Chemical reaction dynamics of F atom reaction with the dimer reconstructed Si{100}(2×1) surface

T. A. Schoolcraft and B. J. Garrison[a)]
Department of Chemistry, 152 Davey Laboratory, The Pennsylvania State University, University Park, Pennsylvania 16802

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We have calculated the initial sticking probability S_0 for near thermal atomic fluorine on the clean dimer reconstructed Si{100}(2×1) surface to be near unity using molecular dynamics simulations. The dependence of the sticking probability on coverage decreases to approximately zero for the fully fluorinated surface. The sticking probability of an F atom on a fully fluorinated silicon surface increases when the kinetic energy of the fluorine atom is above 0.50 eV.

I. INTRODUCTION

Fluorine atoms are the dominant species in plasmas that are used to etch silicon in the fabrication of microelectronic devices. Fluorine reacts with the silicon to produce primarily volatile silicon tetrafluoride, SiF_4, thus transferring one silicon atom from the crystal to the gas phase. However, due to the difficulties involved in making atomic fluorine beams, only a few experiments have explored how fluorine atoms actually react with silicon.[1,2] Engstrom, Nelson, and Engel have recently performed adsorption experiments using atomic fluorine with the dimer reconstructed Si{100}(2×1) surface and report that the initial sticking probability is 0.5 ± 0.3.[1] In this paper, we investigate the use of molecular dynamics computer simulations to elucidate the mechanisms of the F/Si interaction. We also report the dependence of the sticking probability on coverage and on the kinetic energy of the incoming fluorine atom with a Si{100}(2×1) surface covered with one monolayer of fluorine. These results are compared to the experimental data of Engstrom, Nelson, and Engel.[1]

II. DESCRIPTION OF CALCULATION

The Si{100}(2×1) surface was modeled with a microcrystallite of six layers with eight atoms per layer. The top layer was reconstructed into four surface dimers [Fig. 1(a)]. Each atom in the surface dimers has one dangling bond site that is ripe for fluorine atom attachment. The forces on the atoms in the top two layers were determined from the interaction potential. On the next three layers (stochastic region), frictional forces in addition to the forces due to the interaction potential were used.[3] This force dissipates the heat created by the very exothermic reaction between fluorine and silicon and maintains the temperature of the crystal around 300 K. The bottom layer of the crystal was held rigid and was not allowed to reconstruct. Periodic boundary conditions were applied perpendicular to the surface plane to mimic an infinite crystal. The potential energy function used was a many-body potential developed by Stillinger and Weber.[4-6] The initial conditions for an F-atom deposition were a random vibrational phase in the crystal, a random aiming point on the surface, and a gas-phase fluorine atom traveling perpendicular to the surface with a fixed kinetic energy.

A trajectory was considered to be completed when one of three possible results was observed. One result is for the incoming fluorine atom to adsorb on the surface. An atom was counted as adsorbed when its binding energy to the solid is greater than 5.0 eV. (The silicon–fluorine bond energy is between 5.0 and 6.0 eV, whereas the silicon–silicon bond energy is near 2.0 eV.) Another result is for the incoming fluorine atom to be repelled by the surface. The criteria for this event is that the potential energy of the incoming fluorine atom with respect to the surface is greater than zero and its velocity vector is directed away from the surface. These two events are easily identified. The last possible result is for the time of the trajectory to have passed 3 ps (~ 10 000 steps) and for the fluorine atom to have not yet left the influ-

