F$_2$ reaction dynamics with defective Si(100): defect-insensitive surface chemistry

Lawrence E. Carter, Emily A. Carter

Department of Chemistry and Biochemistry, University of California, Los Angeles, CA 90024-1569, USA

Received 26 July 1994; accepted for publication 15 September 1994

Abstract

We have investigated the influence of a variety of dimer vacancy defects on the reactivity of F$_2$ molecules with the clean Si(100)-2 × 1 reconstructed surface via molecular dynamics using an ab-initio-derived Stillinger–Weber-type many-body potential. Our simulations of a wide variety of defective surfaces indicate that vacancy defects have a negligible effect on the reactivity of F$_2$ molecules toward the Si surface. These simulations suggest that the density of accessible Si dangling bonds (i.e., the number of reactive surface sites) is the sole critical factor in determining the reactivity for this highly exothermic surface reaction. Thus, defective Si(100) exhibits essentially the same reactivity toward F$_2$ as a perfect Si(100)-2 × 1 surface.

Keywords: Adsorption kinetics; Etching; Halogens; Models of surface chemical reactions; Molecular dynamics; Silicon; Surface defects

1. Introduction

Although halogen etching of silicon persists as an important processing technique in the semiconductor industry, the underlying mechanism of this reaction still remains in question. Due to the complexity of the etching environment, studies of simplified systems may assist in bringing this surface reaction into focus. With this in mind, we previously used molecular dynamics with an ab-initio-derived potential to study the interaction of single fluorine molecules with the clean Si(100)-2 × 1 surface [1]. This initial study yielded qualitative agreement with current experimental studies as to the initial adsorption probability of F$_2$ with the clean Si(100)-2 × 1 surface. However, this work did not account for the presence of the two most common types of surface irregularities found in this system, namely steps and defects. Further simulations designed to explicitly model the effect of steps in the F$_2$/Si(100)-2 × 1 reaction indicated that single atomic height steps, the most prevalent type, have little influence on the initial adsorption probability [2]. Here we present the results from a similar effort to study the influence of dimer vacancy defects on F$_2$ reaction probabilities.

Experimental evidence for the presence of defects on the Si(100)-2 × 1 surface is derived mainly from scanning tunneling microscope (STM) images. The Si(100)-2 × 1 surface consists of rows of Si dimers. Typical published images of this surface show defect densities on the order of a few percent [3–7], with a 9% defect density reported as a highly defective surface [5]. The most prevalent type of defect observed in these images is referred to as an ‘a-type’
defect, and has usually been interpreted as a Si dimer vacancy. Most of these images also show larger defects consisting of multiple (two or three) dimer vacancies adjacent to each other within a single row. Additionally, one published image [5] exhibits defects comprised of a multiple dimer vacancy separated from a single dimer vacancy by only one dimer in a row, yielding a ‘dimer vacancy complex’ [8]. Local density functional calculations using pseudopotentials by Wang et al. [8] predicted that several of these complexes are more stable than the isolated constituent defects. Another surface defect observed in some STM images is the so-called ‘c-type’ defect [4]; c-type defects have often been interpreted as two Si atoms missing from the same side of adjacent Si dimers in the same row. As with the a-type defect, multiple c-type defects located adjacent to one another have also been observed [4].

More recent evidence, however, suggests that many of the defects observed in STM images are not due to missing atoms at all! Both Chander et al. [6] and Andersohn and Kohler [7] reported that water adsorbed on the Si(100) surface had the same appearance as a true dimer vacancy in STM images. Chander et al. quantified their findings, reporting a true defect density of ~1% for their surfaces [6]. Andersohn and Kohler stated only that the true defect densities for their surfaces were 2–3 times smaller than the apparent densities [7], essentially in agreement with the findings of Chander et al. [6].

