

Influence of single atomic height steps on F₂ reactions with Si(100)-2×1

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We have investigated the effect of single atomic height steps on the reactivity of F₂ molecules with a clean Si(100)-2×1 reconstructed surface via molecular dynamics simulations using an *ab initio* derived Stillinger–Weber-type potential. Of the three types of single atomic height steps thought to commonly exist on Si(100) surfaces, the presence of the lower energy S_A and S_B rebonded steps had a negligible effect on reactivity compared to the perfect (100) surface while the higher energy S_{B'} nonbonded step slightly increased the adsorption probability. These results suggest that current discrepancies between experimental observations and theoretical predictions of the partitioning between reaction channels for F₂ reacting with the Si(100) surface are not due to the presence of steps on the silicon surface in the laboratory.

I. INTRODUCTION

As the demand for faster and higher quality devices continues to grow in the semiconductory industry, the ability to improve upon existing silicon fabrication techniques becomes increasingly important. Continued advancement of workhorse technologies, such as plasma etching of silicon with halogens, ultimately will require an understanding of the atomic level processes involved in these reactions. Although plasma-based halogen etching is widely used in the manufacture of integrated circuits, the basic mechanisms involved in this process still are not well characterized.¹

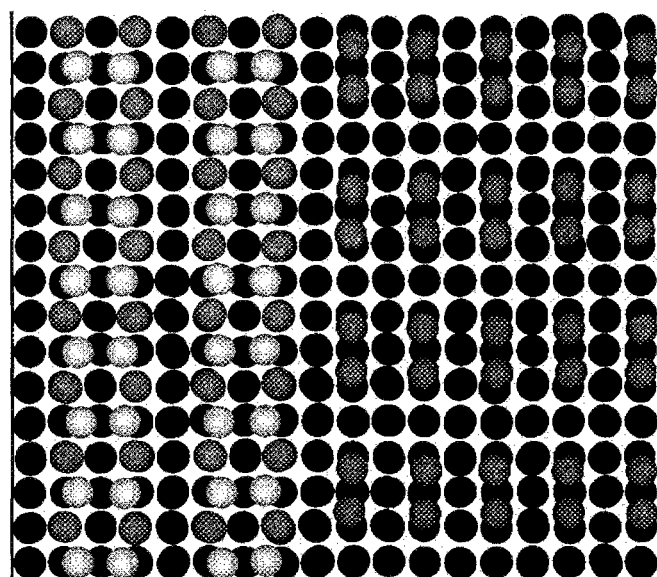
One method for building an understanding of the etching process is first to study the interaction of single atoms and molecules with the silicon surface. With this in mind, we recently examined the interaction of F₂ molecules with a clean reconstructed Si(100)-2×1 surface via molecular dynamics (MD).² We used the Stillinger–Weber potential for silicon³ and fluorine⁴ with a reparameterization of the Si–F cross terms to fit *ab initio* electronic structure data from embedded cluster models of the Si(100) surface.^{5,6} The simulations were designed to determine the effects of increasing translational and vibrational energy on the adsorption probability of F₂ on the clean surface and on the partitioning between reaction channels. Our simulations were in agreement with available experimental data⁷ for qualitative features and trends such as: (a) the negligible number of nonreactive scattering events, (b) the adsorption probability increasing with incident F₂ center-of-mass translational energy, (c) the two major reaction channels being F atom abstraction, where one F atom forms a Si–F bond while the other F atom is ejected from the surface, and dissociative chemisorption, where both F atoms form Si–F bonds to the surface, and (d) the F atoms ejected during abstraction events having hyperthermal escape velocities. However, quantitative agreement of theory with experiment was less satisfactory. We found initial adsorption probabilities for F₂ molecules on the clean silicon surface ranging from 0.58 for our lowest incident energy of 1.8 kcal/mol of F₂ center-of-mass translational kinetic energy to 0.78 for our highest F₂ translational energy of 20.9 kcal/mol. By contrast, for incident

energies in this range, Ceyer and co-workers⁷ used time-of-flight mass spectrometry to ascertain that S₀ was at least 0.83, while Engstrom *et al.*⁸ reported a value for S₀ of 0.46, derived from x-ray photoemission spectroscopy. While it is encouraging that the experimental values bracket our predictions, one major discrepancy between our predictions and the observations of Ceyer and co-workers remains. Namely, we predict the dominant reaction channel to be F atom abstraction from F₂ by the surface (a reverse Eley–Rideal process), while Ceyer and co-workers conclude that dissociative chemisorption dominates over F atom abstraction.

