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Atomic processes during Cl supersaturation etching of Si(100)-(2×1)

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Supersaturation etching starts with Cl insertion into Si-Si bonds of Si(100) and leads to the desorption of $SiCl_2$ pairs. During etching, insertion occurs through a Cl_2 dissociative chemisorption process mediated by single dangling bond sites created by phonon-activated electron-stimulated desorption of atomic Cl. Based on scanning tunneling microscopy results, we identify a surface species, describe its involvement in supersaturation etching, and explore the energetics that control this process. In doing so, we show that insertion occurs at room temperature and that paired dangling bonds of bare dimers also mediate this process.

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The structure and chemistry of Si(100) have been the subject of extensive experimental and theoretical studies. The importance of this surface resides in its use in the integrated circuit technology.[1] In particular, dry etching of silicon is an essential process that requires increasing precision due to the continual miniaturization of devices.

The clean Si(100) surface reconstructs, through dimerization, to remove one of the two dangling bonds (DBs) associated with each atom on the bulk-terminated surface.[2–4] The remaining two dangling bonds, per dimer, control the chemistry of this surface. In principle, the dynamics of etching would seem to be simple since there is only one desorption species, Si dihalide for Cl, Br, and I. However, extensive experimental and theoretical studies have revealed that even this apparently simple process presents a variety of complexities with subtle mechanisms involved. Structural insights into the etching by halogen atoms have come from studies using scanning tunneling microscopy (STM) that reveal the atomic scale morphologies.[5–8] In general, material removal from Si(100) by Cl and Br proceed via step retreat or layer-by-layer etching, resulting in bounded surface roughness.[9–11]

Calculations on the interactions of halogens with Si(100) reveal the atomic-level events involved in surface reactions that lead to dihalide desorption.[12,13] STM studies of the dependence of etch rate on time, flux, and temperature[14,15] have confirmed the reaction pathway for Si(100) proposed originally by de Wijs *et al.*[12,13] Very recently, however, we found another etching mechanism under conditions of supersaturation.[16] By exposing a saturated surface to a flux of Cl_2 at elevated temperature, we determined that etching is possible through a reaction pathway that leads to an unexpected final surface morphology. Here, we extend those studies and identify the structure of a previously mysterious surface moiety, the so-called bright feature (BF) observed during supersaturation etching (SSE),[16] allowing us to propose the sequence of events that control SSE and the energetics involved. Furthermore, we find that halogen dissociation at room temperature leads to insertion on a less than saturated surface and the resulting inserted species are kinetically limited from reaching an available dangling bond site.

The experiments were performed in ultrahigh vacuum (base pressure: 5×10^{-11} Torr) using a room-temperature Omicron STM and RHK electronics. The Si wafers were *p* type, B doped to 0.01–0.012 Ω cm, and oriented within 0.15° of (100). Clean Si(100)-(2×1) surfaces were prepared by standard thermal annealing procedures.[17] A solid-state electrochemical cell made from AgCl doped with 5 wt % Cd Cl_2 provided a constant Cl_2 flux that could be controlled through the applied voltage. After cleaning, the surface was exposed to Cl_2 while slightly above room temperature to reduce the concentration of water and related *c*-type defects.[18] The sample was then annealed at 700 K for 5 min to obtain a saturated Si(100)-(2×1) surface with very low defect density.[19] SSE was achieved by exposing this surface to Cl_2 at 750–825 K. The flux was varied from 3 to 40 $\times10^{-3}$ ML/s, where 1 ML corresponds to the atom density of Si(100).

The accepted reaction pathway for Si(100) etching proposed by de Wijs *et al.*[12,13] is based on first-principles local-density-functional calculations. Within a dimer, a monochloride-dichloride isomerization reaction generates a precursor $SiCl_2$ and a bare Si atom, the so-called Si bystander. The transfer of this Si atom to the terrace creates a vacancy adjacent to the $SiCl_2$, cutting off the reverse isomerization reaction and allowing the $SiCl_2$ unit to ultimately overcome the desorption barrier. In an alternative process, the $SiCl_2$ unit can transfer its Cl adatoms to neighboring Cl-free sites, if such sites exist, and that the now-bare Si atom can also move to the terrace.[20] This gives rise to roughening without etching since there is no desorption. Both etching and roughening reactions produce Si dimer vacancies (DVs) that can grow into dimer vacancy lines (DVLs) and pits. In both cases, the transferred Si adatoms nucleate on the terrace to form regrowth islands. The STM image of Fig. 1(a) shows that heating a Cl-saturated surface at 800 K for 25 min produces pits and islands of different sizes that decorate the surface.

