Fluorine-Silicon Reactions and the Etching of Crystalline Silicon

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The interaction between F atoms and crystalline Si, which is essential for etching processes in semiconductor device fabrication, is investigated with state-of-the-art theoretical techniques. A comprehensive picture of F reactions with the Si surface, the bulk, and the near-surface region is obtained, in terms of which the etching progress is elucidated. Insertion of F into Si-Si bonds becomes possible because of relaxed steric constraints in the near-surface region. Dependence of the etch rate on doping follows naturally, in agreement with observations.

Reactive-ion etching of crystalline Si has become the foremost technique for selective removal of material in microdevice fabrication.[1,2] Fluorine is the primary element used for such etching. Despite extensive scientific investigation and debate, the basic F-Si reactions are not yet understood. Experimental data available thus far have not resulted in a comprehensive description of the atomic processes that underly the etching mechanism. The few theoretical studies that have been reported[3] addressed only a small subset of the interesting questions, and were mostly based on approximate techniques whose reliability for solid-state problems has not been established. The question of how F reacts with a Si crystal is, of course, of fundamental importance since F is the most electronegative atom and virtually no knowledge exists about its behavior as an impurity. Here we present the first systematic study of F-Si interactions, using state-of-the-art theoretical techniques: local-density-functional theory, combined with *ab initio* pseudopotentials and large supercells. The reliability of these methods has been proven in a variety of calculations, and is again tested for the system at hand. A comparable study for hydrogen in Si was recently completed,[4] which provided significant new insights about how H reacts singly or in a collective fashion with the Si network.

The purpose of the present paper is to explore in a quantitative fashion all possible ways in which F can interact with the Si matrix: at the surface, as a single impurity in the bulk, in the near-surface region, and in collective bulk processes. At the surface, F atoms tie off dangling bonds. After penetrating the bulk, the behavior of a single F atom in the Si matrix is described in a total-energy surface (including relaxation of the host atoms) which allows us to identify stable sites and migration paths for various charge states. A single F atom in the perfect crystal diffuses as F^- in the interstitial channel, with a migration barrier of ~ 0.7 eV, and is unlikely to disrupt the network. The extra degrees of freedom available for motion of the Si atoms near the surface turn out to be essential for insertion of F into Si-Si bonds: Unconstrained relaxation of the Si neighbors lowers the energy of a F in the bond center by more than 2 eV. This mechanism initiates the disruption of the network, and leads to the formation of a highly fluorinated layer and ultimately etching. Simultaneously, the presence of large concentrations of negative F ions induces band bending near the surface. These effects interact to produce a dependence of the etch rate on substrate doping.

All calculations are carried out with local-density-functional theory[5] and *ab initio* pseudopotentials,[6] in a supercell geometry.[7] Because of the small size and deep potential of the F atom in comparison with the Si atom, 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 is improved here by generation of a "soft" pseudopotential for F, which requires fewer plane waves while still providing an accurate description of the Si-F interaction.[8] Test calculations on molecules (SiF_2 and SiF_4) and on 8-atom unit cells are used to establish the quality of the representation, and the convergence as a function of energy cutoff. We find that 30 Ry (with waves above 15 Ry included in second-order perturbation theory) suffices to obtain energy differences to within 0.1 eV.

First, we study the behavior of F on the Si surface. It has been established experimentally that F atoms tie off dangling bonds in the chemisorption regime.[2] We calculate the bond strength of Si-F bonds for the configuration in which a (111) surface is completely covered with F atoms in the onefold-atop position. The calculation is carried out in a repeated-slab configuration, with six layers of Si atoms and a F overlayer on each side. The Si-F distance is found to be 1.7 ± 0.1 Å. The total energy of this structure is compared with that of an ideal unreconstructed surface and a F atom in free space. The resulting bond strength is 7.3 ± 1 eV. This is comparable to the calculated bond strength of 7.6 ± 1 eV in a SiF_4 molecule. The experimental bond dissociation energy for removal of a F atom from SiF_4 is 6.95 eV.[9]

Our calculated bond strength somewhat overestimates the experimental value, which is typical in density-functional theory.

