Reaction mechanism for fluorine etching of silicon

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A reaction mechanism is proposed for etching of Si surfaces by F atoms in which SiF_4 is formed. We proposed that in the rate-determining step the F atom attacks the back side of a —SiF_3 moiety with simultaneous Si—F bond formation and Si—Si bond rupture (as in an S_N2 process). The transition state for this process involves charge transfer from the rupturing Si—Si bond to the attacking F atom and is consistent with recent observations that the etch rate is greater for n-type than for p-type silicon.

Chemical etching of solid silicon by reaction with fluorine atoms is a promising technology for maskless fabrication of microstructures in modern electronic devices. Some information on the chemical mechanisms behind this important materials tailoring technique is emerging from a variety of experiments. Although there are many variants of how the F atoms are introduced to the silicon substrate, in general it is predominantly $SiF_4(g)$ that ultimately desorbs from the surface,[1-4] and it is the formation of the product SiF_4 that is believed to be rate determining.[3-8] Photoemission studies have shown fluorine etching of Si leads to a steady-state surface layer of 10–20 Å containing high concentrations of SiF, SiF_2, and SiF_3.[3-8] For etching of heavily doped n-type silicon it is observed that the reaction rate is ~2.5 times faster[9-12] and that the SiF_x layer is slightly thinner[7] than for intrinsic silicon. For heavily doped p-type silicon the etch rate is ~0.8 times slower[9-12] and the SiF_x layer is thicker[7] than for intrinsic silicon. In addition, for p-type silicon the product distribution has significant populations of SiF_3 and Si_2F_6.[2] It is impor-

tant to pin down the mechanisms of such chemical steps in electronic materials processing, since development of the ultimate techniques will require design of new processes in which the chemistry is manipulated *a priori* to attain lower temperature, finer resolution, and three-dimensional devices.

In order to elucidate the fundamental chemical mechanisms, we have carried out a series of theoretical calculations on various Si-F reactions. The steps by which an F atom bonds to unsaturated Si atoms (i.e., an Si atom with a dangling bond or an Si atom with a lone pair of electrons) are exothermic by ~5.5–6.5 eV.[13,14] Thus it is easy for F atoms to attach to Si dangling bonds and form SiF_x, where $x = 1-3$. Consequently, this study is focused on the final rate-determining step in which the product SiF_4 is formed from a F atom and a —SiF_3 species which still bonded to another Si atom.

Based on a series of electronic structure calculations, we propose that in the rate-determining step a F radical attacks the Si—Si bond from the back side to form SiF_4 as in (1),

$$\text{(1)}$$

F Atom + SiF$_3$ Species   **Reaction Intermediate**   **SiF$_4$ + Si Dangling Bond**
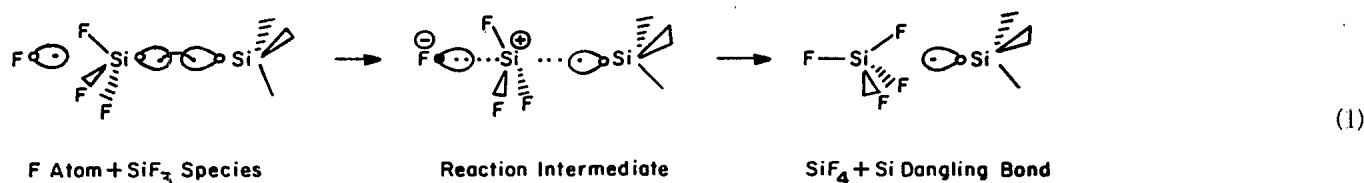
Although this process may appear implausible, it has a strong precedent in organic chemistry where it is known as the S_N2 process (nucleophilic substitution). In addition, upon examination of the silicon lattice and the possible positions of a —SiF_3 species, there are channels to align the F-atom motion parallel to the Si—Si bond. We find for the $F + H_3Si—SiH_3 \rightarrow F—SiH_3 + SiH_3$ analog of (1) that the reaction is exothermic by 3.58 eV with an activation barrier of only 0.27 eV. This reaction is so

exothermic that the transition state has a F—Si distance of 2.35 Å [50% longer than the calculated equilibrium value of 1.65 Å (Ref. 13)], whereas the Si—Si distance in the transition state is within 0.01 Å of the equilibrium value. The distortion of the SiH_3 bond angle is only 3° from the tetrahedral value. As discussed below, we estimate that for the reaction $F + F_3Si—SiH_3 \rightarrow SiF_4 + SiF_3$ has a comparable exothermicity with a barrier of 1.0 ± 0.2 eV.

