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Mechanistic Predictions for Fluorine Etching of Si(100)

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Abstract: We present results of highly correlated ab initio electronic structure calculations on embedded silicon clusters containing 0–4 fluorine atoms that are designed to mimic the Si(100) surface in the initial stages of the fluorine etching reaction. We predict that fluorine atoms initially saturate all the dangling bonds with no activation barrier and with a large release of heat into the solid (6.1–6.4 eV per Si–F bond formed). Above $\theta_F = 1.0$ ML (ML = monolayer), Si–Si bonds start to break, with the reaction still exothermic by 2.9 eV up to $\theta_F = 1.25$ ML. Reaching a coverage of 1.5 ML is either downhill or activated, depending on how the F atoms are deposited. Beyond a coverage of 1.5 ML, we predict that adjacent SiF_2 groups are highly destabilized and should be preferentially etched. These results are consistent with recent experiments involving F atom adsorption on Si(100) and offer the first ab initio heats of reaction for elementary steps in silicon etching by atomic fluorine.

The processing of silicon during the preparation of microelectronic devices often utilizes fluorine plasmas, which provide the means to remove (etch) Si atoms.[1] Fluorine etching is thought to proceed via the formation of intermediate SiF_x species en route to production of SiF_4 (the primary gaseous product).[2–6,9] The current drawback of fluorine etching is that it does not differentiate between various sites in silicon itself and hence cannot yet be controlled on the atomic level. Development of a fundamental understanding of the mechanism by which SiF_x species are produced in the fluorosilyl layer may lead to etching selectivity on a site-by-site basis, by learning which silicon atom sites are most vulnerable to etching and by exerting lateral control over production of those sites. This latter goal prompted both our present work and other experimental[2–9] and theoretical[10–18] studies of the interaction of F atoms with silicon.

Most of the experimental studies have yielded important qualitative information about intermediates in F etching. Photoemission and Auger suggest that dissociative chemisorption of XeF_2 (a clean source of F atoms) leads to SiF, SiF_2, and SiF_3 surface species, which can then react to produce SiF_4.[2,6] A buildup of 2–6 layers of fluorinated silicon (SiF_x) is necessary before etching will commence,[4] with a 10–20 Å thick fluorosilyl layer during steady-state etching.[6] Thermal desorption studies[5,9] have shown that SiF, SiF_2, Si_2F_6, and SiF_3 desorb in addition to SiF_4, albeit at much lower levels.

Previous theoretical investigations of F atom interactions with Si have included semiempirical MNDO models that predicted bridging F atoms are preferred over dangling bond adsorption,[11,18] Hartree–Fock (HF) cluster calculations for F on Si(111),[10,14] configuration interaction (CI) or perturbation theory on clusters containing one or two Si atoms to model formation of SiF_4 from SiF_3[12] or to model HF etching,[17] local density functional theory (DFT) that predicted F saturation of surface dangling bonds followed by insertion of F atoms into Si–Si bonds in the near-surface region,[13] and classical molecular dynamics (MD) simulations with an empirical potential that predicted thermal F atoms will only saturate dangling bonds and that energetic F atoms are needed to induce etching (contrary to experiment).[15,16]

These previous theoretical studies utilized either very small clusters (typically two atoms) that may not represent a surface properly, methods not known to be reliable for predicting relative energetics (e.g., HF, DFT, and MNDO), or an empirical potential that appears to be physically unrealistic. Experimentally, it has been exceedingly difficult to characterize the initial stages of etching beyond a qualitative level because of limitations in experimental probes and because the reaction itself is so complex. Herein we present the first ab initio calculations relevant to F atom etching of Si on fully optimized large clusters along with high-level CI calculations designed to yield reliable energetics. The results from this study provide the first accurate thermochemical data for adsorption/reaction of F with Si(100) as a function of F coverage (θ_F).