F atoms which approach the surface after all dangling bonds have been saturated can penetrate the bulk. The affinity level for F is so low that it readily attracts an extra electron when immersed as an interstitial in an electron-rich environment such as the Si bulk. We indeed find that all F-related energy levels in the band structure are buried in the Si valence band, and the impurity inevitably is negatively charged. Charge neutrality requires that the extra negative charge on the F be compensated by a hole at the top of the valence band. Such holes can be attracted to and bound by the F^- in effective-mass states, or become unbound at finite temperature. The presence of these holes is associated with band bending in the near-surface region, which plays an important role in the kinetics of the etching process, as we shall see later on.

We map out the total-energy surface for a single F in the Si crystal. The calculations are performed for a finite set of F positions in a supercell with 16 Si atoms. Convergence as a function of cell size is checked by performance of calculations on 8-, 16-, and 32-atom supercells. The relevant energy differences change by less than 0.2 eV when we go from a 16- to a 32-atom supercell. For each position, the surrounding Si atoms are relaxed in order to find the minimum-energy configuration. In the 16-atom cell, only the nearest Si neighbors of the impurity are relaxed. Relaxation of other shells of Si atoms is studied in a 32-atom cell, at energy cutoffs which are sufficient to analyze the Si-Si interactions that are relevant for these relaxations. Relaxations of additional shells lead to very small differences in the total energy, as checked with a Keating model.[10]

The resulting energy values, which are a function of the F position $\bar{r}$ only, give rise to an energy surface $E(\bar{r})$. An analytical representation of such a surface can be given by a recently developed technique, which takes the full symmetry of the host crystal into account in the generation of the surface.[4] The surface is expanded in a set of basis functions with the symmetry of the crystal. Figure 1 shows a contour plot of such an energy surface of F^-, with the F coordinates confined to the (110) plane through the atoms. The lowest-energy state is for F at the tetrahedral interstitial site, in the negative charge state. F^- can diffuse through the lattice, with a saddle point at the hexagonal interstitial site and an energy barrier smaller than 0.7 eV. No experimental investigations of isolated F impurities in Si have been reported so far to allow a comparison. Our predictions regarding the charge state, stable site, and migration path could be verified using standard experimental techniques for point defects.

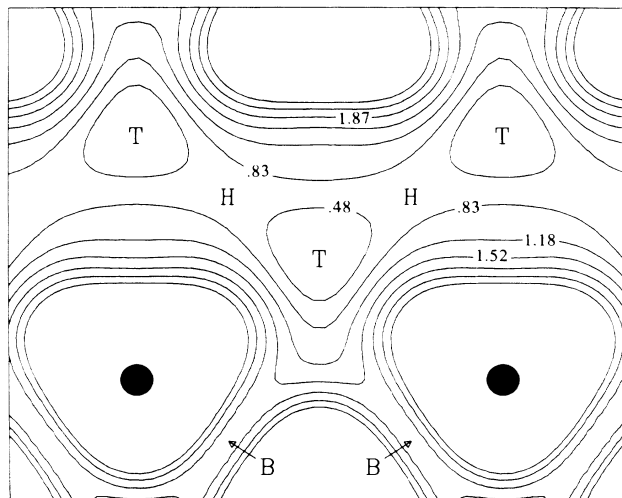We carefully examine all positions in which a single F atom might want to bond to a Si atom, but find no evi-

FIG. 1. Contour plot of the energy surface in the (110) plane for F^- in Si. Atomic positions are indicated by filled circles, as well as the points T (tetrahedral interstitial site, chosen as reference, $E=0$), H (hexagonal interstitial site, $E=0.68$ eV), and B (bond center, $E=1.50$ eV). The energy difference between adjacent contours is 0.34 eV. The migration path through the interstitial channel is clearly visible.