The calculations performed here are for gas-phase molecules, not for —SiH$_3$ and —SiF$_3$ moieties in a heavily damaged and distorted real environment. Since the reactions of interest are highly exothermic, one would believe that any distortions in the solid would tend to weaken the Si—Si bond or make the F ligands on the Si atom more amenable to inversion, thus the net effect would be to lower the activation energy. Our value of 1.0±0.2 eV for the activation energy is thus an upper bound for the real processes of interest.

It is important to note that the barrier for (1) is low because the attacking F atom is a *radical*. One can visualize the reaction as the attacking F atom having a singly occupied orbital which accepts an electron from the Si—Si bond in the transition state, weakening the Si—Si bond and allowing the SiF$_3$ species to transfer to the F atom. This mechanism provides a *microscopic* explanation for the differences between the etching rates in *n*-type and *p*-type silicon. In *n*-type silicon there is a larger electron density available to promote this reaction, and hence product formation is more facile. On the other hand, in *p*-type silicon there is a deficiency of electron density, and the reaction will be inhibited, leaving an abundance of —SiF$_3$ species in the solid. Of note is that the analog of process (1) with a F$^-$ ion rather than a F radical would proceed much slower.

In order to test these ideas, we carried out a sequence of quantum-mechanical calculations designed to obtain accurate bond energies of Si-F species and the activation energy of process (1). The important feature to be described accurately in the calculation is the change in spin coupling as the middle —SiX$_3$ (X=H,F) species starts to bond to the F atom and lessens its interaction with the other Si atom. The application generalized valence bond (GVB) and dissociation-consistent (DC) configuration-interaction (CI) wave functions[15–17] to silicon fluoride systems has been previously delineated.[13] The spirit of the GVB-DC-CI procedure is to include the same level of electron correlation in the wave functions that describe the reactants, products, and any possible transition states. With this approach we have obtained excellent bond energies for Si-F systems, a sample of which are given in Table I with relatively small CI wave functions.[13] The GVB-DC-CI prescription is used here because our goal is to reliably calculate the overall exothermicities and activation barriers of the F + Si$_2$H$_6$ reaction to form FSiH$_3$ + SiH$_3$.

For the collinear reaction of F with Si$_2$H$_6$ the important geometrical parameters are the Si—F distance, the Si—Si distance, and the F—Si—H angle, θ. Here $\theta=70.53°$ is the tetrahedral angle corresponding to the reactant Si$_2$H$_6$, $\theta=109.47°$ is the tetrahedral angle of the product F-SiH$_3$, and $\theta=90°$ has the Si—H bonds perpendicular to the F-Si-Si axis. We assume that all Si—H bond lengths are constant at 1.5 Å and the SiH$_3$ moiety away from the F atom remains in a tetrahedral configuration. From the studies on the SiF$_x$ and SiF$_x$H$_y$ species,[13] we found that the dominant electron correlation effects are the F atom intrapair correlation, the correlation within the three-electron σ space (the bonding electrons), and instantaneous correlations between the F lone pairs and the σ space electrons. Each of the F valence orbital pairs is described within the generalized valence bond prescription by two optimized orbitals. Further correlation is introduced by using a GVB restricted CI (GVB-RCI) wave function. In this wave function all three occupations [(20), (11), and (02)] of two electrons in the two GVB orbitals are allowed.

The three electrons in the radical orbitals of the F atom and the two SiH$_3$ species need special consideration since the spin coupling changes as the reaction proceeds. In order to avoid bias in describing the three sigma orbitals we include all seven configurations of three electrons in three orbitals [a seven-configuration wave function—also referred to as a CASSCF (Ref. 18)]. Preliminary testing showed that to best describe both the wave function and the activation energetics, a true multiconfiguration self-consistent-field (MCSCF) wave function for all active electrons is necessary. Thus the calculations presented here were performed using a 189 (3×3×3 configurations of the F lone pair GVB-RCI wave function times 7 configurations of the σ-bonding space) MCSCF calculation for the proposed reaction. The 189 MCSCF has been designed to calculate the overall reaction energetics where there is always one bond present. To accurately describe the individual bond strengths of SiH$_3$-SiH$_3$ and F-SiH$_3$, additional electron correlation terms that include higher-order excitations from the orbital of the bond being broken must be included.[13,15,17]

TABLE I. Dissociation energies for Si—F bonds with all species in their ground state.

