incident to the surface along the surface normal. Instead, the distribution is broadly peaked between 10 and 30° for an incident energy of 0.906 eV and between 40 to 55° for 2.5 eV. We believe that these distributions show inelastic scattering, influenced
by the corrugation present on the surface, which causes a continued depression in scattering angle with increasing incident energy.

Fig. 4a is more difficult to explain. While showing maximum intensity at 10° away from the surface normal, this distribution has a broad maximum which extends all the way to the normal itself. The best analysis of this distribution relies on the presence of two types of scattering. A great deal of direct, inelastic scattering is still present. However, the presence of precursor-mediated adsorption for low incident energy F atoms provides for the possibility of equilibrated F atoms escaping the surface. The classic scattering model would give these equilibrated F atoms a cosine-like distribution, which would account for the high intensity along the surface normal.

This immediately raises a question about the data shown in Fig. 2. If the angular distributions confirm the presence of precursor-mediated adsorption at low energies, why is there not similar evidence available in the average exit energies of the scattered F atoms? This problem arises due to the quick decline in precursor-mediated events as a function of incident energy. At the lowest incident energy, 0.078 eV, the exit energy of an F atom equilibrated with the surface temperature of 298 K, approximately 0.03 eV, is about the same as the exit energy of an F atom which loses more than 50% of its energy during an inelastic scattering event. Thus, at the lowest energies the escape energies of scattered F atoms do not distinguish between the precursor-mediated and direct inelastic scattering mechanisms. By the time the incident energy has risen enough to clearly differentiate between these two mechanisms, the number of
precursor-mediated events has become relatively few in number, preventing it from greatly influencing the average value.

Up to this point we have said little about the nature of the products formed on the surface when chemisorption occurs. Formation of an Si–F bond on the surface causes the release of large amounts of energy, due to the \( \approx 6 \) eV strength of an Si–F bond \([11,12]\). For low incident energy F atoms, this energy generally does not produce any lasting disruption of the dimer row structure on the surface. While the Si atom involved in the Si–F bond may vibrate more strongly around its equilibrium position, even this usually persists for only one or two hundred femtoseconds. In a few trajectories, the dimer bond is disrupted completely, resulting in an increased separation of the two dimer atoms from the \( \approx 2.4 \) Å characteristic of a dimer bond to \( \approx 3.8 \) Å, which is more typical of the unreconstructed surface. In these cases, however, if the simulation is allowed to proceed for an additional 1–2 ps, this defect will heal and regenerate the underlying 2 \times 1 dimer row structure for the surface Si atoms.

Only at higher incident energies do the impinging F atoms cause significant disruption of the surface. At incident energies \( > 1 \) eV, the additional energy imparted by the impact of the incoming F atom increases the likelihood of breaking an Si–Si bond to a subsurface atom, allowing greater movement of a surface Si atom away from its original position in the dimer row. These Si atoms will often settle on the surface in a location which is stable relative to the thermal fluctuations occurring in a 300 K Si(100) lattice. This stable defect creates a "vacancy" in the original position of this moving Si atom, leaving open the possibility of subsequent attack of lower layer Si atoms by F atoms. Further surface damage or etching is of course not seen in these simulations since we are working in the limit of zero flux, in order to predict initial reaction probabilities. At high fluxes, etching precursors are formed even by low energy F atoms, as shown previously \([13]\).

So far we have considered surface defects and disorder caused by formation of Si–F groups on the surface. For the most part, our simulations predict that F atoms exclusively attack Si atoms which are not already participating in Si–F bonds. However, at incident energies of \( \geq 2.5 \) eV on the \( \theta_L = 0.5 \) ML and \( \theta_L = 1.0 \) ML "disordered" surfaces, and of \( \geq 3.5 \) eV on the \( \theta_L = 1.0 \) ML ordered surface, we observe that up to 50% of the Si–F bond formation events result in production of SiF\(_2\). In our previous simulations of F\(_2\) molecules impinging on Si(100) surfaces, we observed that the only SiF\(_2\) species formed during our simulations were due to both F atoms from the incoming F\(_2\) molecule attacking a bare Si dimer atom. (This mechanism was later reproduced in the simulations of Schoolcraft et al. \([19]\).) Clearly this method of SiF\(_2\) formation is not available with only F atoms impinging on the surface. Thus, at high incident energies we are seeing a new mechanism of reaction, as F atoms are finally forming additional Si–F bonds with pre-existing Si–F groups. This probably accounts for why Schoolcraft and Garrison \([9]\) chose 3.0 eV F atoms for their study, as this was the lowest energy where this critical step for etching occurs.