There is agreement that the etching/roughening reactions are hindered on halogen-saturated Si(100) (Refs. 6, 7, and 21) because Cl atoms on neighboring dimers preclude the escape of the Si bystander. However, Trenhaile *et al.*[22,23] demonstrated that bare dimers (BDs) can be generated on a saturated surface by phonon-activated electron-stimulated desorption (PAESD) of atomic Cl. Once this occurs, the surface will etch/roughen through the conventional reactions, as shown in Fig. 1(a).

Until recently, it was believed that any etching would not be possible if the surface was exposed to a Cl_2 flux at high temperature to replenish the Cl lost via PAESD. Experiments

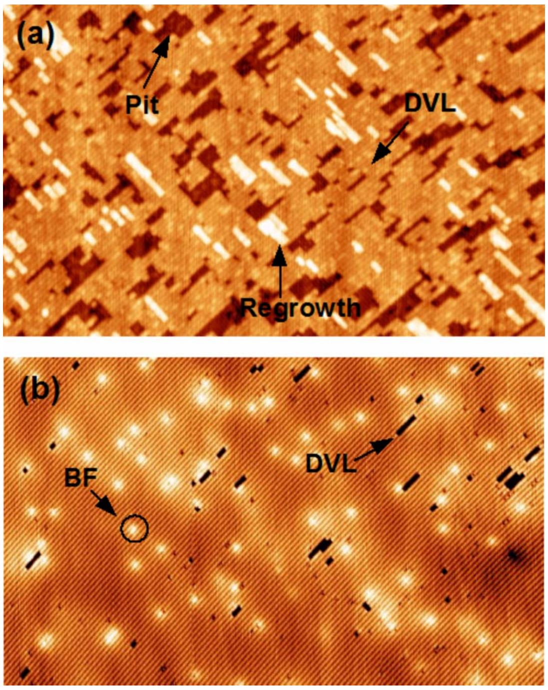

FIG. 1. (Color online) STM images of Si(100)-(2×1) acquired at room temperature. The dimer rows run from the lower left to the upper right. (a) Conventional etching/roughening for a Cl-saturated surface heated to 800 K for 25 min with dimer DVLs, pits, and Si island regrowth feature (90×55 nm^2; −3.0 V sample bias). (b) Surface that was heated to 800 K while being exposed to a Cl_2 flux of $\sim6\times10^{-3}$ ML/s for 40 min. Etching has produced DVLs that have occasionally branched but there is no evidence of regrowth. BFs that extend over three rows such as that within the circle represent moieties related to inserted Cl (90×55 nm^2; −1.4 V sample bias).

showed, however, that etching does occur and this required a new reaction pathway.[16] Figure 1(b) shows a saturated surface after being heated to 800 K for 40 min while being exposed to a Cl_2 flux of 10^{-2} ML/s. Despite the longer time at elevated temperature, compared to Fig. 1(a), the surface is less damaged as DVLs formed but without the concomitant regrowth islands. Significantly, the surface of Fig. 1(b) shows that there are no Cl-free dimers,[24] implying that the Cl_2 flux was sufficient to replenish the Cl lost via PAESD and thereby preventing the conventional reactions. These findings led Agrawal *et al.*[16] to propose another type of surface mechanism, termed supersaturation etching.

The etch pits observed on terraces exhibit size and shape distributions that reflect energy anisotropies around an existing pit.[12] Although energy differences are small compared to the desorption energy, they are sufficient to account for the patterns observed during etching. Once a single vacancy is created on a terrace, it destabilizes its neighbors and vacancy growth will tend to produce a linear vacancy. The fact that they are linear indicates that they are produced by vacancy extension since DVs and DVLs are nearly frozen on a saturated surface.[25] In the early stages of etching, as in Fig. 1(b), this gives rise to a dominance of linear pits that are one row wide. Steps are not expected to play a role in the observed pits as care was taken to acquire images on large *A*-type terraces far away from steps. Therefore, the diffusion and annihilation of existing DVs at a step is frustrated during the supersaturation etching and the cooling down process since the Cl coverage is always ≥1 ML.

