VOLUME 62, NUMBER 18 PHYSICAL REVIEW LETTERS 1 MAY 1989

Fluorination of the Dimerized Si(100) Surface Studied by Molecular-Dynamics Simulation

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(Received 2 December 1988)

A computer simulation has been carried out to illuminate atomic processes in the fluorination of a dimerized Si(100) surface. Distinctly different outcomes arise from a pair of 130-ps runs that employ identical initial and boundary conditions. For one of these energy is conserved, the heat released by reaction causes substrate melting, and volatile SiF_3 and SiF_4 products emerge. The other is nonconservative due to periodic reduction of Si momenta to approximate thermal conduction into a bulk substrate; it just avoids melting, yields a passivated surface with all dangling bonds fluorinated, and fails to produce volatile products.

PACS numbers: 68.45.Ax, 61.20.Ja, 81.60.Cp, 82.20.Wt

A wide range of powerful experimental methods is available for fundamental surface science, including Rutherford backscattering, electron and helium diffraction, photoelectron and Auger spectroscopy, and scanning tunneling microscopy. The resulting body of observations and data has encouraged intense theoretical effort to aid in the interpretation and understanding of surface phenomena at the atomic level. In particular, molecular-dynamics computer simulation has been employed to a moderate extent to model nonreactive surface scattering, adsorption and desorption kinetics, and surface mobility of various gaseous species.[1-3] But to the best of our knowledge such simulation heretofore has not been applied to cases where the substrate reacts with, and can be etched by, an ambient fluid reactant.

Our purpose here is to report such an example, namely simulation of the exothermic reaction between crystalline silicon and diatomic fluorine gas. This case bears significance due to widespread interest in fluorine etching processes for production of patterned silicon substrates in very-large-scale-integration device manufacture.[4]

The calculations reported here utilize our prior molecular-dynamics modeling for pure silicon[5] and for pure fluorine,[6] but extend those studies by including the necessary additional cross interactions. The potential energy Φ used in this mixed system comprises two-atom and three-atom interactions ($A \equiv \mathrm{Si}$, $B \equiv \mathrm{F}$):

$$\Phi = \sum v_{AA} + \sum v_{AB} + \sum v_{BB} + \sum v_{AAA}^{(3)} + \sum v_{AAB}^{(3)} + \sum v_{ABB}^{(3)} + \sum v_{BBB}^{(3)} . \tag{1}$$

Structural chemistry requires a delicate balance between terms in this expression, specifically to enforce the monovalency of fluorine and the tetravalency of silicon.

Our study has adopted the silicon interactions from Ref. 5 without change, thereby automatically committing us to that prior convention for energy and length units. The fluorine interaction functions from Ref. 6 consequently were rescaled in order to conform to those units. The new pair interaction required for the silicon-fluorine bond was given in the form

$$v_{AB}(r) = \begin{cases} 21.23414138(0.5695476433 r^{-3} - r^{-2}) \exp[1.3(r-1.8)^{-1}] & (0 < r < 1.8) , \\ 0 \quad (1.8 \leq r) , \end{cases} \tag{2}$$

which produces the correct bond length, bond strength, and vibrational frequency for the SiF molecule. The depths of v_{AA}, v_{AB}, and v_{BB} are -1.000, -2.640, and -0.766 in the silicon-based reduced units employed.

It is convenient (and entails no loss of generality) to express each $v^{(3)}$ as a sum of three triad functions $h_{XYZ}(r,s,\theta)$, where θ is the vertex angle at atom Y and r and s are distances of the two "legs."[5-7] The four new heteroatomic triad functions have been assigned as follows:

$$\begin{aligned} h_{AAB} &= 15(\cos\theta + \tfrac{1}{3})^2 \exp[(r-1.8)^{-1} + (s-1.8)^{-1}] , \\ h_{ABA} &= 50 \exp[1.3(r-1.8)^{-1} + 1.3(s-1.8)^{-1}] , \\ h_{ABB} &= 2.5 \exp[(r-1.8)^{-1} + (s-1.8)^{-1}] , \\ h_{BAB} &= [24(\cos\theta - \cos 103°)^2 - 3.2] \exp[(r-1.8)^{-1} + (s-1.8)^{-1}] , \end{aligned} \tag{3}$$

where each becomes identically zero for $r,s \geq 1.8$.

With this set of interactions the lowest-energy structures of the gas-phase species SiF_2, SiF_3, and SiF_4, respectively, are bent (C_{2v}), pyramidal (C_{3v}), and tetrahedral (T_d) in agreement with experiment, and exhibit moderately good bond lengths and energies. The SiF_4 molecule in this modeling scheme exhibits virtually no tendency to add a fifth fluorine atom; i.e., the silicon valency indeed saturates at four. Full details concerning these and other Si_xF_y species will be published elsewhere.