Chander et al. also noted that all of the c-type defects observed in their images were due to adsorbed water, leaving no real c-type defects on their surfaces [6]. This suggests that the c-type defects may not have a true missing atom counterpart. Other evidence against the presence of c-type defects comes from Zhang and Metiu [9], who used the empirical many-body Stillinger–Weber potential to calculate barriers to diffusion pathways for single atom and dimer vacancies. Based on these barriers, they concluded that any single atom vacancies on the Si(100)-2×1 surface would rapidly become dimer vacancies, as the remaining undimerized atom should have high mobility on the surface.

In addition to theoretical studies of vacancy diffusion rates, such as the work of Zhang and Metiu mentioned above [9], local density functional calculations using pseudopotentials have been used to investigate the stability of dimer vacancies on the Si(100)-2×1 surface, as well as other structures which might produce the STM pattern of an a-type defect [8,10,11]. Roberts and Needs [10] calculated the relative stabilities of various Si(100) surface reconstructions, including several which involved dimer vacancies. Their calculations indicated that the perfect surface was slightly favorable energetically relative to a surface containing a dimer vacancy, but that the difference was small enough that single dimer vacancy defects could play an important role on the Si(100)-2×1 surface. Ihara et al. [11] used local density functional molecular dynamics with local pseudopotentials to investigate an alternate metastable structure for the a-type defect known as the ‘dimer interstitial model’. They reported that this new structure was close enough in energy to the dimer vacancy that the dimer interstitial should account for some number of the a-type defects on a surface. However, Wang et al. [8] improved upon Ihara et al.’s calculations by using non-local pseudopotentials with local density functional theory to show that the dimer interstitial model does not result in even a metastable structure. Their results also indicate that dimer vacancies are still the best current model for the structure of a-type defects.

In this work, we present the results of MD simulations designed to investigate the interaction of F₂ molecules with a variety of vacancy defects that have been proposed in the literature. Section 2 describes the methods used to carry out this study. The results and analyses of the simulations reside in Sections 3 and 4, respectively, while Section 5 contains our concluding remarks.

2. Simulation details

As in our previous work, we used the Stillinger–Weber (SW) potential for silicon [12] and fluorine [13] to model the homoatomic interactions within our simulations. For the heteroatomic interactions, we used a Stillinger–Weber-style potential that was reparameterized to fit ab initio data [14,15]. The base slab used in these simulations consisted of 1080 silicon atoms distributed equally in nine layers in a tetragonal unit cell of 46.08 Å × 38.40 Å × 10.86 Å. The slab was oriented such that reconstruction of the
clean, perfect surface yielded six dimer rows each containing ten dimers. The (100) face of the crystal was exposed in the direction of the shortest cell dimension. Periodic boundary conditions were enforced in the remaining two directions in order to represent an infinite surface.

Defects were introduced to the surface by removing an appropriate pair of atoms: either both atoms of a single dimer for an a-type defect, or two atoms from the same side of neighboring dimers within a dimer row for a c-type defect. Once all of the defects were introduced, the slab was equilibrated to 298 K with an induced $2 \times 1$ reconstruction where appropriate for the surface atoms as well as for lower layer atoms exposed by creation of the defects. This was accomplished by giving the silicon atoms initial velocities generated randomly from a 298 K distribution followed by equilibration using Nose's equations of motion for canonical ensemble (constant particle number, volume, and temperature (NVT)) dynamics [16]. After roughly 6 ps of propagation in the NVT ensemble, the slab was further equilibrated in the microcanonical ensemble (constant particle number, volume and energy (NVE)) via the Verlet [17] integrator for 3 ps, in order to prevent any possible simulation artifacts, due to switching ensembles, from influencing our results. In all trajectories, the bottom layer of silicon atoms was held fixed in bulk lattice sites, as in our previous work [1,2,14,15].

In all of the simulations, the initial center-of-mass position of the $\text{F}_2$ molecule parallel to the surface as well as its orientation were chosen randomly, while the height above the surface was set at 5.0 Å, beyond the range of the Si–F potential. The $\text{F}_2$ molecule was given 1.8 kcal/mol of center-of-mass translational energy with the incident center-of-mass velocity directed normal to the surface, but no initial vibrational or rotational energy. This mimics a supersonic molecular beam experiment [1].