Agrawal *et al.*[16] studied the dependence of the SSE etch rate on flux in the range of 750–825 K, finding that it became flux independent for high enough Cl_2 fluxes. This implied that Cl_2 does not simply dissociate and insert at any terrace site, but that insertion was mediated by special surface sites, namely, DBs that facilitate dissociation to produce an adsorbed Cl atom on the surface.[13,26,27] Before the flux-independent regime, the etch rate increased with the Cl_2 flux, indicating that not all of the DBs created by PAESD see impinging Cl_2 molecules. The etch rate increases until all of the DBs react with incoming Cl_2. Since Cl desorption creates the DBs, the PAESD rate should limit uptake and the subsequent etching reactions. When chemisorption takes place, one Cl atom ties up the DB and the second can be incorporated into the surface corresponding to uptake beyond 1 ML. These inserted Cl atoms, termed Cl(i), can diffuse to form $SiCl_2$ units that constitute the desorbing species.

In the flux-independent regime, the etch rate must be equal to the insertion rate and an Arrhenius plot measured in the flux-independent regime should be directly related to the PAESD rate. Agrawal *et al.*[16] showed that the activation energy (2.27 eV) obtained from SSE rate measurements was in excellent agreement with that determined directly from PAESD rate measurements on Cl-saturated Si(100). They also showed that there was ~1 insertion event for every ten Cl_2 dissociation events at DBs.

The SSE reaction path, as proposed by Agrawal *et al.*,[16] is portrayed in Fig. 2. The alternative pathway including species f was not proposed before and will be discussed below. SSE starts with a Si dimer with two terminally bonded Cl atoms, 2SiCl (species a). Such species constitute most of the surface. The desorption of atomic Cl through PAESD generates Si_2Cl (species b). This species has a DB that facilitates the dissociation of an impinging Cl_2. When this happens, one Cl atom goes to the lowest-energy adsorption site, the DB, while the second can be inserted into the surface, Cl(i), starred in the figure. We represent the inserted Cl as a dimer with three Cl atoms (species c), but we do not imply that this is the actual configuration since Cl(i) could insert at the valleys between dimer rows or in the Si backbonds, as discussed below. Cl(i) atoms can diffuse easily[13] and pair up on a single dimer to form $2SiCl_2$, labeled e, which is energetically more favorable than two units of species c. If the impinging Cl_2 flux is not high enough, however, it is possible for Cl(i) atoms to find a dangling bond before encountering another Cl(i). This is described in Fig. 2 as a reaction that annihilates a Si_2Cl to form 2SiCl.[28,29] Desorption of one $SiCl_2$ unit produces species g, which has a single silicon atom. A DV is created with the desorption of the second $SiCl_2$ unit and, thus, there is no residual Si to produce regrowth chains or islands. DVs are nearly frozen on a Cl-saturated surface, implying that they do not diffuse to annihilate at steps during SSE.[25] Since etching is slightly more favorable near a DV than in a defect-free part of the surface, single DVs evolve into DVLs.

Within the described reaction path, two units of species c

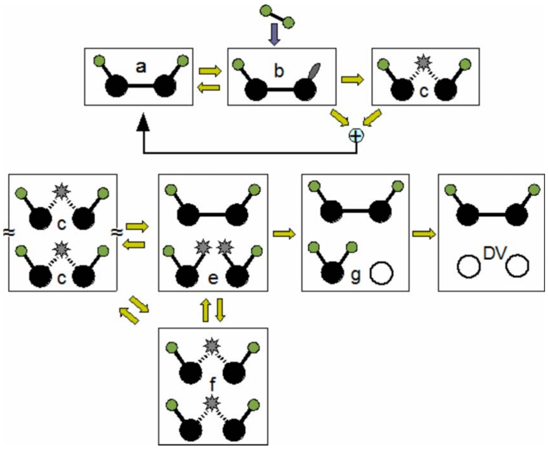

FIG. 2. (Color online) Species and mechanisms during SSE as proposed in Ref. 16 and in the present work. Large solid circles represent Si atoms, smaller circles depict Cl atoms, and Cl(i)'s are shown as stars. The oval in b is a dangling bond. SSE starts with a chlorinated dimer (species a). Species b is generated by Cl atom desorption. Thereafter, an impinging Cl_2 can dissociate at the dangling bond with one Cl atom attaching to the dangling bond and the second inserting into the surface as Cl(i) (species c). As discussed in the text, insertion is depicted as a bridge bond (dashed lines in c and f) but there are other local energy minima. For low Cl_2 flux, a Cl(i) atom can find a dangling bond before pairing with another Cl(i) atom. If this takes place, species b and c convert into species a. Cl(i) can diffuse and pair to form species e, as per Ref. 16, or, in an alternative pathway proposed here, form first species f and then e. Species e loses a $SiCl_2$ molecule to form species g. The desorption of the second $SiCl_2$ unit generates a dimer vacancy without leaving residual Si for regrowth.