Our molecular-dynamics investigations have employed an initial configuration with a crystalline slab of 160 silicon atoms and an ambient gas of 50 diatomic fluorine molecules. These were housed in an elongated rectangular cell with reduced dimensions $7.328 \times 7.328 \times 50.000$. Periodic boundary conditions were used in all three directions. The silicon slab, 10 layers deep, stretched across the short dimensions and was oriented to expose (100) surfaces on top and bottom, each reconstructed by dimerization in a $p(2\times 1)$ pattern. Each of the 32 exposed atoms in top and bottom layers consequently formed three bonds to other silicon atoms, and possessed a dangling bond (unsatisfied valence). The fluorine gas initially was kept just out of contact with the slab but was otherwise in a random configuration. The initial temperatures assigned to the slab and reactant gas were relatively low, about 62 and 75 K, respectively. In this state the initial pressure of the fluorine was estimated to be about 20 atm, and it would eventually have condensed to a liquid in the absence of the subsequent exothermic reaction.

Two molecular-dynamics runs have been generated, both using identically the same initial and boundary conditions just specified. The first of these (designated I) followed the Newtonian conservative dynamics for the 260-atom system, using the fifth-order Gear algorithm[8] with a step size of 0.004 reduced time unit (3.065×10^{-16} s). The second run (II) was identical in all respects *except* that every 8000 steps (2.452 ps) the silicon atom momenta were scaled downward by the factor 0.97. The reason for this distinction was to modulate the influence of the heat of reaction, and the momentum reduction in II was a simple way to approximate thermal conduction into a massive substrate slab that would have been impractical to simulate directly. Runs I and II both spanned 424000 time steps (130.0 ps).

The initial phases of I and II were quite similar, as expected. Random collisions of fluorine molecules with the surfaces fluorinated dangling bonds with release of reaction energy that heated the slab and, with a time lag, the ambient fluorine gas as well. Fluorination occurred both by nearly simultaneous addition of the two ends of a diatomic F_2 to neighboring unbonded sites, and by single fluorine addition from an F_2 with vigorous ejection of its partner back into the gas phase.

But in spite of the initial similarity, the final outcomes from I and II were dramatically different. In the energy-conserving scenario I the extent of reaction is sufficient to melt the silicon slab (the melting point of our model silicon has been determined to be 1691 ± 20 K,[9] compared to the measured value 1683 K). The molten layer continued to stretch across the cell throughout the simulation but fluctuated in shape enough to continue exposing silicon atoms to the reactive fluorine. As a result the volatile products SiF_3 and SiF_4 emerged, a process that surely would have continued were I to have been extended to longer times. By contrast, the nonconservative scenario II retained slab crystallinity to the end, in spite of slight momentary superheating at an intermediate stage. Fluorination proceeded only to the extent of occupying the initial 32 dangling bonds. Subsequently the surface was chemically passivated. No volatile silicon fluorides were produced in II.

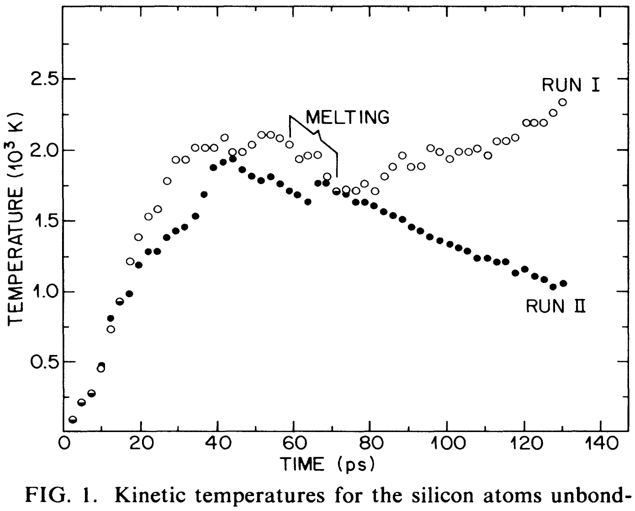

FIG. 1. Kinetic temperatures for the silicon atoms unbonded to fluorine during the two molecular-dynamics runs. The points shown represent averages over 8000-step intervals (2.452 ps).

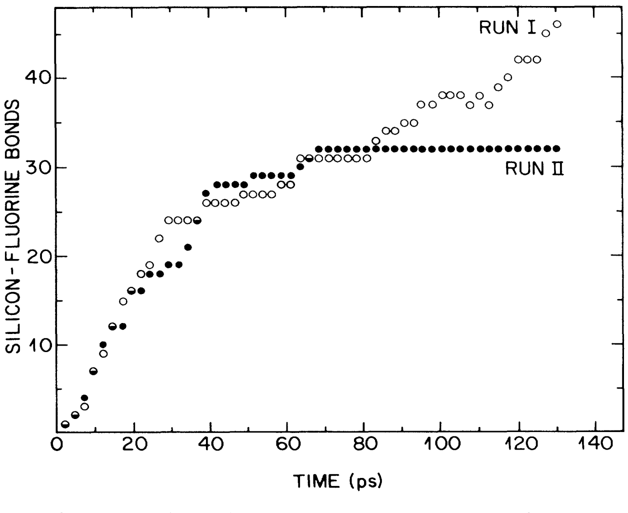

FIG. 2. Total numbers of Si—F bonds vs time for the two molecular-dynamics runs. A bond is counted if the atom pair distance is less than $\frac{4}{3}$ the equilibrium bond length of $v_{AB}(r)$.