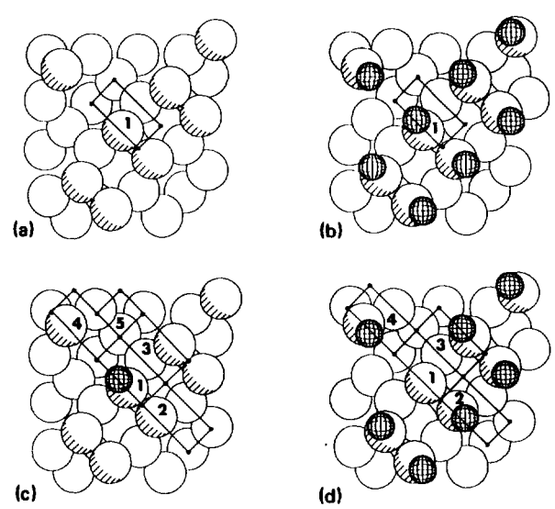

FIG. 1. Fluorine coverages on Si{100}(2×1). The shaded atoms are the surface dimers and the open circles are the subsequent layers of silicon. Only the top four layers of silicon are shown. The hatched atoms are the fluorine atoms adsorbed to the silicon dangling bonds. The boxed regions shown were used in determining the sticking probability for each coverage and the same region size was used for all coverages. The coordinates for the aiming regions are determined from 0 K atom positions and therefore, the regions may not dissect the dimers perfectly because the dimers in each figure are in a different part of their vibrational phase. (a) $\theta = 0$. (b) $\theta = 1$. This surface was also used to determine the dependence of the sticking probability on the kinetic energy of the incoming fluorine atom. (c) $\theta = 1/8$. One occupied dangling bond. (d) $\theta = 7/8$. One unoccupied dangling bond.

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ence of the surface. This cutoff was used to conserve computer time. The fluorine in these trajectories was labeled as "leaving". This event was not observed for the clean surface, but was occasionally found when the incoming fluorine atom came within the range of a fluorine adatom. A sampling of these leaving trajectories was calculated for longer time periods and the fluorine atom in the majority of the cases was found to be out of the potential energy range of the surface before 5 ps. In a few trajectories, the atom did not leave after 5 ps and when their motions were calculated up to 11 ps, they still had not adsorbed or repelled. The fluorine atoms appeared to "diffuse" approximately 3.2 to 4.2 Å above the surface around a F adatom with a potential energy between -0.04 and 0.14 eV. These trajectories were not calculated further since this could be an artifact of the potential energy function. We chose to count diffusing and leaving fluorine atom trajectories as nonsticking events. The low number of the diffusing trajectories does not significantly alter our conclusions. The sticking probability S was therefore calculated as the number of favorable events of F-atom adsorption divided by the total number of trajectories.

The dependence of the sticking probability on coverage θ was investigated using five different coverages for 0.039 eV F-atom adsorption. For the clean surface [Fig. 1(a)] and the fully fluorinated surface [Fig. 1(b)], the surface possesses a translational symmetry and therefore the entire surface can be represented by randomly aiming the F atom in the rectangular region shown. A fully fluorinated surface, $\theta = 1$, corresponds to one fluorine per dimer atom. Experimental evidence for the fluorine atom adsorption to the silicon-dimer dangling bonds was obtained by electron-stimulated desorption ion angular distribution experiments.[7]

The next two coverages investigated were 1/8 and 7/8, Figs. 1(c) and 1(d), respectively. These two surfaces lack translational symmetry. To facilitate the calculation of the sticking probability for these coverages, each surface was divided into 16 regions. All these regions have the same dimensions as those used for $\theta = 0$ and $\theta = 1$. Therefore, the sticking probability for these coverages is the sum of the sticking probability contribution from each region, which is the sticking probability in the region multiplied by the fraction of area of the surface that region represents. In calculating the sticking probability of $\theta = 1/8$ (7/8), we assumed that any region sufficiently far away from the region containing the fluorine adatom (vacancy) would have a sticking probability equal to the clean (fully fluorinated) surface. Therefore, the regions shown in Figs. 1(c) and 1(d) are the only regions where trajectories were performed. For $\theta = 1/8$, the purpose of calculating the sticking probability in the regions around the adatom is to investigate the magnitude of repulsion created by the F adatom. Conversely, for $\theta = 7/8$, the purpose is to determine the accommodation of any atoms that may diffuse from a region surrounding the unoccupied dangling bond and adsorb onto the dangling bond.

The last coverage investigated was $\theta = 1/2$. To our knowledge, ordered overlayer structures of fluorine on Si{100}(2×1) with a coverage of $\theta = 1/2$ have not been experimentally observed. Therefore, we assumed four symmetrical arrangements of fluorine atoms [Fig. 2(a)–2(d)]. In each case there are only two unique regions for aiming the incoming F atom.