The classical equations of motion for microcanonical (NVE) dynamics were propagated forward in time via a simple Verlet [17] integration algorithm using a time step of $3.06536 \times 10^{-16}$ s. The trajectories were propagated for 4000 time units, or 1.2261 ps, which generally provided sufficient time for collision with the surface to occur and for the system to advance forward in time far enough to classify the outcome of the trajectory.

In this work, we express the defect density as the total number of atoms missing from the surface layer. Thus, if 1 out of every 10 atoms is missing, we define the defect density to be 10% regardless of whether the missing atoms are located in one large defect or many smaller defects.

The results presented in Table 1 are based on 400 trajectories for each surface, where the silicon atoms' initial positions and velocities were the same for each $\text{F}_2$ trajectory, derived from the NVT/NVE equilibration described above. In order to generate error bars for our calculated values, each set of 400 trajectories was arbitrarily divided into eight sets of 50 trajectories. Quantities of interest were computed for each set of 50 and the results from the eight sets

<table>
<thead>
<tr>
<th>Surface type</th>
<th>Non-reactive scattering</th>
<th>F-atom abstraction</th>
<th>Dissociative chemisorption</th>
<th>Complex formation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface 1, 10% a-type vacancies</td>
<td>0.5 ± 0.9</td>
<td>77.3 ± 5.8</td>
<td>16.5 ± 6.2</td>
<td>5.7 ± 3.3</td>
</tr>
<tr>
<td>Surface 2, 10% a-type + c-type vacancies</td>
<td>1.0 ± 1.5</td>
<td>69.0 ± 7.5</td>
<td>20.8 ± 6.6</td>
<td>9.2 ± 2.8</td>
</tr>
<tr>
<td>Surface 3, 15% a-type + double dimer vacancies</td>
<td>0.5 ± 0.9</td>
<td>75.5 ± 5.0</td>
<td>15.8 ± 5.5</td>
<td>8.2 ± 3.5</td>
</tr>
<tr>
<td>Surface 4, 15% dimer vacancy complexes</td>
<td>1.0 ± 1.1</td>
<td>68.8 ± 11.9</td>
<td>23.7 ± 9.8</td>
<td>6.5 ± 3.3</td>
</tr>
<tr>
<td>Surface 5, 24% 'pit' defects</td>
<td>0.2 ± 0.7</td>
<td>69.0 ± 7.6</td>
<td>22.8 ± 7.7</td>
<td>8.0 ± 4.4</td>
</tr>
<tr>
<td>Surface 6, Perfect surface (from Ref. [2])</td>
<td>0.5 ± 1.0</td>
<td>74.5 ± 6.0</td>
<td>15.5 ± 3.4</td>
<td>9.5 ± 3.8</td>
</tr>
</tbody>
</table>
were used to find an overall value with a standard deviation.

3. Results

Studying the interaction of a single molecule with a crystalline surface allows us to easily categorize the possible results of each trajectory. For a single F$_2$ molecule interacting with the clean Si(100)-2 $\times$ 1 surface, two possible outcomes dominate the reaction. One is F-atom abstraction, where one Si–F bond is formed at the expense of the F–F bond [1]. The remaining unbound F atom is ejected away from the surface. This pathway, while rare in most diatomic molecule chemisorption processes, is highly probable here due to the high exothermicity of the reaction. The F–F bond is extremely weak ($D$(F–F) = 37 kcal/mol) [18] while the Si–F bond is extremely strong ($D$(Si–F) = 150 kcal/mol) [19,20]. The other dominant pathway in this reaction is (the expected) dissociative chemisorption, where both F atoms in the F$_2$ molecule form Si–F bonds, once again at the expense of the F–F bond. A third