		D_e (eV)	
	E_{act}	Theory	Expt.
Si + F→SiF	0	5.45[a]	5.62[b]
SiF + F→SiF$_2$	0	6.38[a]	6.76[c]
SiF$_3$ + F→SiF$_4$	0	6.34[a]	6.71[c]
H$_3$Si-SiH$_3$ + F→H$_3$Si + H$_3$Si-F	0.27[d]	3.58[d]	3.42[c]
H$_3$Si-SiF$_3$ + F→H$_3$Si + F$_3$Si-F	1.0±0.2[e]	~3.5[e]	

[a]Reference 13.

[b]K. P. Huber and G. Herzberg, *Constants of Diatomic Molecules* (Van Nostrand, New York, 1979). This value has been corrected for vibrational zero-point energy.

[c]Taken from tables and references in Ref. 13.

[d]Values from the 189 MCSCF wave function.

[e]Estimates.

The basis set used for the F atom is the Dunning $(9s\,5p\,/3s\,2p)$ double-ζ contraction[19] of the Huzinaga[20] Gaussian basis set with an added set of d functions without the s linear combination of exponent 1.34. The effective core potential of Rappe et al.[21] and valence double-ζ basis with an added set of d functions, again without the s linear combination of exponent 0.3247, was used for the Si atoms. The Dunning $(4s\,/2s)$ unscaled contraction of Gaussian orbitals[22] was used for the H atoms. All calculations were performed in C_{3v} symmetry.

The energetics for the F + H_3Si-SiH_3 reaction near the transition state are displayed as a contour plot in Fig. 1. The overall reaction is exothermic by 3.58 eV at the 189 MCSCF wave-function level. Given this large exothermicity it is not surprising that the transition state occurs in the reactant channel. As seen in the right portion of Fig. 1, for large Si—F distances the —SiH_3 umbrella bend or pyramidal inversion motion is energetically constrained to $\theta \approx 70°$, or tetrahedral of the reactants. The umbrella motion becomes quite facile when the Si—F distance is 2.4 Å. (Equilibrium Si—F distances in small molecules are typically much shorter at 1.6–1.65 Å.) In fact, at this Si—F distance there are two minima in the θ direction, one corresponding to reactants and one to products with a small barrier in between. The transition state occurs at $R(Si—F)=2.35$ Å and $\theta=75°$. An optimization of the Si—Si distance was performed at the transition state with the resulting distance the same as for reactants. Cursory optimization of the Si—Si distance in the product channel, i.e., the geometries in the upper left corner of Fig. 1, predicts that the Si—Si bond should be longer and of course the energies are lower.

The calculated activation energy is 0.27 eV. We feel that this is an upper bound to the true value. In general, correlation effects tend to lower activation energies, so that any neglected interactions will aid the ease of reaction. In this case the transition state occurs where there is little distortion of the F—Si—H angle, thus one would not expect that the neglected correlations of the electrons in the Si—H bonds or Si—H bond-length optimization would be significant.

Of note is that the product can be formed with virtually no distortion of the lattice. Because of the large exothermicity the product will, of course, want to escape if there are no geometrical restrictions. This lack of distortion is in contrast to, for example, a mechanism where the F atom would be inserted directly into the Si—Si bond. In this latter case the SiF_3 species would have to move several tenths of an angstrom for the product to form. Houle has recently measured the velocity distributions of the SiF_3 species that eject from the solid and finds that there are two components, one in equilibrium with the surface and one that is more energetic.[23] The hot molecules could arise from reactions of the surface with the SiF_4 desorbed immediately with the reaction exothermicity in the translational degree of freedom.