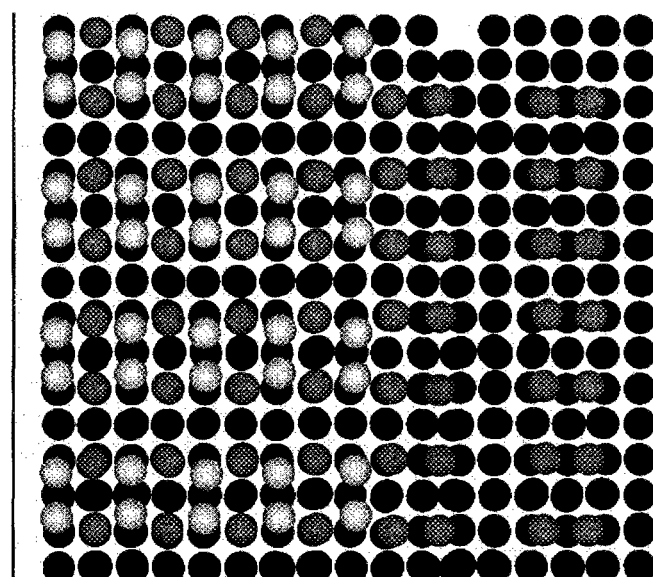
One of the most notable differences between the conditions in our models and a typical experimental environment was the lack of irregularities on our surface, such as steps, since we modeled a perfectly flat Si(100)-2×1 surface. Current scanning tunneling microscopy (STM) images⁹ of both flat (negligible miscut angle) and vicinal Si(100) surfaces clearly show the presence of both single and double atomic layer steps, with single layer steps being more prevalent for surfaces with low miscut angles.¹⁰ As our initial simulations neglected the presence of steps on the silicon surface, we hypothesized that this might play a part in accounting for the differences between our theoretical predictions of the reactivity of F₂ with the Si(100) surface and the time-of-flight mass spectrometric data. This article presents the results of new MD simulations performed to determine the effect of steps on the reactivity of F₂ molecules with the Si(100) surface.

Chadi¹¹ provided an important framework for the study of steps on Si(100) surfaces via semiempirical tight binding-based total energy calculations of various Si(100) step structures. Chadi used these calculations to predict the relative stability of the most probable single and double atomic layer step configurations. Double atomic layer steps were found to be significantly higher in energy for surfaces with low miscut angles, therefore we have chosen to focus on the reactivity of single layer steps. Figure 1 shows the three common types of single layer steps predicted to occur on the Si(100) surface. Chadi's calculations indicated that the S_A step [Fig. 1(a)] should be slightly lower in energy than the S_B "rebonded" step [Fig. 1(b)], with both only slightly less stable than a perfectly flat surface. The S_{B'} "nonbonded" step [Figure

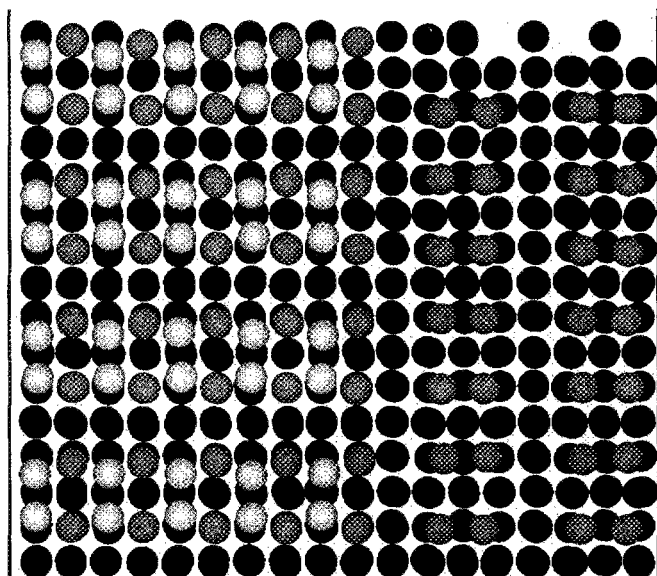
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(a)



(b)



(c)

