

## Summary Abstract: Theoretical investigations of fluorine-silicon systems

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The interaction of Si and F is essential for understanding the mechanisms of etching Si with F compounds. Photoemission experiments<sup>1</sup> show that fluorine etching creates a surface layer of up to 25 Å which contains SiF, SiF<sub>2</sub>, SiF<sub>3</sub>, and SiF<sub>4</sub>. The latter product is the one that desorbs from the surface. The presence of a F-rich layer of this thickness indicates that penetration of the F into the bulk occurs before any stripping of the outermost layer takes place. Experiment has also shown that etching does not depend on the substrate orientation. All this indicates that the F-Si interactions that are relevant for etching can be studied in a bulk environment.

Here we will address two important issues concerning the initial phases of the etching process. First, we will examine the behavior of a single F atom in crystalline Si. For that purpose, we map out the total-energy surface and determine stable sites, migration paths, and barriers. Second, we explore how and why F atoms will disrupt the Si network; this involves the collective behavior of several F atoms. The results we report here are based on state-of-the-art theoretical techniques: density-functional theory combined with the local-density approximation (LDA) for exchange and correlation,<sup>2</sup> norm-conserving *ab initio* pseudopotentials,<sup>3</sup> and large supercells<sup>4</sup> for the solution of the relevant Schrödinger equation. Due to the small size and deep potential of the F atom in comparison with the Si, large numbers of plane waves are needed in the expansions of wave functions and potentials, presenting computational requirements near the limit of presently available computer systems. The convergence as a function of basis set size can be improved by using a "soft" pseudopotential for F, which requires fewer plane waves while still providing an accurate description of the Si-F interaction.<sup>5</sup> We have established the convergence properties of our pseudopotentials in extensive tests on molecular structures (SiF<sub>2</sub> and SiF<sub>4</sub>), as well as on small-size unit cells. Our final results were obtained from calculations on supercells containing 16 Si atoms, with an energy cutoff of 30 Ry. Relaxation of the Si atoms around the defect sites is essential for obtaining the minimum-energy configurations; displacements of the first shell of Si atoms were included in the full calculations, while the outer shells were treated with a Keating model.

A comparable study for hydrogen in Si was recently completed,<sup>6</sup> which provided significant new insights about how H reacts singly or in a collective fashion with the Si network. It was found that H can diffuse very easily, and that H atoms in a collective fashion can create local defects. The basic driving force for defect generation is the strength of the Si-H bond; we found that when an interstitial H atom passivates a

dangling bond by forming a Si-H bond, the gain of energy is ~2.2 eV. When sufficiently many H atoms are available, it becomes energetically favorable to eject Si atoms and form Si-H bonds at the resulting dangling bonds.

For fluorine, we first mapped out the total-energy surface for a single F atom in Si, using the novel symmetry-exploiting technique described in Ref. 6. We evaluate the total energy for the F at different positions in the lattice, taking relaxation of the surrounding Si into account. The global energy minimum occurs at the tetrahedral interstitial site. In this state, F is negatively charged<sup>7</sup>; the impurity-related energy levels are indeed well below the top of the valence band. F<sup>-</sup> can diffuse easily through the lattice, with a saddle point at the hexagonal site and an energy barrier smaller than 0.5 eV. At the bond-center site, which involves large relaxation of the surrounding Si atoms, F<sup>-</sup> is found to be 1.5 eV higher in energy than at the tetrahedral site. A F-related energy level appears in the band gap for the bond center and adjacent sites; depending on the Fermi-level position, the defect could therefore also be neutral or even positively charged. This particular configuration of F is believed to exist in amorphous Si.<sup>8</sup>

For sufficiently high fluorine concentrations, cooperative interactions of several F atoms with the Si network will occur. It is tempting to invoke a mechanism based on the strength of the Si-F bond, similarly as described above for Si-H. (The Si-F bond is one of the strongest single bonds, with a bond strength of more than 5 eV in molecules,<sup>9</sup> while the Si-H bond in molecules has a strength of ~4 eV.) When a single F atom approaches a Si surface, it bonds to one of the undercoordinated Si atoms (dangling bonds) at the surface; this has been established experimentally in the chemisorption regime.<sup>1</sup> After all dangling bonds are passivated, F atoms will penetrate the bulk. The lowest-energy configuration of a F atom in a Si network is a Si-F bond. This result was obtained from a calculation of a Si vacancy with four F atoms saturating the four dangling bonds. Clearly, however, a single F atom cannot lead to the formation of a single Si-F bond in perfect crystalline Si. When several F atoms are available on the other hand, the creation of Si-F bonds is possible. The simplest case is through the ejection of a Si atom, i.e., F-assisted Frenkel pair formation as discussed earlier in the case of H.<sup>6</sup> More generally, several F atoms can induce local amorphization where isolated Si-F bonds can be accommodated. The precise atomistic processes that lead to amorphization may be quite complex. After amorphization of a near-surface layer, etching proceeds via the ejection of SiF<sub>x</sub> molecules, a process which usually needs to be enhanced by energetic particle beams.

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<sup>2</sup>P. Hohenberg and W. Kohn, *Phys. Rev.* **136**, B864 (1964); W. Kohn and L. J. Sham, *ibid.*, **140**, A1133 (1965); exchange and correlation potentials are based on the data from D. M. Ceperley and B. J. Alder, *Phys. Rev. Lett.* **45**, 566 (1980), as parametrized by J. Perdew and A. Zunger, *Phys. Rev. B* **23**, 5048 (1981).

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<sup>4</sup>Following the methodology of Y. Bar-Yam and J. D. Joannopoulos, *Phys. Rev. B* **30**, 1844 (1984).  
<sup>5</sup>The approach is the same as that followed for oxygen by Y. Bar-Yam, S. T. Pantelides, and J. D. Joannopoulos (to be published).  
<sup>6</sup>C. G. Van de Walle, Y. Bar-Yam, and S. T. Pantelides (to be published).  
<sup>7</sup>In principle,  $F^-$  attracts and binds a hole in an effective-mass state. At finite temperature, such holes may be ionized.  
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<sup>9</sup>R. Walsh, *Acc. Chem. Res.* **14**, 246 (1981).