---

**Fig. 1.** Surface 1. The lightest colored spheres represent the top layer of atoms on the surface. The next lightest colored spheres are second layer atoms, while the remaining layers all have the darkest color. Atoms denoted with an ‘a’ are second layer atoms exposed to the surface due to the removal of atoms from the top layer. The same gray-scale and labelling schemes are used in Figs. 1–4. All of the defects on this surface are a-type (single dimer vacancies). The total defect density is 10%.
outcome which is also possible when a diatomic molecule interacts with a surface is non-reactive scattering, where no Si–F bonds form and the intact F₂ molecule bounces away from the surface. However, due to the highly exothermic nature of Si–F bond formation, and the plethora of reactive sites (the Si dangling bonds) present on the clean surface, this latter reaction is rare (typically < 1%). One other low probability event we observe in our simulations is formation of an Si–F–F complex, where one Si–F bond is formed but the F–F bond is not completely broken. Rather, the two fluorines also remain together in a metastable state that is long-lived relative to the length of the trajectory (~1.2 ps).

Obviously, this complex will break apart on the picosecond time scale, resulting eventually in either an abstraction or dissociative chemisorption event.

Table 1 contains the results of our simulations for various types of defective surfaces as well as for a clean, perfect Si(100) surface. Our first four surfaces attempt to recreate the effect of monolayer vacancy defects. Figs. 1–4 depict these four surfaces, with subsurface atoms exposed due to the vacancies marked with the letter ‘a’. Surface 1 has a 10% defect density of only a-type defects. Surface 2 also has a 10% defect density, but on this surface half of the defects are a-type and half are c-type. Surface 3 once again uses only a-type defects, but this time

---

Fig. 2. Surface 2. Half of the defects on this surface are a-type (single dimer vacancies), while the remaining defects are the proposed structure for the c-type defect. The total defect density is 10%.
half of the defects are single dimer vacancy a-type, while the other half of the defects are double dimer vacancies. Thus, while surface 3 has the same total number of defect regions as surfaces 1 and 2, the number of atoms removed from the surface has increased to 15%. The relative locations of these defects on these surfaces were chosen to maximize the distances between the defects, and each dimer row contains only one defect feature. Surface 4 has the same number and type of vacancies as surface 3, but the vacancies have been rearranged to yield 'dimer vacancy complexes' of a single vacancy and a double vacancy separated in a row by only one dimer. This was the most commonly observed dimer vacancy complex in the STM image from Alerhand et al. [5] It is worth mentioning that all of these surfaces have defect densities that are considerably larger than the ~ 1% value suggested by Chander et al. [6]. We have chosen these artificially high defect densities in order to accentuate any changes in reactivity which might occur.

Due to the dominance of dissociative chemisorption and F atom abstraction in our simulations, any changes in reactivity will have the form of an increase/decrease in dissociative chemisorption with a concomitant decrease/increase in the F-atom abstraction channel. Thus an examination of the dissociative chemisorption percentages for surfaces 1–4

Fig. 3. Surface 3. This surface contains three a-type defects and three double dimer vacancies (two a-type defects adjacent within a row). The total defect density is 15%.
and the perfect surface (surface 6) in Table 1 should provide information about the relative reactivities. The most obvious trend in the dissociative chemisorption numbers in Table 1 is that they are the same to within the statistical accuracy of the calculation, indicating that defects have little influence on the reactivity of $F_2$ molecules toward the clean Si(100)-2 $\times$ 1 surface. We will discuss this in greater detail shortly. The only apparent deviations in the data come from the surfaces containing the dimer vacancy complexes and the c-type defects, which both show slight increases in reactivity. Aside from the fact that these increases still lie within the statistical accuracy of our calculations, given the unusually high defect densities present on our surfaces, such a minimal increase in reactivity would probably go undetected for a more realistic, less defective surface.