FIG. 1. The white circles represent surface atoms in the upper terrace while the grey circles are atoms on the level of the lower terrace. Black circles depict atoms in lower layers. (a) Example of an S_A type step. The step edge is oriented parallel to the dimer rows on the upper terrace while it is perpendicular to the dimer rows on the lower terrace. Note that no surface dimer atoms in the lower terrace participate in bonds with atoms in the upper terrace. (b) Example of an S_B type step. The step edge is oriented perpendicular to the dimer rows on the upper terrace while it is parallel to the dimer rows on the lower terrace. This step is comparable energetically to the S_A step. Note that for the row of dimers closest to the step edge on the lower terrace, only one atom in each dimer has a dimer dangling bond. The other atom in the dimer has two bonds to atoms in the layer below, the dimer bond, and a bond to an atom participating in a surface dimer on the upper terrace. (c) Example of an $S_{B'}$ type step. The step edge is oriented perpendicular to the dimer rows on the upper terrace while it is parallel to the dimer rows on the lower terrace. This step is higher in energy than either the S_A or S_B steps. Note that the lower terrace atoms in the single row closest to the step edge have only three bonds, consisting of two bonds to atoms in the layer below and one bond to a surface dimer atom in the upper terrace.

1(c)] was predicted to be the least favorable conformation, but still close enough in energy to be an important structure. Note in Fig. 1(b) that the S_B step has fewer dangling bonds than either the S_A or $S_{B'}$ steps since the Si dimer atoms closest to the lower step edge have no dangling bonds. However, strain due to formation of Si-Si bonds at the step between upper terrace dimers and lower terrace dimers probably cancels any reduction in surface energy due to the decrease in dangling bonds. This helps to explain why the S_A and S_B steps are so close in energy.

In an effort to expand upon the restricted size of quantum mechanical calculations, many studies have been performed using empirical potentials, especially the Stillinger-Weber (SW) potential for silicon. Poon *et al.*¹² used Chadi's results to confirm the suitability of the Stillinger-Weber silicon potential for studying steps on the Si(100) surface, and then expanded upon Chadi's work via atomistic simulations. Using the conjugate gradient energy minimization method, they found that for flat surfaces both S_A and S_B steps could be

energetically favorable relative to a smooth surface given sufficient separation between ledges on the surface. The S_A steps become energetically favorable first at roughly 16 Å, but by about 20 Å, the S_B "rebonded" step is not only favorable relative to a smooth surface but drops below the S_A step in energy as well. Of the remaining studies of Si(100) steps using the SW potential, the molecular dynamics simulations of Roland and Gilmer¹³ are relevant to our discussion as they dealt with the reactivity of the silicon atoms in a step toward Si adatoms. They found that atoms in the S_A and S_B rebonded steps did not show any increase in reactivity, while atoms in the $S_{B'}$ nonbonded step were more reactive than those in a perfectly flat surface.

II. SIMULATION DETAILS

As before,² we used the Stillinger-Weber (SW) potential to model both the pure silicon³ and pure fluorine⁴ interac-

tions, while for the Si-F interactions we used a reparameterization fit to *ab initio* data.^{5,6} Poon *et al.*'s¹² studies of step stability were critical for providing confidence in the SW Si-Si potential for describing steps on Si(100). As for the Si-F potential, due to the directional bonding found in silicon, the electronic structure of atoms near the steps should not significantly differ from the electronic structure of atoms in the terrace regions. Because the Si-F potential was fit to a wide variety of geometries involving fluorine atoms interacting with silicon surface dimers and isolated surface atoms, the potential should be able to model the Si-F interactions correctly near a step. The Si(100) surface was modeled using a slab of nine layers of Si atoms each having 144 atoms per layer. This slab was placed in a tetragonal unit cell having dimensions $69.12 \text{ \AA} \times 30.72 \text{ \AA} \times 10.86 \text{ \AA}$. The cell was oriented so that the (100) face of the crystal was exposed in the direction of the shortest cell dimension. In the other two directions, periodic boundary conditions were enforced. Either 64 or 72 atoms were then removed from the top layer, in order to create a symmetric, one atom deep trench in the middle of the cell having either two S_A , S_B , or $S_{B'}$ steps at the trench edges. Since periodic boundary conditions connected the upper terraces on each side of the lower terrace, this created a slab of alternating upper and lower terraces each having approximately the same surface area. The distance between any two steps was roughly 30 \AA , which, according to the calculations of Poon *et al.*,¹² is far enough apart that both the S_A and S_B rebonded steps are energetically favorable relative to a smooth surface. Only 64 atoms were removed from the S_A slab while 72 were removed from the S_B slab so that the S_A and S_B rebonded steps would have the same number of dimer dangling bonds on the lower height terrace and so that all of the terraces would have roughly the same amount of surface area exposed in the lower trench. For the $S_{B'}$ slab the same number of atoms were removed as for the S_B slab, causing the $S_{B'}$ slab to have the equivalent of an additional full row of dimer dangling bond sites on its lower height terrace [see Fig. (1c)]. Once the atoms were removed, the surface was equilibrated to achieve the proper (2×1) reconstruction of the surface atoms and to yield velocities for the atoms appropriate for a surface at 250 K, in order to compare directly with the substrate temperature in Ceyer and co-workers' experiments. The exception to this is the bottom layer of atoms, which were held fixed in their equilibrium bulk lattice sites both during equilibration and during the simulations, in order to represent the bulk crystal.