The calculations were performed on Si clusters (Si_xH_y, $x = 1$–9, $y = 2$–12) chosen to represent truncated pieces of the Si(100)–2×1 surface. Each surface Si atom on Si(100) is directly bonded to two Si atoms in the second layer and each has two dangling bond orbitals pointing up toward the vacuum in the unreconstructed surface. The surface layer forms surface Si dimers upon reconstruction,[19] via formation of an Si–Si bond between adjacent surface Si atoms, leaving two dangling bonds per dimer that are weakly singlet coupled.[20a]

The largest cluster employed, Si_9H_{12}, has parts of four layers of Si atoms with one surface Si dimer. All of the subsurface Si atoms are saturated with hydrogens so that these Si remain tetrahedrally coordinated (roughly equivalent to embedding the

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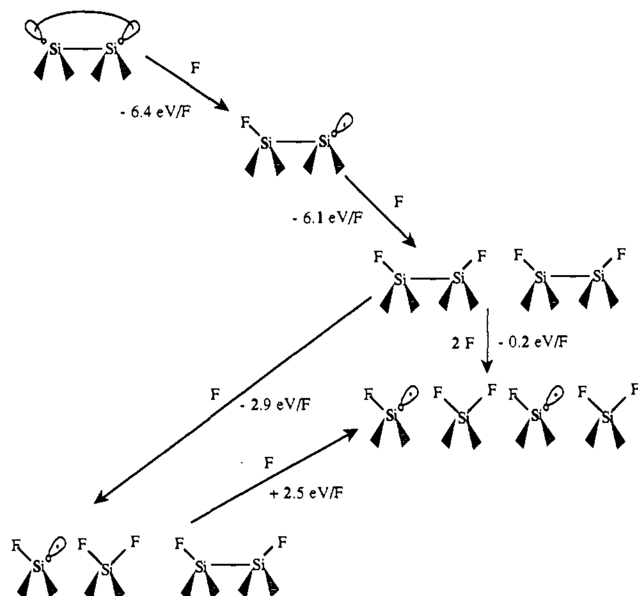

Figure 1. Ab initio GVB/CCCI energetics (in eV) for sequential adsorption of fluorine atoms during the initial stages of etching the Si(100)–2×1 surface.

cluster in the bulk crystal). The minimal basis set used to describe the H atoms was optimized to maintain charge neutrality on all of the Si atoms in the cluster, in order to avoid spurious charge transfer that would be present if a real H atom basis set was used.[20b,24] The surface Si atoms were described by an effective potential for the core electrons and a double-ζ plus polarization (DZP) basis set for the valence electrons (ζ^d = 0.3247).[21] Subsurface Si atoms were treated similarly except that the polarization function was removed. The Dunning–Huzinaga[22] valence DZP basis set (ζ^d = 1.347) with an added set of diffuse s and p functions [ζ^s = 0.112; ζ^p = 0.076] was used to describe the F atoms. Equilibrium reconstructed geometries of the large clusters were obtained by using analytic gradients of generalized valence bond (GVB-PP) wave functions.[23a,24]

A new theoretical strategy for obtaining reliable adsorption energetics is also used here, with details for implementation presented elsewhere.[24] The fully optimized structure of the Si_9H_{12} cluster was mapped on to a smaller Si_2H_4 cluster (where we have replaced all lower Si layers with modified H atoms) when performing configuration interaction (CI) calculations to obtain bond energies and heats of reaction. On the basis of the largest CI calculations performed on both the large and small silicon clusters (essentially a complete active space (CAS)-CI), we estimate the error in relative energetics incurred by this "geometry-mapping" to be ≅0.1 eV.