Because surface defects seem to have little, if any, effect on the reactivity of $F_2$ with the Si(100)-2 $\times$ 1 surface, we decided to investigate the influence of larger scale 'pit' defects, possibly representing defects present on a surface damaged by energetic ion bombardment (see Fig. 5). In order to represent larger, deeper defects on the surface, we first created a larger size slab containing 144 atoms per layer, as

---

Fig. 4. Surface 4. All of the missing dimers on this surface are concentrated into three dimer vacancy complexes of the type reported to be most common in Ref. [8]. These consist of a double dimer vacancy separated from a single dimer vacancy within the same row by only one dimer. The total defect density is 15%.
Fig. 5. Surface 5. The lightest colored spheres represent the top layer of atoms on the surface. Unmarked spheres of the next lightest color represent second layer atoms not exposed to the surface. Atoms marked with ‘a’ represent second layer atoms exposed to the surface due to the removal of first layer atoms. Atoms marked with ‘b’ or ‘c’ represent third and fourth layer atoms, respectively, which have been exposed to the surface due to removal of upper layer atoms. All remaining atoms have the darkest shading. See text for description of the types of defects on this surface. The total defect density is 24%.

compared to 120 atoms per layer for the other surfaces. A large pit was then placed in the surface by removing atoms from successive layers of the slab. Creation of the pit initially involved removing six contiguous dimers (three dimers each from two adjacent rows, 12 atoms in all) from the surface, followed by removing eight and six atoms from the second and third layers, respectively. The second and third layer atoms removed were chosen so that no undercutting of an upper layer occurred. In addition to the large pit, two other multiple layer defects were created; one involving the removal of eight atoms from the surface layer (two dimers from two adjacent rows) and four atoms from the second layer, and one where three dimers within one row were removed along with four second layer atoms below them. Finally, one double dimer vacancy and two single dimer vacancies were created to bring the total surface defect density to about 24%. Note that at this defect density, it is no longer possible to place each
defect feature in its own row. As a result, although we once again placed the defects in such a way as to maximize the distances between them, the two single dimer vacancies were placed in rows which already contained other defect features. As Table 1 shows, however, even this surface failed to show any statistically significant change in reactivity.

As a final check to confirm the lack of influence of vacancy defects on Si(100) surface reactivity toward F$_2$ molecules, we performed simulations where an individual defect site was specifically targeted. Rather than allowing the initial position of the incident F$_2$ molecule to be anywhere above the surface, this initial position was constrained to be within a small rectangular box directly above the location of the defect. The edges of the target area were aligned with the equilibrium positions of the nearest first layer atoms to the defect both along the dimer row and perpendicular to it. This created a target area which tested not only the reactivity of the exposed second layer atoms, but the reactivity of the nearest neighbor first layer atoms as well. We propagated 120 trajectories for each of six different defects using this directed beam technique: (a) an a-type defect; (b) a c-type defect; (c) a double dimer vacancy; (d) a triple dimer vacancy; (e) a dimer vacancy complex of the type found on surface 4; and (f) two a-type defects positioned next to each other in adjacent rows. Once again, none of the targeted defects yielded a statistically significant difference in reactivity from the perfect Si(100)-2 × 1 surface.