directly convert into one unit of species e upon their encounter. Although a viable pathway, it is incomplete in that it does not identify BF in Fig. 1(b). BFs are not present in conventional etching/roughening experiments and are thought to be associated with moeities related to Cl(i). De Wijs *et al.*[13] determined three local minima (LM) binding sites for Cl(i) on a saturated surface. In the one with the lowest energy, LM1, the Cl(i) resides in the valley between two dimer rows bonded to a Si atom of the second layer. In LM2, Cl(i) can break a dimer bond to bridge two Si atoms. In LM3, a Si-Si backbond is broken and Cl(i) binds to a dimer Si atom. The Cl_2 adsorption energy for two Cl(i)'s in independent LM1 states is 0.9 eV; both LM2 and LM3 are 0.2 eV higher in energy than LM1. The diffusion of Cl(i) along the rows can take place on top of the dimers and through the valleys between dimer rows. When diffusing along a valley, Cl(i) must move from an LM1 to the next LM1 and the activation energy is ~0.3 eV; while diffusing along a row, it must move from an LM2 to the next LM2 with an activation energy of ~0.4 eV. It is within reason to argue that due to the low diffusion barrier, species c is too mobile even at room temperature to be observed with STM. As such, BFs cannot be artifacts of a single Cl(i).

To confirm this, we prepared a surface that was ~97% saturated with 3% of BDs and no BFs as shown in Fig. 3(a). We exposed this surface at room temperature to a flux of 4×10^{-3} ML/s of Cl_2 for 25 s, an amount of Cl_2 corresponding to 0.1 ML, to produce the surface shown in Fig. 3(b). From Fig. 3(b), the BD concentration decreased from 3% to 0.67%, and the surface had 0.24% of BFs (referred to as the surface dimer density). BDs can be distinguished from BFs because they are one dimer in width, in contrast to BFs that extend over 2–3 dimer rows. The surface was then annealed at 650 K for 5 min to facilitate the diffusion of Cl(i). Figure 3(c) shows that the BD concentration decreased from 0.67% to 0.42% and the BF concentration decreased from 0.24% to 0.03%. This indicates that BFs are related to a Cl-rich species that can provide Cl atoms for the available DBs. The changes in surface concentration were 0.25% for BD and 0.21% for BFs. Given the small densities and the variations in the densities on the surface, we estimate an error in the difference in number of about 0.03%. To determine these percentages, we analyzed several images of 50×50 nm^2 (~8500 dimers) for each data point, and from the dispersion in the number of features observed we estimated the error reported. We ran the experiment three times with similar results. Since each BF saturates a BD, which has two dangling bonds, we conclude that each BF must have two Cl(i) atoms

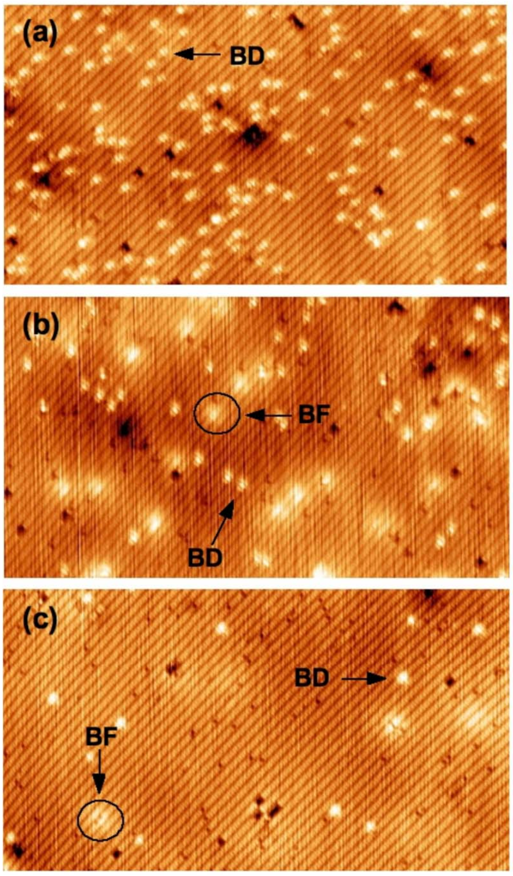

FIG. 3. (Color online) Image (a) represents a surface with ~97% Cl coverage with BDs constituting ~3% of the total surface. Image (b) shows the surface after exposure to 0.1 ML Cl_2 flux at room temperature. The BD concentration decreased substantially and the surface displays many BFs. Image (c) shows the surface after annealing at 650 K for 5 min, demonstrating that the concentrations of both BDs and BFs decrease. These results indicate that each BF has two Cl(i) atoms associated.