dence for any tendency to weaken specific Si-Si bonds or form a Si-F bond. The bond-center site, with its large charge density, seems particularly likely for a F atom to bind to Si. We find, however, that F^- is ~ 1.5 eV higher in energy at the bond center than at the tetrahedral interstitial site. The nearest Si atoms have to move out over an appreciable distance (~ 0.7 Å) when the F is placed at this site. An energy level is introduced in the upper part of the band gap; it is derived from an antibonding combination of the "dangling bonds" on the neighboring Si atoms which have been moved apart by the introduction of the F. Zero, one, or two electrons can occupy this level in the positive, neutral, or negative charge state, depending on the Fermi-level position. Whatever its charge state, however, the configuration with F at the bond center in *perfect* crystalline Si is always higher in energy than the interstitial site. Nevertheless, the bond-center site offers at least in principle the possibility of transferring from a negative to a neutral charge state, which is essential for the formation of a Si-F bond. We are then left with the question of determining the actual structure in which such a Si-F bond is formed. To answer that, we have to go back to the region near the surface.

From our results on F diffusion in the Si lattice, it is clear that a single F atom in the perfect crystal is not likely to break a Si-Si bond. The bond-center site in perfect crystalline silicon is energetically unfavorable mainly because the tight geometrical constraints imposed by the surrounding Si network levy a high-energy cost for
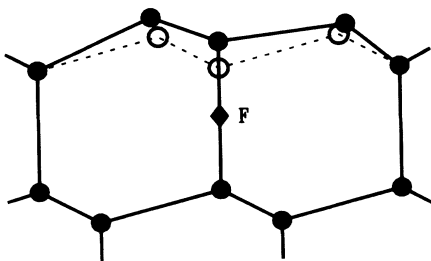
FIG. 2. Schematic representation of the configuration near a (111) surface used to study insertion of F into Si-Si bonds. In the "constrained" structure (open circles and dotted lines), the surrounding crystal opposes relaxation of the Si atoms near the F interstitial. Near the surface, these constraints are removed, the Si atoms move outward, and a F atom can insert at the bond center.

the outward motion of the Si atoms needed to accommodate the F atom and allow the formation of a Si-F bond. These constraints can be relaxed in the immediate neighborhood of the surface, where Si atoms in the uppermost layers have large freedom to move outwards, as schematically illustrated in Fig. 2. We mimic this type of near-surface environment in a series of calculations in which the displacements of Si atoms around a bond-center F atom are not constrained by the surrounding network, i.e., Si atoms on both sides of the F are allowed to relax without energy cost. This is accomplished by performance of the calculations in a (111) superlattice configuration, with six Si atoms and one neutral F atom in each cell. Interactions between neighboring impurities, and the particular incorporation of the strain fields (two dimensional instead of three dimensional) differ from the real system, but the basic features of this model should qualitatively apply to the situation that we wish to study. We find that the lowest-energy configuration occurs for a F atom symmetrically located between two Si atoms, with a Si-F distance of ~ 1.9 Å. For comparison, we also perform superlattice calculations for the "constrained" bond-center structure, similar to the environment for a single F at the bond center in the otherwise perfect network. By comparison with this "constrained" structure, the energy gained through relaxation is ~ 2.3 eV. This energy is clearly sufficient to make the Si-F-Si configuration more stable than interstitial F^-.

Now we turn to a discussion of our results in the context of etching. Experiments[1] have established that F atoms cause spontaneous etching: Gas-phase F reacts with solid silicon to produce primarily SiF_4 (gas). It was shown that the exposure of Si to XeF_2 results in the formation of a fluorosilyl layer on the surface, which contains SiF, SiF_2, SiF_3, and SiF_4. The latter product is the one that desorbs from the surface. The thickness of this layer, under steady-state conditions, is between 10 and 30 Å.[2] 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. Doping of the substrate can have a profound effect on the etch rate.[11,12] Heavily doped n-type Si (n^+) etches fastest, while the etch rate is lowest for heavily doped p-type (p^+). The etch rates for lightly doped n- or p-type Si are very similar.