4. Discussion

The lack of influence of vacancy defects on the reactivity of the Si(100)-2 × 1 reconstructed surface toward F$_2$ molecules follows a trend found in our other recent studies of the F$_2$/Si(100) reaction. Previous MD simulations of the interaction of F$_2$ with both clean, perfectly flat, defect-free Si surfaces [1] as well as clean, defect-free, stepped Si surfaces [2] suggested that the dominant factor determining the extent of reaction is simply the density of accessible dangling bonds on the surface. These simulations predicted that the reaction of F$_2$ with the Si(100)-2 × 1 surface proceeds in a stepwise manner, with one Si–F bond forming first, followed quickly by the breaking of the F–F bond. The remaining F atom will either escape from the surface or form a second Si–F bond if it finds another dangling bond site nearby. The simulations also indicated that essentially all F atoms that come into contact with a Si dangling bond react to form Si–F. Thus, an increase in dangling bond density on the surface will increase the likelihood of a second Si–F bond forming and increase the reactivity, while a decrease will lead to the opposite effect. As we will detail below, the presence of defects does not significantly alter the dangling bond density, so we would expect a minimal influence on the reactivity. This is in agreement with the results found in Table 1, where all of the surfaces show the same reactivity to within the limits of statistical significance.
For the case of a single a-type defect, removing a dimer from the surface reduces the density of dangling bonds available for reaction. Although the removal of a surface dimer initially exposes four atoms from the second layer, each having an unsatisfied bonding site, these second layer atoms can reconstruct to form dimers in the second layer. Local density functional theory calculations of defect stability [8,10] also have predicted such a reconstruction to be favorable. This satisfies the dangling bonds created upon the removal of the surface dimer, leading to a net loss of two dangling bonds from the surface (the two present on the original surface dimer). Thus, it is not surprising that the presence of 10% a-type defects, which leads to a 10% reduction in dangling bond density on the surface (one per missing atom), does not yield any increase in the reactivity of individual \( \text{F}_2 \) molecules with the surface (see surface 1 versus surface 6 in Table 1). Indeed, we might expect to see, if we sampled enough trajectories, a 10% decrease in the reactivity of this surface. We discuss later why such a decrease was not observed here.

Analysis of the structure of a double dimer vacancy yields a slightly different result (see Fig. 6). Four dangling bonds are lost from the surface layer, but this is offset by the fact that not all of the exposed second layer atoms may reconstruct, leading to a gain of four dangling bonds in the second layer. As a result, the double dimer vacancy causes no net loss in dangling bond density. Therefore, we would expect the reactivity of our surfaces with both single and double dimer vacancies to show once again the same or slightly less reactivity than that for the perfect surface, due to the previously discussed influence of the single dimer vacancies. Examination of the data in Table 1 for surface 3 versus surface 6 supports this analysis. Larger defects involving only dimers missing from the first layer will show the same patterns as the single and double dimer vacancies in terms of either having two fewer dangling bonds or the same number of dangling bonds as the perfect surface.

This type of general analysis does not apply to defects with atoms missing from below the first layer, such as our ‘pit’ defects. For multi-layer defect structures, the number of dangling bonds within the defect depends strongly on the number and location of the missing atoms in each layer. All of the multi-layer defects found on surface 5 have a net increase in the number of dangling bonds. For example, for the large defect in the center of Fig. 5, 12 dangling bonds were lost by the removal of the 12 surface atoms while removal of atoms from lower layers caused no additional loss, since they had no dangling bonds to begin with. In return, eight dangling bonds were created in the second layer (atoms labeled ‘a’), four were created in the third layer (‘b’ atoms), and six were created in the fourth layer (‘c’ atoms), for a net gain of six dangling bonds. In a similar manner, the defect in the upper right corner of Fig. 5 gained four dangling bonds while the defect in the lower left corner gained two. Even after accounting for the four dangling bonds lost due to

![Diagram](https://via.placeholder.com/150)

**Fig. 7.** Schematic of the reconstruction of a c-type defect. As before, the ‘Si’ s depict second layer atoms exposed to the surface due to the removal of first layer atoms, whose former locations are indicated by the X’s. The ‘Si’ s represent the undimerized surface layer atoms left behind after the creation of the defect. The lobes indicate either dangling bonds (one dot) or 3s lone pairs on the remaining surface silicon atoms (two dots). Only two dangling bonds are generated in the second layer, while four are lost from the first layer.
the presence of the two single dimer vacancies, this surface shows an increase of eight dangling bonds per 144 surface atoms relative to a perfectly flat, defect-free surface. Because of this, we would expect the reactivity of surface 5 to be slightly higher than the reactivity of the perfect surface, consistent with the results in Table 1.