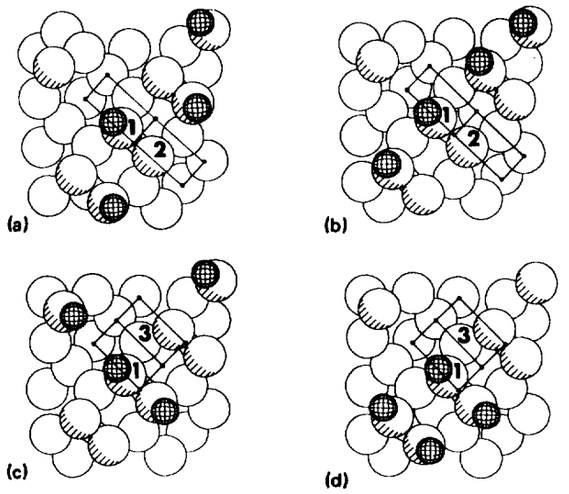

FIG. 2. Fluorine overlayers used in calculating the sticking probabilities for $\theta = 1/2$. In all cases there are only two unique regions for aiming the incoming fluorine atom.

The total number of trajectories calculated for different regions varied from 50 to 200. Most sticking probabilities for an individual region converged to approximately 1% within 150 trajectories. To demonstrate the validity of only calculating the results using 200 trajectories, up to 300 trajectories were calculated on the clean surface. The cumulative initial

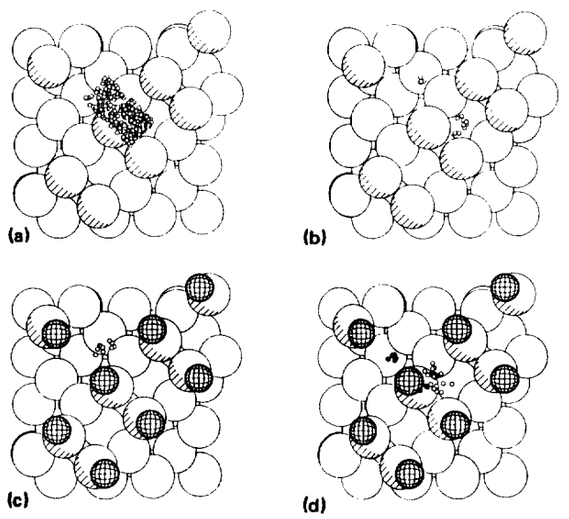

FIG. 3. (a) Example of 200 random aiming points (small circles) for the clean surface. (b) The aiming points on the clean surface, which resulted in nonsticking trajectories. The surface shown is that of the initial condition and does not represent the nuclear positions of the silicon atoms in their random vibrational phase when each fluorine starts its motion towards the surface. (c) The aiming points on the fully fluorinated surface using a beam energy of 3.0 eV, which resulted in sticking to a second-layer atom. (d) The aiming points on the fully fluorinated surface using a beam energy of 3.0 eV, which resulted in the formation of a silicon dimer atom with two fluorine adatoms.

sticking probabilities S_0 tabulated every 50 trajectories were 1.0, 0.970, 0.947, 0.955, 0.956, and 0.953. By 150 trajectories, the sticking probability is within 0.01 of a converged value of 0.95. Figure 3(a) shows an example of the randomness of 200 aiming points. In the case of region 5 for $\theta = 1/8$, only 50 trajectories were calculated to assure that an assumption of $S = S_0$ was valid.

The dependence of the sticking probability on the kinetic energy of the incoming fluorine atom where the surface is fully fluorinated was also investigated. For each kinetic energy 100 trajectories were calculated. The initial conditions are the same as above, except the kinetic energy of the incoming fluorine atom was varied from 0.5 to 3.0 eV in steps of 0.5 eV for different sets of trajectories.

III. RESULTS AND DISCUSSION

The results of the computer simulations for the F-atom deposition on the Si{100}(2×1) surface for various coverages of fluorine atoms are summarized in Table I. The initial sticking probability of atomic fluorine on Si{100}(2×1) is calculated to be 0.95. Since the silicon dimer atoms have one dangling bond per atom and the SiF bond strength is 5–6 eV, this value near unity is not unexpected. The calculated sticking probability dependence on coverage is shown in Fig. 4.