In all of the simulations, the center of mass of the F_2 molecule was initially placed 5.0 \AA above the highest terrace of the surface, out of the range of the Si-F potential. The initial center-of-mass position of the F_2 molecule parallel to the surface was chosen randomly. The orientation of the F_2 bond axis relative to the surface was chosen from a spherically symmetric distribution in order to model a real distribution of orientations. The F_2 molecule was always given initially 1.8 kcal/mol of center-of-mass translational energy, but the direction of the initial velocity of the F_2 molecule was chosen from one of three initial conditions. A third of the simulations were carried out with the F_2 molecule incident

normal to the surface, as in the experiments of Ceyer and co-workers. In order to check for corrugation effects, the remaining simulations were carried out with the F_2 incident velocity directed 75° from the surface normal (as in Engstrom *et al.*'s experiments) and directed either parallel to the step edge or perpendicular to the step edge. In all cases, the diatomic was given zero initial vibrational and rotational energy.

The classical equations of motion were propagated forward in time via a simple Verlet¹⁴ integration algorithm using a time step of $3.06536 \times 10^{-16} \text{ s}$. For trajectories where the incident F_2 center-of-mass velocity was oriented perpendicular to the surface, the system was propagated for 4000 time units, or 1.2261 ps. This generally provided sufficient time for the collision with the surface to occur and for the system to propagate forward in time far enough to classify the outcome of the trajectory. For the few exceptions where the outcome was not fully determined, the trajectory was propagated for another 4000 time steps. By contrast, the trajectories with a grazing angle of incidence required longer simulations times just to allow the F_2 molecule to reach the surface. Under the latter initial conditions, all of the trajectories were propagated for 8000 time steps. Once again, any trajectories whose outcomes were still not determined by this point were propagated for an additional 4000 time steps.

We calculated 200 trajectories for each type of surface with each type of initial direction for the F_2 incident velocity, i.e., 600 trajectories for each of the three types of stepped surfaces. In order to generate error bars for our calculated values, each set of 200 trajectories was arbitrarily divided into four sets of 50 trajectories. Quantities of interest were computed for each set of 50 and the results from the four sets were used to find an overall value with a standard deviation.

III. RESULTS

Table I shows the partitioning between reaction channels for F_2 molecules with 1.8 kcal/mol of center-of-mass translational energy reactively scattering from Si(100) surfaces having each of the three types of single atomic height steps (see Fig. 1) and for a perfectly flat surface, as was used in our previous work.² We have already mentioned two of the possible reaction channels for the scattering of F_2 molecules from a clean Si(100) surface. In *F-atom abstraction*, one of the F atoms forms a Si-F bond with a dimer dangling bond on the surface. The F-F bond is then broken and the other F atom is ejected away from the surface. In *dissociative chemisorption*, the F-F bond is also broken, but both F atoms form Si-F bonds to the surface. A third possible outcome is *non-reactive scattering*, where the F-F bond remains intact and the molecule bounces off of the surface without forming a Si-F bond. As in our previous simulations,² we find this outcome to be extremely unlikely, as it occurred only 5 times in the 2400 trajectories performed for this study. The other possible outcome is *complex formation*, where one Si-F bond is formed but the F-F bond does not completely break. Instead, the second fluorine remains loosely bound to the first fluorine. We believe that these complexes are metastable states, but the lifetime of this state on a clean Si(100) surface is simply long relative to the length of our simulations (1.2

TABLE I. Percentage per F₂ reaction channel vs Si(100) surface type.