Surface 3, containing c-type defects, also shows a slight increase in reactivity, in spite of an apparent decrease in the number of dangling bonds for this surface. For each c-type defect, the effective dangling bond density is reduced by four in the first layer due to recoupling of dangling bonds to form two closed shell Si 3s electron pairs on each of the remaining two surface Si atoms (see Fig. 7). Only two additional dangling bonds are gained in the second layer after reconstruction to form a second layer dimer occurs, leading to a net loss of two dangling bonds per defect site, similar to the result for a-type defects. Normally we would expect such a defect to lead to a decrease in reactivity. However, the two 3s lone pairs on the surface Si atoms neighboring the c-type defect should be reactive toward F₂, albeit slightly less reactive than a normal dangling bond. The extreme exothermicity of the reaction will still allow chemisorption at these isolated Si atom sites. The presence of this new, distinct type of reactive specie on the surface may account for the slight increase in reactivity for surface 2 in Table 1.

A similar explanation for increased reactivity for surface 4 is more elusive. Based solely on the dangling bond argument, we would expect this surface to show identical reactivity to surface 3. At this time, we are still unable to account for the apparent slight increase in reactivity shown in Table 1, although it is interesting to note that the results for this surface have the largest error bars of any of the surfaces studied.

One remaining question is why the introduction of dimer vacancies did not lead to a measurable decrease in reactivity in our simulations. Although a single dimer vacancy creates a region with low dangling bond density, the size of this region is only slightly larger than the F₂ molecule. Unless an incident F₂ molecule struck the surface almost exactly at the center of this region of depleted dangling bond density, nearly every F₂ which approached the surface formed at least one Si–F bond. Thus, any loss of reactivity would have to be due to an increase in F atom abstraction at the expense of dissociative chemisorption. Since the dissociative chemisorption percentage is already quite small (<25%) at these F₂ incident energies, it may be that the difference in reactivity is not large enough statistically to make itself evident at an incident energy of 1.8 kcal/mol. Possibly this difference would be accentuated at higher F₂ incident energies, where the dissociative chemisorption and F atom abstraction channels have comparable probabilities for the clean, perfect surface [1].

5. Concluding remarks

The presence of dimer vacancies on the clean Si(100)-2×1 surface, the most commonly proposed defect, exerts a negligible effect on the reactivity of the surface toward F₂ molecules. As was the case for single atomic height steps, the dominant factor in determining reactivity appears to be the dangling bond density. Although dimer vacancies cause a modest reduction in dangling bond density on the surface, nearly every incident F₂ molecule still forms at least one Si–F bond. Note that this insensitivity to defects depends heavily on the highly exothermic nature of this reaction. The fact that the reaction of F₂ with Si surface dangling bonds has no barrier and is highly exothermic means the reactivity will be directly proportional to the number of reactive sites on the surface (i.e. dangling bonds) with little or no sensitivity to any other aspects of the surface structure. We fully expect reactions involving either an activation barrier or a net endothermic process to show much greater sensitivity to surface defects. The special, highly exothermic nature of the etching reaction is responsible for the insensitivity of the reaction to steps and defects, as long as the dangling bond density remains nearly constant. Work in progress has shown that when the dangling bond density is depleted, e.g., by adsorption of F atoms, the reactivity of the surface towards F₂ drops precipitously. Indeed, this was found to be true also for the reaction of F atoms with a partially fluorinated silicon surface [15]. Therefore, while initial F₂ adsorption probabilities (S₀) are unaffected by steps and defects, the F₂ adsorption probabilities are found to depend greatly
on the coverage of fluorine, because it drastically alters the population of dangling bond sites on the surface. These latter findings will be published elsewhere [21].

Acknowledgements

This work was funded by the Air Force Office of Scientific Research. E.A.C. is also grateful to the National Science Foundation, the Camille and Henry Dreyfus Foundation, and the Alfred P. Sloan Foundation for partial support via their Presidential Young Investigator, Teacher-Scholar, and Research Fellow Awards, respectively.

References