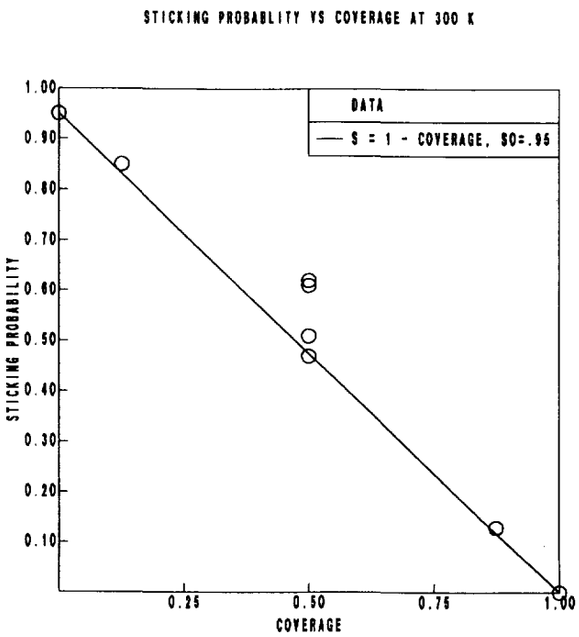

FIG. 4. The sticking probability for fluorine atoms having 0.039 eV kinetic energy vs coverage. The circles are the data points calculated by our simulations. The solid line is the Langmuir adsorption curve $S(\theta) = S_0(1-\theta)$, where $S_0 = 0.95$.

TABLE I. Sticking probabilities S calculated for each region investigated for each coverage. The sticking probabilities are reported as the number of trajectories where the fluorine adsorbed over the total number of trajectories calculated. The labels of a–d for a coverage of 1/2 correspond to Fig. 2. In all cases the incoming F atom had 0.039 eV of kinetic energy.

Coverage	Region	Number of F atoms that adsorb	Number of trajectories	S	S_{total}
0	1	286	300	0.95	
					0.95
1/8	1	50	200	0.25	
	2	184	200	0.92	
	3	176	200	0.88	
	4	184	200	0.92	
	5	49	50	0.98	
					0.85
1/2a	1	33	200	0.17	
	2	168	200	0.84	
					0.51
1/2b	1	62	200	0.31	
	2	184	200	0.92	
					0.62
1/2c	1	49	200	0.25	
	3	191	200	0.96	
					0.61
1/2d	1	39	200	0.20	
	3	148	200	0.74	
					0.47
7/8	1	138	200	0.69	
	2	16	200	0.08	
	3	30	200	0.15	
	4	25	200	0.13	
					0.13
1	1	0	200	0.00	
					0.00

The solid line is the Langmuir adsorption curve, $S(\theta) = S_0(1-\theta)$, where $S_0 = 0.95$. The circles are the data points that were calculated from the information in Table I. The calculated points follow the Langmuir prediction rather well, thus the adsorption of fluorine atoms on silicon depends on the availability of a vacant site. Interestingly, the sticking probability on the clean surface is not 1.0. The aiming points of the F-atom trajectories, which did not stick, are over third layer atoms in the trough and in between dimers, see Fig. 3(b). Note that Fig. 3 displays the aiming points with respect to the initial coordinate set for the surface and not with respect to the vibrational phase of the surface, which has evolved for a random amount of time before the F atom is introduced into the trajectory. The sticking probabilities for $\theta = 1/8$ and 7/8 are comparable to the Langmuir prediction. Therefore, for these coverages, surface diffusion does not play a role and the sticking probability is determined by the fraction of adsorption sites available. There is a strong correlation between the aiming point of an incident F atom and the dimer atom to which it adsorbs.

The sticking probabilities for the four $\theta = 1/2$ configurations shown in Fig. 2 vary from 0.47 to 0.62. The two values larger than that predicted by the Langmuir isotherm, i.e., the surfaces in Figs. 2(b) and 2(c), warrant special attention as it appears that surface diffusion might now be important. We chose the surfaces in Figs. 2(a) and 2(c) to represent the $\theta = 1/2$ overlayers, which yielded the lower and higher sticking probability results, respectively. In order to obtain an approximate dynamical representation of the fluorine reactivity to these surfaces in a static contour plot, we have calculated minimized energy contour plots as shown in Figs.