From our calculations it is evident that F atoms which penetrate the Si crystal are negatively charged. This means that an electron must be removed during the reaction which starts from an isolated (negative) F atom and leads to a neutral Si-F bond, or, alternatively, a hole must be present to annihilate the extra negative charge: $F^- + Si + h^+ \rightarrow SiF$. We propose that the breakup of the Si lattice is initiated by the introduction of a F atom in a Si-Si bond near the surface. This process will occur more efficiently if holes are available to capture the excess electron. Otherwise, the excess electron would be placed in the conduction band, at a cost of ~ 1.2 eV.

The presence of a large concentration of F^- at or near the surface sets up an electric field which forces the semiconductor bands to bend upward. Alternatively, the band bending can be regarded as a way to generate holes in the region near the surface, providing the positive charge to neutralize the negative charge of the F^-. The F^- concentration can be estimated to be of the same magnitude as the concentration of Si atoms on the surface, which is close to 10^{15} cm^{-2}. The amount of band bending depends on the doping of the material. The dependence of the etch rate on doping can then be explained in a natural fashion, through our observation that a large concentration of holes in the near-surface region enhances the reaction probability. For lightly doped n- and p-type material, the band bending and the hole concentration near the surface are similar, leading to similar etch rates. In n^+-type material, the bands show stronger bending, in order to create an inversion layer at the surface. This inversion layer creates a large concentration of holes in a narrow layer near the surface, exactly in the region where holes are required in order to make the insertion of F into Si-Si bonds possible. For a donor concentration larger than 10^{19} cm^{-3}, a hole concentration equal to the F^- concentration (i.e., $\sim 10^{15}$ cm^{-2}) will be confined in a region less than 100 Å from the surface. In p^+-type material, on the other hand, a small amount of band bending, extending over a large distance, is sufficient to create an accumulation layer which neutralizes the F^-. Holes are therefore not preferentially confined near the surface, explaining why this type of material exhibits the lowest etch rates. Indeed, even an acceptor concentration of larger than 10^{19} cm^{-3} only gives rise to $\sim 10^{13}$ cm^{-2} holes in the region within 100 Å from the surface, i.e., 2 orders of magnitude smaller than in the case of n^+ material.

Winters and Haarer have suggested that the transport of negative ions under the influence of an electric field determines the etch rate.[11] They assumed that the

affinity level for F lies below the top of the valence band, but only by ~0.5 eV. Our calculations show that it is hard to associate any particular level in the band structure with the F and that very little F character is present in the energy region between the top of the valence band and 1.8 eV below that. Winters and Haarer stated that, if that were indeed the case, the mechanisms described in their paper would have to be reconsidered. Furthermore, the mechanism proposed by Winters and Haarer neglects the chemistry, and only concentrates on the transport of negative ions through the reaction layer. Such an assumption, however, leads to consequences that are in contradiction with experiment, as discussed in Ref. 12. In our description, the experimentally observed thinner reaction layer for n^+ is a consequence of the enhanced reactivity in the near-surface layer, due to the presence of a large hole concentration in the inversion layer.

Finally, we turn to a comparison between hydrogen and fluorine. For H, we found that Frenkel-pair (vacancy-interstitial pair) formation is exothermic when H is present to tie off dangling bonds.[4] We have explored a similar spontaneous-defect-generation mechanism in the presence of F, but found it to be energetically unfavorable. Clearly, therefore, Frenkel-pair creation is not responsible for etching. Hydrogen etches silicon, but not as efficiently as F does. We attribute this fact to H's ability to diffuse rapidly into the material,[4] so that no large concentrations of H in the near-surface region can be achieved. The barrier for migration of F is higher, leaving larger concentrations of F at or near the surface available for etching. In addition, F "dopes," i.e., becomes F^- and introduces free holes, concomitantly bending the bands and inducing F to etch as described above. If, however, the difference in diffusion properties between H and F is indeed a major factor in the etch rate, it should be confirmed by the temperature dependence of the etching process. Raising of the temperature should make F etching less effective, since F atoms would have more energy to diffuse away from the near-surface regin. Also, H etching would become more effective at lower temperatures. Unfortunately, variation

of the temperature may have other effects than simply changing the mobility of H or F. Nonetheless, at least one experimental study[13] has observed a *decrease* in F etch rate with *increasing* temperature, consistent with the above considerations.

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