To estimate the effect of F-atom substitution for the H atoms, we performed lower-level calculations for the

F + H_3Si-SiH_3 and F + F_3Si-SiH_3 reactions where the three lone pairs on the reactant F atom and the bond pair were described at the GVB(4/8)PP level. This description yields either a bond in the reactant channel or a bond in the product channel, that is, the diabatic potential curves are determined. Each diabatic GVB-PP wave function in the transition-state region was then used for a GVB-RCI calculation in which all 189 configurations described above were included. The main difference between these calculations and the 189 MCSCF calculation is that the spin coupling in the σ space does not change continuously with distance of the F atom from the reactant molecule.

The transition state for this level of calculation can be approximated by finding the geometry where both the reactant and product diabatic states energies are equal. This procedure yields a transition state for the F + H_3Si-SiH_3 reaction at $R(Si—F)=\sim2.36$ Å and $\theta=80°$ with an energy of ~0.77 eV. The reaction energy found using the diabatic potentials for the F + F_3Si-SiH_3 is ~1.67 eV with $R(Si—F)=\sim2.17$ Å and $\theta=80°$.

These diabatic calculations do not allow for the proper treatment of the changing spin coupling in the three-σ electron-orbital space. If we assume that this effect in the disilane reaction accounts for the difference in activation energies for the two disilane calculations (diabatic versus 189 MCSCF), then its value is ~0.5 eV $(=0.77-0.27$ eV). Adjusting the F + F_3Si-SiH_3 value by 0.5 eV results in an estimate of the activation energy of ~1.2 eV $(=1.7-0.5$ eV). We feel that we have made a very conservative estimate of the activation energy for SiF_4 formation from F + F_3Si-SiH_3, and that the activation energy is probably in the range 1.0 ± 0.2 eV.
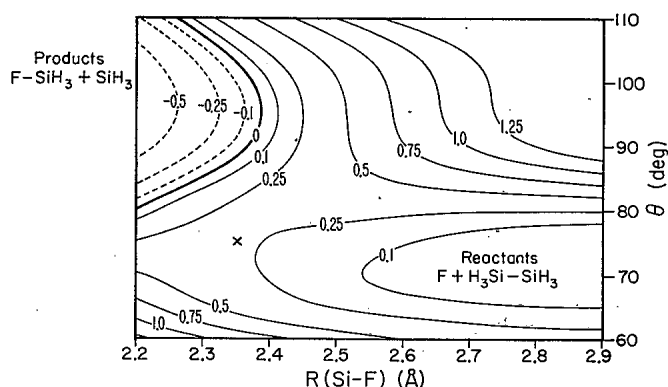

FIG. 1. Contour plot of the reaction energetics in eV near the transition state. The axes are the F—Si—H bond angle θ and the Si—F distance. The Si—Si distance is fixed at 2.41 Å. The transition state is denoted by $\times$. The lines should be interpreted for qualitative and not quantitative features as they have been generated by a bicubic spline from ~40 calculated values. The zero of energy corresponds to the reactant state (lower right corner). The zero-energy contour in the product channel (upper left) is shown as a bold line. Negative energies are shown as dashed lines. The absolute values of the energies at (R (Si—Si), R(Si—F),θ) points are (2.41 Å, 8.00 Å, 70.53°): $-680.75524h$; and (2.41 Å, 2.35 Å, 75°): $-680.74537h$.

Of interest is the possibility of experimentally testing the proposed mechanism. McFeely *et al.* have found that —SiF_3 species could be formed on specific surfaces.[5] By designing a beam experiment where the angle and energy of the F-atom approach to the surface are varied, one can determine if the reaction probabilities were enhanced with a collinear approach of the F atom along the Si—Si bond. In addition, the activation barrier can be measured.

A phenomenon of importance to etching is the observation that the etch rate can be enhanced by at least an order of magnitude if the substrate is simultaneously dosed with F atoms and bombarded with a beam of heavy keV particles.[1] The beam enhancement has been shown to affect the rate of formation of the SiF_4 product. Our mechanism is consistent with that observation in that the beam would break Si—Si bonds allowing direct F-atom attachment. In addition, any damage to the solid in the form of weakened Si—Si bonds or distorted —SiF_3 angles would lower the activation energy. Molecular-dynamics studies are planned to examine the etching process both without and with the keV beam.

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