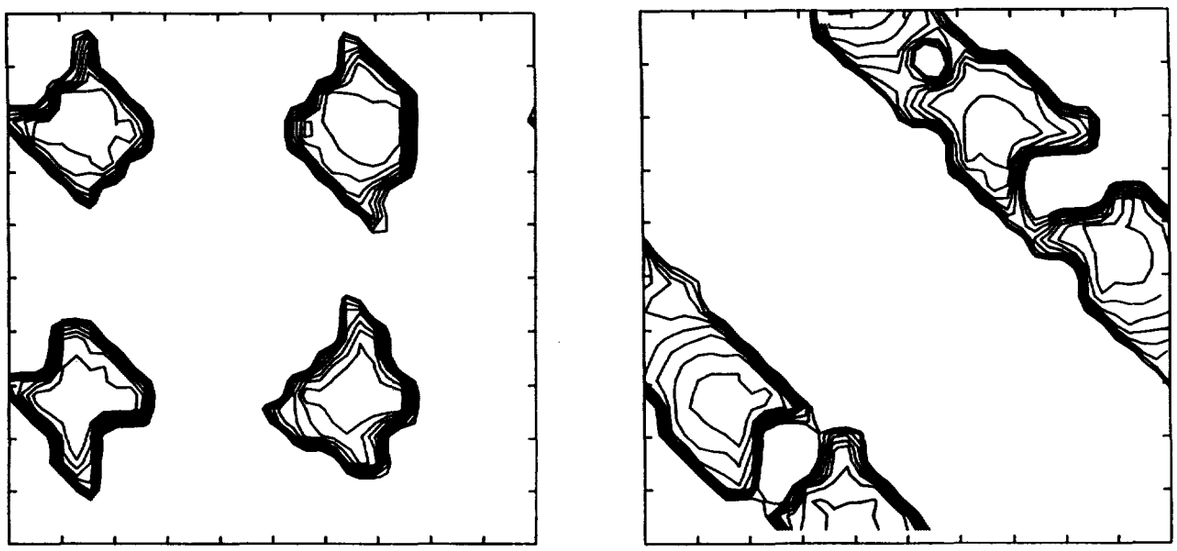

FIG. 5. Minimized energy contour plots for two $\theta = 1/2$ surfaces with respect to an incident fluorine atom. Constant energy contour lines are from -2.5 to -5.3 eV in steps of 0.4 eV (a) The contour is for the zigzag coverage shown in Fig. 2(a). (b) The contour is for the chain coverage shown in Fig. 2(c).

5(a) and 5(b) for the surfaces in Figs. 2(a) and 2(c), respectively. In each case, the square region represents the entire crystal as shown in Fig. 2. The goal is to identify the regions of the surface that are attractive to an incoming fluorine atom. A grid of 21×21 points was used in making the contour plots. At each point, a fluorine atom was placed above the surface outside the influence of the potential energy function with a kinetic energy of 4.6×10^{-4} eV directed towards the surface. The incident fluorine atom's lateral positions were fixed. The system minimized its energy by changing the coordinates of the atoms in the substrate and the perpendicular coordinate of the incident fluorine. The energy minimum was found by integrating the equations of motion for the combined system for 2000 timesteps at 300 K and then zeroing the velocities for an additional 2000 timesteps. The adsorption energy was obtained by subtracting the energy of the initial crystal from the energy value found by the above procedure. The energies resulting from the minimization indicated that an aiming point was either attractive (having an energy difference between -2.35 and -5.59 eV) or not attractive (having an energy difference between 0.00 and -0.12 eV). Therefore, we feel that this type of contour plot gives a reasonable qualitative representation of the dynamical reactivity of an incident fluorine atom with the surface. We have plotted energy contours between -2.5 and -5.3 eV in steps of 0.4 eV. The attractive regions of the surface are those that have the highest density of lines.

The energy contours in Fig. 5 for the configurations in Figs. 2(a) and 2(c) show distinct differences. Figure 5(a) shows discreet areas of attraction over the dangling bond sites, which are formed by the zigzag fluorine overlayer in Fig. 2(a). The contour in Fig. 5(b) for the chain of fluorine adatoms in Fig. 2(c) shows that the attractive dangling bond sites are connected by troughs of attractive interactions. We conclude that the chain-like fluorine overlayers permit the formation of attractive bridges between dangling bond sites. Therefore, these bridges increase the sticking probability since a fluorine atom that is aimed at these positions will feel some attraction and can therefore be pulled towards a dangling bond.