Figure 1 shows a record of the time-dependent temperatures for silicon atoms in I and II that were not directly involved in bonds to fluorine. The points shown are 8000-step averages. Figure 2 provides a corresponding record of the numbers of silicon-fluorine bonds, from which the passivation in II after about 66 ps is very clear. For the purposes of these calculations we have defined a "bond" to exist between two atoms whenever their distance is less than $\frac{4}{3}$ the equilibrium separation for their pair potential.

Identification of melting in I is based on several unmistakable observations. First, the ten-layer density profile through a crystalline slab (which remains throughout II) transforms to a featureless profile with a single broad maximum. Second, the number of silicon-silicon bonds suddenly increases owing to the higher coordination number of the liquid compared to the crystal.[5,10] Third, it is clear that the silicon atoms undergo relatively rapid self-diffusion in the slab only after the melting event has occurred.

In neither case do we find any tendency for fluorine atoms to penetrate into the interior of the silicon slab. Fluorine atoms attached to silicons that have not yet volatized are confined to layers just outside the slab, whether it is in the crystalline or the molten state. However, this observation does not exclude the possibility of fluorine invasion if a defective crystal were present, or over longer times than that spanned by our runs.

Structural interpretations of condensed-phase phenomena are often facilitated by mapping instantaneous system configurations to potential energy minima by mass-weighted gradient descent on the potential hypersurface.[11-13] This is especially true where chemical bonding and reactivity are at issue.[6,7,14] Consequently, we have applied this mapping to the final configurations of both molecular-dynamics runs. This removes the distracting influence of thermal vibrations that are present in both cases, but are especially severe for run I. Table I specifies the bonding patterns and potential energies at the two relative Φ minima encountered. The last five rows in the table state the numbers of silicons found with exactly 1, . . . , 5 bonds to fluorines.

TABLE I. Bonding properties for the Φ minima obtained by mass-weighted gradient descent from final configurations of molecular-dynamics runs.

Property	Run I	Run II
Φ[a]	−419.56634	−408.08341
Si−Si bonds	385	304
Si−F bonds	48	32
F−F bonds	24	33
SiF	32	32
SiF_2	1	0
SiF_3	2	0
SiF_4	2	0
SiF_5	0	0

[a] Φ values in silicon-based reduced units.

The SiF_3 and SiF_4 species listed in Table I for run I occur in the gas phase well away from the slab, while the SiF_2 unit is an unvolatilized component of the molten slab surface. These multifluorinated units appeared only after the melting event occurred, consistent with their nonoccurrence in the unmelted run II. For both runs the ambient fluorine gas was partially dissociated, since the observed numbers of F−F bonds, 24 and 33, were less than the maximum possible for the respective numbers of available fluorines, namely 26 and 34 F−F bonds. We have also verified the presence of fluorine exchange reactions in the gas phase for both runs.

The number of Si−Si bonds listed in Table I for run II, 304, is exactly the number with which both runs began. Examination of the mapped configuration shows that the initial bonding pattern was undisturbed, with all surface dimers surviving the fluorination process. At longer times these dimers might break to add more surface fluorines. The potential energy listed for this final mapped configuration is roughly estimated by the sum of optimal pair-bond energies:

$$304(-1.000)+32(-2.640)+33(-0.766)=-413.758\,, \qquad (4)$$

the discrepancy with Table I arising from a combination of bond strain in the silicon substrate and fluorine crowding in the bonded monolayers. The corresponding estimate for run I,

$$385(-1.000)+48(-2.640)+24(-0.766)=-530.104\,, \qquad (5)$$

is considerably farther off the mark due to the disorder in the amorphous slab.

We are well aware that the specific model interactions used in this study probably could be significantly improved in their ability to describe the pure elements as well as the reaction pathways and products. However, we believe that the dominant theme of our results is robust, namely that substrate melting exerts a powerful influence on surface reaction rates and products.

Beside attempting to improve potential functions for the silicon-fluorine system, it would also be valuable to incorporate alternative means for supplying fluorine to the silicon surface. An experimentally convenient choice is the reagent XeF_2 which is much easier to handle and control than F_2.[4,15] We believe that the same general Φ format as applied here utilizing two-atom and three-atom interactions could be invoked to describe this case as well.

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