Since the cluster model of chemisorption normally treats the limit of zero coverage, we also developed a new means of estimating binding energies for chemisorption at high coverages.[24] Essentially, this involves evaluating the lateral interactions between coadsorbates via calculating the interaction energy (normally nonbonded repulsions) between adsorbates on two small clusters as a function of distance between the clusters. These clusters are oriented in such a way that the dominant contributions to nonbonded repulsions are due to the adsorbates. The repulsive forces are evaluated at the GVB-PP level, which should provide an upper bound to the repulsion energy (since dynamical correlations not included in this wave function would tend to decrease this repulsion). We are also careful to evaluate counterpoise corrections[25] as a function of distance for basis set superposition errors that are often present in weakly interacting systems. Since we calculate this repulsive interaction as a function of distance, we are able to use a criterion of minimal repulsions to establish equilibrium adsorbate–adsorbate distances on the surface.[24]

The predicted energetics and mechanism for the interaction of F atoms with these Si clusters at the GVB/correlation-consistent CI (CCCI) level[23b] are depicted in Figure 1. First, we find that F atoms initially attack the dangling bonds of the Si dimers on Si(100)–2×1, with the process being unactivated and more than 6 eV exothermic per Si–F bond formed (6.4 eV for the first Si–F bond and 6.1 eV for the second). Although we cannot compare directly to experimental surface thermochemistry, we can compare to the experimental Si–F bond strength in SiH_3F, which is 6.7 ± 0.4 eV,[26] indicating our predictions are physically reasonable. The F atoms prefer to add to dangling bonds, rather than insert into Si–Si bonds.

Once the dangling bonds are saturated, the surface is covered with Si–F groups only, with the dimer bonds intact (θ_F = 1.0 ML). Saturating the second dangling bond is 2.1 eV more exothermic than forming an SiF_2 group in the second step, which requires breaking the Si–Si bond. (This cost of 2.1 eV provides a rough estimate of the Si dimer bond energy.) Adding a third F to this region of the surface now requires cleaving the Si–Si bond to form an SiF_2 and an SiF group on the surface; this is downhill only 2.9 eV, because of the cost to break the dimer bond and increased F–F repulsions. The most favorable configuration for an SiF_2 is predicted to be adjacent to an F–Si–Si–F saturated dimer and to one SiF radical whose F is pointed away from the SiF_2. Addition of another F to this repeating p(4×1) structure is found to be endothermic by 2.5 eV, because of 6.2 eV/p(4×1) unit cell repulsions for a surface with half SiF radicals and half SiF_2 groups. Thus, at low exposures or with a dilute beam of F atoms, *the p(4×1) structure involving an SiF_2, an SiF, and an F–Si–Si–F dimer may be a stable intermediate phase (θ_F = 1.25 ML).* However, if two F atoms attack neighboring F–Si–Si–F dimers simultaneously at θ_F = 1.0 ML, it is favorable by 0.4 eV to form alternating SiF and SiF_2 groups on the surface (θ_F = 1.5 ML). Such a deposition mechanism may be operative when F_2 is used as the F source.[9]

Finally, we find a significant barrier to addition of F atoms above θ_F = 1.5 ML, because adjacent SiF_2 groups suffer huge nearest-neighbor repulsions (17 eV). This is easy to understand, because the unreconstructed Si–Si distance of 3.84 Å leads to a nonbonded F–F distance of only 1.19 Å for eclipsed SiF_2 groups. (For comparison, the bonding F–F distance in F_2 is 1.41 Å.) This predicted barrier to addition of more F atoms beyond 1.5 ML is consistent with the observed sharp decrease in rate of adsorption of fluorine above this same coverage.[9] We find that concerted twisting of the SiF_2's minimizes this repulsion at a 30° twist but causes considerable subsurface layer strain (since these are distortions toward square-planar Si). Thus, *although SiF_2 is an extremely stable species in the gas phase, it is predicted to be much less favorable than SiF on the surface due to repulsive lateral interactions.* Photoemission data for low exposures of XeF_2 on Si(100)–2×1 also support these predictions.[6b] Thus, further *fluorination/etching may have to proceed sequentially, whereby patches of Si are etched away before others, due to the propensity of SiF_2 to etch more quickly because of its instability.*

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