The results of the simulations aimed at investigating the sticking probability dependence on the kinetic energy of the incoming fluorine atom with the fully fluorinated surface are shown in Fig. 6. The sticking probability is seen to increase with kinetic energy above a threshold value between 0.50 and 1.00 eV. The fluorine atoms that adsorb when the kinetic energy is less than 2.0 eV stick almost exclusively to silicon atoms in the second layer as shown in Fig. 7(a). Sticking to a second-layer atom occurs when the fluorine atom is aimed at a third-layer atom in the trough as shown in Fig. 3(c). In the formation of this $-$SiF adspecies, the silicon atom that reacts with the incoming F atom undergoes an S_N2-like mechanism, as proposed by Garrison and Goddard.[8] The F atom attacks from one side of a Si atom and this Si atom is pulled toward the F atom, breaking the bond on the opposite side. As stated previously, the Si–F bond strength is approximately twice the Si–Si bond strength. Since the other three ligands are attached to the solid, the umbrella-type motion occurs by the central atom moving. The second-layer silicon atom to which the incident fluorine atom has adsorbed still has a coordination of four, whereas the third-layer silicon atom below this second-layer atom has a coordination of three, due to the broken bond between the second and third-layer atoms. The coordination of a silicon atom is defined as the number of atoms within a sphere of radius 2.95 Å of that silicon. When the fluorine atom has a kinetic energy of 2.0 eV and greater, the probability that the fluorine will adsorb to a silicon dimer atom increases, thus forming a silicon

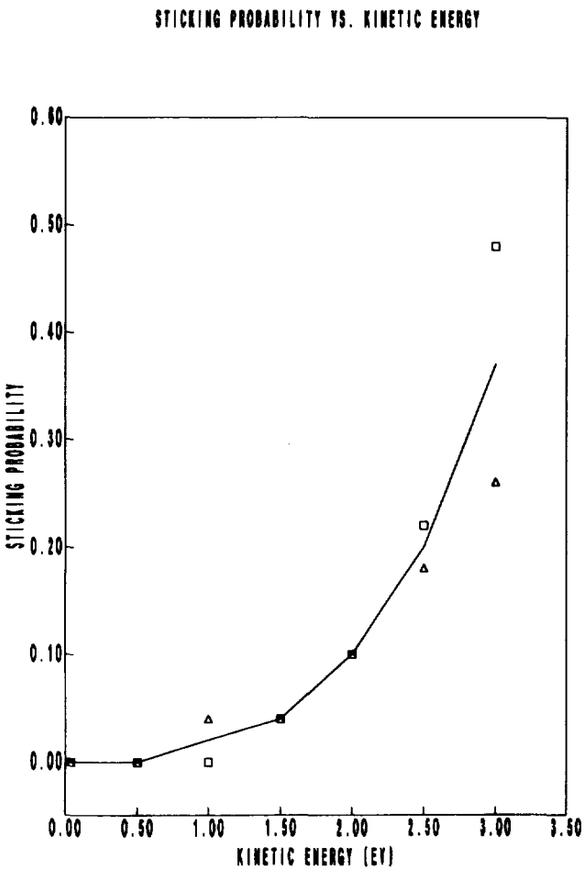

FIG. 6. The sticking probability dependence for a fully fluorinated surface on the kinetic energy of the fluorine atoms. The symbols are the sticking probability results for different sets of 50 trajectories. The solid line is drawn through the average sticking probability at each kinetic energy.

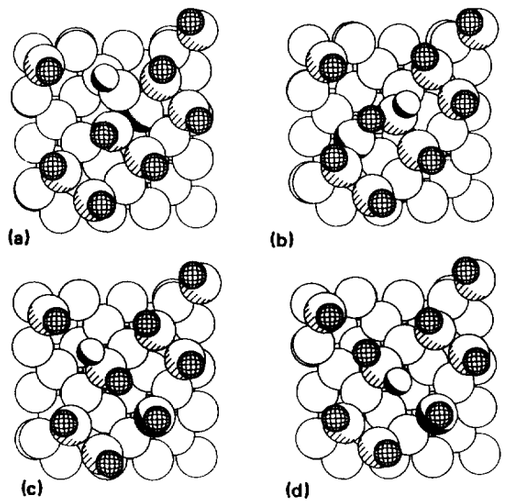

FIG. 7. The resulting surfaces when a 3.0 eV beam of fluorine atoms is aimed at the fully fluorinated Si{100}(2×1) surface. The small hatched atoms are the fluorine adatoms of the original monolayer coverage. The small shaded atom is the fluorine atom from the beam. The large densely shaded atom is a silicon atom that has a coordination of three. (a) The incident F atom is adsorbed to a second-layer silicon atom. A Si–Si bond between second and third-layer atoms has been broken. (b) The incident F atom is adsorbed on an occupied dimer atom, which results in an $-SiF_2$ adspecies. A Si–Si bond between first and second-layer atoms is broken. (c) The incident F atom is adsorbed on the trough side of an occupied dimer atom. The Si–Si dimer bond is broken. (d) The incident F atom is adsorbed between the original dimer atoms and the Si–Si dimer bond is broken.