We further characterized this SiF\(_2\) formation according to whether the Si–Si dimer bond or one of the bonds to a subsurface Si was broken to allow for the formation of the second Si–F bond. For \( \theta_L = 0.5 \) ML, roughly equal numbers of SiF\(_2\) groups formed by breaking the dimer bond versus breaking one or both subsurface bonds. Note that in the case of breaking both subsurface bonds, the resulting SiF\(_2\) group has only two Si–F bonds and one Si–Si bond, yielding what should be a highly reactive etching intermediate on the surface. By contrast, for the \( \theta_L = 1.0 \) ML ordered surface, breaking of a single subsurface bond was almost exclusively responsible for the formation of SiF\(_2\). The difference between the \( \theta_L = 0.5 \) and 1 ML cases appears to be primarily a steric effect. For the \( \theta_L = 0.5 \) ML surface, breaking of either the dimer bond or one of the subsurface bonds is driven primarily by the bias in the interaction potential toward a tetrahedral environment around a Si atom. If the attack direction of the incoming F atom favors breaking the dimer bond, then the Si atom simply moves away from its dimer partner. Conversely, if the geometry of the incoming F atom dictates that breaking a subsurface Si–Si bond is more favorable, the Si atom can similarly
move to accommodate this. On the \( \Theta_F = 1 \) ML surface, the individual Si–F groups have limited mobility, as all of the neighboring Si–F groups compete for space. When an SiF\(_2\) group forms, the new SiF\(_2\) species is constrained by the presence of the nearby SiF groups. Breaking the dimer bond in this case would require the Si atom to move laterally toward a neighboring Si–F group, resulting in large repulsions between dimer rows. As a result, breaking of a subsurface bond is favored, as part of the motion for the Si atom can be out of the plane of the surface, thus reducing the amount of steric hindrance. Regardless of the method of creation, SiF\(_2\) groups formed on the surface tend to create defects in the dimer row structure which are stable at 300 K, meaning that any subsurface atoms exposed due to the creation of an SiF\(_2\) group will remain exposed.

4. Discussion

The quality of our prediction for F atoms interacting with the Si(100) surface mirrors that of our previous predictions for F\(_2\) molecules. In particular, our simulations had their greatest success in predicting trends in reactivity, and characteristics of ejected or scattered species. For atomic fluorine, we successfully reproduced the qualitative observations of inelastic scattering and non-cosine exit angle distributions reported by Giapis et al. [2]. For our surfaces with \( \Theta_F = 1 \) ML, we also confirmed Engstrom et al.’s [5] trend of increasing reactivity with increasing incident energy. Additionally, we predicted the presence of a precursor-mediated adsorption channel, similar to what Engstrom, et al. [5] found for F\(_2\) on fluorinated Si(100) surfaces. For F\(_2\) molecules, we also matched the trends seen by Behringer et al. [24], Jensen et al. [25], and Ceyer and co-workers [26] for increased reactivity due to increased center-of-mass translational kinetic energy in the impinging F\(_2\), as well as matching Li et al.’s [27] observation of the atom abstraction pathway which leads to ejection of hyperthermal F atoms from the surface and Jensen et al.’s [25] observation that F atom abstraction dominates at low energies.

Where our modeling has the most trouble is in the prediction of reactive events which occur at high coverages, especially those which lead to more highly fluorinated species like SiF\(_2\). The most notable of these problems is our prediction of no SiF\(_2\) formation for F atoms impinging on a fluorinated Si(100) surface below 2.5 eV of incident energy. Similarly, for incident F\(_2\) molecules, achieving SiF\(_2\) formation by addition of a second Si–F bond to a pre-existing Si–F group requires 5.5 eV of translational incident energy, based on preliminary calculations [28]. Another shortcoming of these simulations concerns the creation of disordered surfaces. While our simulations suggest that disorder is important for real etching processes, based on the low reactivities predicted for \( \Theta_F = 1 \) ML ordered surfaces, our simulations do not generate such disordered surfaces unless extreme conditions (high incident energies or high pressures) are used for the incident F atoms or F\(_2\) molecules. As described in our simulation details, even consecutive bombardment with 1.5 eV F\(_2\) molecules resulted only in a surface which would eventually saturate at \( \approx 1.1 \) ML. Experimentally, F\(_2\) molecules with \( > 0.2 \) eV of incident energy will continue to react with the surface up to coverages greater 1.5 ML [24,29,30].

Both of these difficulties within the simulations can be traced back to the initial fitting of the Si–F potential, which was not designed to handle these cases. The original calculations by Wu and Carter [11,12] explicitly modeled (a) the approach of F atoms toward a bare or monofluorinated silicon dimer, and (b) the repulsions between F atoms already participating in Si–F bonds on the surface. However, for example, the explicit approach of a gas phase F atom toward an F–Si–Si–F species was not studied. (F–Si–Si–F represents the structure present on the \( \Theta_F = 1 \) ML ordered surface.) Thus all of the information in the ab initio calculations dealing with F atoms interacting with each other consisted of the highly repulsive interactions between neighboring SiF and SiF\(_2\) groups. These interactions may not be representative of the interactions felt by gas phase F atoms approaching surface F–Si–Si–F species. These higher repulsions could account for the inability of F atoms and F\(_2\) molecules to form SiF\(_2\) species except at high energies as, even though the end products would be favorable, the barrier to formation would be
too great. Similarly, having large Si–F–F repulsions could also lead to a general lowering of reactivity, as incoming F atoms and F₂ molecules would be scattered away more strongly. Interestingly, for F atoms ejected during abstraction for F₂, the hyperthermal exit energies predicted in our simulations are somewhat higher than those measured by Ceyer and co-workers [26]. A softening of the repulsions between gas phase F atoms and surface Si–F groups would correct this trend in the right direction.