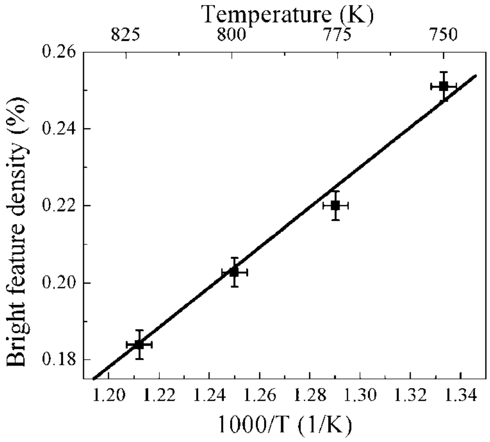

FIG. 4. Arrhenius plot of the bright feature density giving an activation energy of 0.2 eV.

associated with it. However, we cannot rule out that some could have more than two Cl(i)'s. Moreover, the fact that BFs are created at room temperature suggests that Cl_2 dissociation and insertion have a very low barrier.

Species e contains two Cl(i)'s and, if it corresponds to the observed BFs, an Arrhenius plot of the BF density should give the difference in activation energies for Cl insertion (or, similarly, Cl atom desorption) and etching. This can be derived as follows. Since each Cl(i) leads to etching of one Si atom as $SiCl_2$, in the flux-independent regime, the insertion rate must equal the etch rate. Also, the insertion rate is a fraction σ of the rate of creation of DBs via PAESD. Thus, $[\mathrm{BF}]\nu_{\mathrm{et}}\exp(-E_{\mathrm{et}}/k_BT)=\sigma\nu_d\exp(-E_d/k_BT)$, where [BF] is the density of BFs, ν_{et} and E_{et} are the prefactor and the activation energy for the etch rate, and ν_d and E_d are the prefactor and the activation energy for the Cl desorption via PAESD. In the range of 750–825 K, Fig. 4 yields an activation energy of 0.2 eV. This means that the etching activation energy for species e should be ~2.5 eV (0.2 eV higher than that for insertion, which is 2.27 eV) if this species corresponds to the BFs.

De Wijs *et al.*[13] determined two possible atomic configurations resulting in two $SiCl_2$ units on a single dimer by breaking either the dimer bond or a backbond and inserting Cl(i). The activation energy to desorb the first $SiCl_2$ was 1.4 or 1.9 eV and the second was 2.9 eV for the dimer-bond breaking case. The bottleneck to create a dimer vacancy is clearly this second activation energy. Alternatively, Cl_2 from an incident flux could dissociate and saturate the DBs created by the first $SiCl_2$ desorption in the second layer before the second $SiCl_2$ desorption event. The second $SiCl_2$ desorption event then occurs at a cost of 2.5 eV.

In Ref. 13, we also learn that the adsorption energy of Cl_2 to produce any of the configurations with two Cl(i) atoms is 1.9 eV. A single unit of species e is then 1 eV more favorable than two units of species c. For the described reaction scheme of Fig. 2, the energetics would be those shown in Fig. 5(a) reflecting that once species c are formed, they diffuse to form species e and gain 1 eV. To generate a dimer vacancy, once species e is formed, a $SiCl_2$ unit would desorb readily even at 600 K (1.4 eV barrier). Due to its short lifetime, it is unlikely that configuration e would be seen by STM and we conclude that it is not the BF.