dimer atom that has two adsorbed fluorine atoms. The adsorption of the F atom to an occupied silicon surface dimer atom breaks either a bond between the first and second-layer silicon atoms [Fig. 7(b)] or the dimer bond [Fig. 7(c) and 7(d)]. Figure 3(d) shows the aiming points for a 3.0 eV atomic F beam, which forms the $-SiF_2$ adspecies. The hollow aiming points result in the breaking of a bond between the dimer atom and a second-layer atom [Fig. 7(b)]. The filled points over the fourth-layer atom in the trough give an open dimer bond with the incoming F atom adsorbing on the trough side of the silicon atom [Fig. 7(c)]. These two reactions also occur by an S_N2-like mechanism. The last mechanism observed that produced an $-SiF_2$ adspecies occurred when the F atom broke the dimer bond and adsorbed between the original dimer atoms, as shown in Fig. 7(d). The aiming points for this mechanism are the filled ones over the dimer atom shown in Fig. 3(d). In the formation of the $-SiF_2$ adspecies, the silicon atom of the adspecies retains its coordination of four and leaves a silicon atom undercoordinated in the first or second layer. Of the three unique surfaces depicted in Fig. 7, 7(c) and 7(d) are lower in energy than 7(b) by 0.39 eV and 7(a) is higher in energy than 7(b) by 0.74 eV. As the configuration shown in Fig. 7(c) and 7(d) is the lowest in energy, it is quite possible that if atoms are initially in arrangements as shown in Figs. 7(a) and 7(b), then they will rearrange to obtain the lowest energy state. A surface where Si atoms have both one and two adsorbed F atoms is consistent with x-ray photoelectron spectroscopy studies.[9] The probabilities that a fluorine atom will adsorb to a silicon dimer atom or to a second-layer atom are approximately equal when the beam has an energy around 2.5 eV. Obviously, the higher translational energy is needed to overcome barriers to adsorption.

Engstrom, *et al.*[1] have experimentally determined the sticking probability of atomic fluorine on the clean Si{100}(2×1) surface to be 0.5 ± 0.3. The large uncertainty of their result was attributed to the low concentration (17%) of atomic fluorine in the beam, which also contained molecular F_2 and a seed gas. To obtain the atomic sticking probability, the sticking probability due to pure F_2 had to be subtracted from the total signal. Our result of near unity for the sticking probability on the clean surface seems more logical considering the density of dangling bonds on the surface and the large exothermicity of the reaction. Our simulations show that the sticking probability depends on coverage, whereas experimentally the dependence is found to be weak.[1] This discrepancy could be due to an unrealistic potential energy function or to the inability to obtain an experimental crystal that is totally free of contamination and defects. We also find that the probability of adsorption becomes activated when the atomic beam has an energy be-

tween 0.50 and 1.00 eV. This concurs with experimental results that observe a difference in the sticking probabilities between a 0.10 and a 0.56 eV beam.[1]

IV. CONCLUSIONS

We have calculated the dependence of the sticking probability of atomic fluorine on Si{100}(2×1) on coverage using near thermal fluorine atoms. We found the initial sticking probability to be near unity. Our values for the sticking probability versus coverage are close to those predicted by Langmuir adsorption for low and high coverages, thus surface diffusion does not play a dominate role. However, for some assumed geometries of a half monolayer coverage we note that diffusion leads to an enhanced sticking probability. For a fully fluorinated surface, we found that the sticking probability of fluorine can be enhanced by increasing the translational kinetic energy of the atomic fluorine beam. At a beam energy of around 2.0 eV, 1/2 of the fluorine atoms that stick, bond to a second-layer atom. The other half bond to a surface dimer atom.

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