Step type and incident angle	Nonreactive scattering	F-atom abstraction	Dissociative chemisorption	Complex formation
<i>S_A</i> Normal ($\theta=0^\circ$) incidence	0	76.0±6.7	16.0±1.6	8.0±5.4
Perpendicular to step edge, $\theta=75^\circ$	0	71.0±3.5	21.5±7.7	7.5±4.3
Parallel to step edge, $\theta=75^\circ$	0	72.0±4.0	19.0±3.5	9.0±5.8
<i>S_B</i> Normal ($\theta=0^\circ$) incidence	1.0±2.0	70.5±5.5	17.5±1.9	11.0±4.8
Perpendicular to step edge, $\theta=75^\circ$	0	77.0±4.2	15.0±1.2	8.0±3.7
Parallel to step edge, $\theta=75^\circ$	0	76.5±5.3	17.5±7.7	6.0±4.9
<i>S_B'</i> Normal ($\theta=0^\circ$) incidence	0	69.0±5.0	22.5±3.0	8.5±4.1
Perpendicular to step edge, $\theta=75^\circ$	1.0±1.2	71.5±3.8	22.5±5.3	5.0±2.6
Parallel to step edge, $\theta=75^\circ$	0	69.0±4.8	27.0±3.5	4.0±1.6
Flat Normal ($\theta=0^\circ$) incidence	0.5±1.0	74.5±6.0	15.5±3.4	9.5±3.8
Perpendicular to dimer rows, $\theta=75^\circ$	0	76.5±3.0	17.5±2.5	6.0±2.3
Parallel to dimer rows, $\theta=75^\circ$	0	79.5±3.4	14.5±6.6	6.0±3.7

or 2.4 ps). Note that primarily we see prompt formation of Si–F bonds, as should be expected from the high exothermicity of both reaction channels.²

Due to the dominance of the F atom abstraction and dissociative chemisorption reaction pathways, increased adsorption probability of F₂ on the silicon surface can only come about by increasing the number of dissociative chemisorption trajectories at the expense of F atom abstraction trajectories. A comparison of the number of dissociative chemisorption trajectories quickly shows that for the *S_A* and *S_B* rebonded steps compared to the perfectly flat surface, the presence of the step has little influence on the overall reactivity of the surface. Only the higher energy *S_B'* nonbonded step structure consistently shows higher amounts of dissociative chemisorption, although the difference still lies on the edge of statistical significance. These results match well with the findings of Roland and Gilmer,¹³ who also reported that only the *S_B'* nonbonded step caused a change in the reactivity of the surface toward Si adatoms.

The fact that steps do not affect the adsorption probability also agrees well with the conclusions of our previous work,² where we concluded that during F₂ reactive scattering from the Si(100) 2×1 clean surface, any F atom which was given

an opportunity to reach a dimer dangling bond on the silicon surface would result in the formation of a Si–F bond. (This is confirmed by the lack of nonreactive scattering events.) A combination of factors, however, including local regions of low reactivity on the surface directly above the centers of each dimer and high ejection velocities imparted to one F atom when the other F atom forms a Si–F bond, lead to a large number of atom abstraction trajectories. To achieve a significant increase in the adsorption probability would require an increase in the number of dissociative chemisorption trajectories at the expense of atom abstraction events. However, our results indicate that the nature of the reaction itself causes the high number of atom abstraction trajectories, not a lack of favorable bonding sites on the surface. The new results presented here demonstrate that the local nature of the reaction is more important than the overall surface geometry in determining the reaction channel partitioning for this case.

While these simulations indicate that the adsorption probability is not influenced by single atomic height steps, they do not discount the possible importance of these features in the etching reaction. Especially for the *S_B'* nonbonded step, the increase in the number of dissociative chemisorption events makes a stepped surface an interesting target for a study of spontaneous etching via F atoms or F₂ molecules.¹⁵

IV. CONCLUSIONS

The presence of a moderate density of single atomic height steps on the clean Si(100)-2×1 reconstructed surface gives rise to only small changes in the adsorption probability of F₂ molecules compared with a perfectly flat surface. The partitioning between reaction channels remains constant for the lower energy single atomic height steps, independent of the type of step or the angle of incidence of the F₂ molecule relative to the step, while the dissociative chemisorption channel is slightly enhanced for the higher energy *S_B'* nonbonded single atomic height step structure. This suggests that the differences between current experimental and theoretical values for the adsorption probability and the importance of F-atom abstraction are not due to the influence of steps. These results, however, do not yet discount the possible importance of these features in the etching process.

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