Another aspect of the ab initio calculations is that they only dealt with surface Si–F interactions. The high levels of theory used in Wu and Carter's [11,12] cluster calculations precluded models which would be large enough to include an F atom bonded to a subsurface silicon. As this was not the original goal of the calculations, it would be unrealistic to expect the resultant interaction potential to be able to handle F atoms bonded to Si atoms significantly below the surface. As a result, the potential most likely has a high preference for forming, exclusively, surface SiF and SiF₂ groups. This is in contrast to experimental observations of fluorosiloxyl layers ≈10 Å thick in silicon slabs subjected to fluorine etching environments [31]. This high preference for surface SiF and SiF₂ groups also contributes to the lack of disorder predicted in the calculations. Creation of realistic disordered surfaces with high concentrations of F atoms will require the ability to model accurately F atoms in subsurface locations.

What this suggests is that the WWC potential worked well for those cases represented by the ab initio data, and that the shortcomings of the potential can be understood in direct relation to limitations in the ab initio data set used to fit the potential. This may seem to be a trivial result, but it provides an opportunity for expansion of this method. These calculations show that the ab initio data used to fit the Si–F interaction terms were successfully incorporated into the potential. Furthermore, given the direct relation of the ab initio data to both the successes and failures, additional calculations describing, for example, the approach of gas phase F atoms toward an existing F–Si–Si–F group should lead to direct quantitative improvements in the results of dynamics simulations.

5. Summary and conclusions

We have carried out simulations of atomic fluorine impinging on clean and partially fluorinated Si(100) surfaces. On the clean Si(100) surface, atomic fluorine adsorbed with unit probability for all F atom incident energies, as was expected based on previous simulations of F₂ impinging on clean Si(100) surfaces. Introduction of pre-adsorbed fluorine on the surface reduced the adsorption probability, as non-reactive scattering became a viable reaction outcome. It also produced two intriguing reaction features that correlate with previous experimental findings. The first is the presence of precursor-mediated adsorption for low incident energy F atoms on the ΘF = 0.5 ML surface. Although the adsorption probability stays relatively close to 0.7 for most incident energies, a dip to 0.6 occurs near 0.906 eV which indicates a crossover from precursor-mediated adsorption to a direct chemisorption mechanism. This type of mechanism has been previously observed by Engstrom et al. [5] for F₂ on fluorinated Si(100) surfaces. The fact that the adsorption probability is above 0.5 for the ΘF = 0.5 ML surface is also noteworthy, as this deviates from what would be predicted by Langmuir-type kinetics and is consistent with the presence of a precursor. On the ΘF = 1.0 ML disordered surface, any influence of precursor-mediated adsorption on the reaction probability is obscured by the large number of trajectories which remain in the precursor state on the time-scale of our simulations. Translational activation is also effective for increasing the reaction probability at energies above 1 eV. This coincides with the barrier to reaction predicted for the ΘF = 1 ML ordered surface. The other major reaction feature involves the F atoms which are non-reactively scattered from the fluorinated surfaces. These F atoms are inelastically scattered and do not have cosine-like distributions, similar to the recent experimental observations of Giapis et al. [2]. However, formation of SiF₂, a precursor for etching, only occurred for F atoms with greater than 2.5 eV of incident energy, in contrast to experimental observations.

In spite of some difficulties in reproducing certain experimental results, the overall technique of
incorporating ab initio data into interatomic potentials for simulating Si–F interactions appears to have been successful. Shortcomings in reproducing the formation of highly fluorinated SiF$_x$ species or overestimating the F atom exit velocities can be directly related to limitations in the ab initio data set used to initially fit the Si–F potential. While additional ab initio calculations could be performed to improve agreement of MD simulations with experiment, the real potential of this technique lies in simulation of processes which cannot be easily observed experimentally, such as direct observation of reaction mechanisms and characterization of possible structures for the fluorosilyl layers that form during etching. This latter goal would require simulation of structures involving fluorine atoms bonded to subsurface Si atoms, which would involve costly calculations using the formalism of Wu and Carter [11,12]. However, given the direct correlation between the successes of these MD simulations with the ab initio data used to fit the WWC potential, the effort required to generate ab initio data for subsurface bonded Si–F groups appears to be warranted.

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