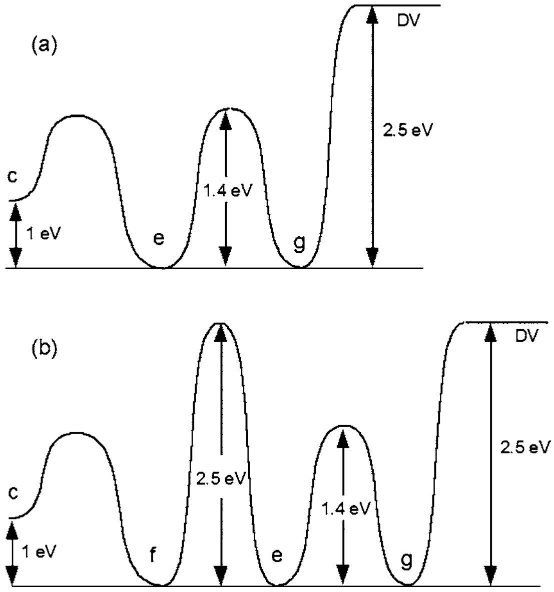

FIG. 5. Energetics during SSE as proposed in (a) Ref. 16 and (b) within the proposed reaction path in which species f, corresponding to the bright features, has been included. In (a), Cl(i) species diffuse and form species e, gaining 1 eV. Species e loses a $SiCl_2$ unit by overcoming a barrier of 1.4 eV to form species g. The second $SiCl_2$ unit must overcome a barrier of 2.5 eV to generate a dimer vacancy without leaving residual Si for regrowth. In (b), inserted Cl atoms diffuse and pair up to form species f. BFs need ~2.5 eV to evolve to species e, which has two volatile $SiCl_2$ units. Once species e is formed, the first $SiCl_2$ unit can desorb with an activation energy of 1.4 eV. Species g, which is more stable than species e, produces a second volatile $SiCl_2$ unit, with a cost of ~2.5 eV, and a dimer vacancy is formed.

Species g is much more stable than species e (2.5 eV barrier to desorb as opposed to 1.4 eV). Though it might be tempting to associate g with the BFs, there are two additional considerations that indicate this is not the case. First, the annealing experiments show that BFs can annihilate BDs, so that BFs must have more than a single Cl(i). This is not compatible with configuration g with a missing silicon atom and a single Cl(i). Second, BFs can be formed at room temperature, as was shown in Fig. 3. At room temperature, there is not enough energy to overcome the 1.4 eV barrier to desorb the first $SiCl_2$ unit from species e to produce species g. Accordingly, we propose that the BFs constitute a precursor of species e as depicted by f in the alternative pathway of Fig. 2.

In the flux-independent regime, we are dealing with a series of reactions, one following the previous one. This means that species c converts to f, f converts to e, e converts to g, and finally g to DVs. The net reaction rates in any of these steps must be the same and constitute the etching rate. We must note that the reactions involving desorption are irreversible because reverse reactions to the conversion of e into g and g into a DV are not possible.

Species e converts very easily into g by desorbing a $SiCl_2$ unit with an activation energy of 1.4 eV. This means that once formed, e evolves very fast into g, leaving its concentration [e] very low. As such, the inverse reaction rate for the conversion of e to f is negligible and the etching rate is then given by the rate at which f converts into e. By reinterpreting the results of Fig. 4 to account for species f, we find that this species is robust since its conversion to species e costs ~2.5 eV, which is 0.2 eV higher than that for insertion, which is 2.27 eV.

In short, the proposed sequence of events taking place during SSE is the following. After insertion, the Cl(i)'s diffuse and pair up to form species f, the BFs. In this picture, it is likely that two or more Cl(i)'s in close proximity attract each other to constitute a BF. BFs convert to species e with an activation energy of 2.5 eV. Once species e is formed, the first $SiCl_2$ unit desorbs easily, thereby cutting off the decay route back to species f. The final $SiCl_2$ unit desorbs at a cost of 2.5 eV; thus, two $SiCl_2$ units desorb in irreversible reactions to create a DV.

These results also demonstrate that Cl insertion and BF formation are not restricted to the realm of SSE, i.e., elevated temperatures and saturated surfaces. Rather, insertion is dictated by the presence of DBs and coincides with dissociative chemisorption. Here, we showed that insertion occurred at room temperature and was mediated by the paired DBs of BDs on a less than saturated surface. However, at lower Cl coverages, the abundance of DBs facilitates the decay route shown in Fig. 2. The barriers for decay were calculated to be ~0.15 eV from LM1 and ~0.3 eV from LM2.[28] At room temperature, these small barriers are easy enough to overcome on a nearly bare surface resulting in the Cl adsorption configurations described by Lyubinetsky *et al.*[30] As a result, we only find evidence of Cl insertion as the Cl coverage nears 1 ML at room temperature and above from the presence of BFs. However, Cl insertion would account for the detection of a bridge-bonded Cl species, LM2, reported by Gao *et al.*[31] after exposing Si(100) to Cl_2 at 100 K. At such low temperature it is quite reasonable that the decay route would be cut off, effectively freezing in the LM2 configuration despite the availability of nearby DBs. This interpretation indicates a very small barrier for insertion and exhibits the need for this process to be taken into account in the dissociative chemisorption of halogens.

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