

Cl Insertion on Si(100)-(2 × 1): Etching Under Conditions of Supersaturation

Abhishek Agrawal, R. E. Butera, and J. H. Weaver

Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801, USA

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We use scanning tunneling microscopy to show that Cl₂ dosing of Cl-saturated Si(100)-(2 × 1) surfaces at elevated temperature leads to uptake beyond “saturation” and allows access to a new etching pathway. This process involves Cl insertion in Si-Si dimer bonds or backbonds, diffusion of the inserted Cl, and ultimately desorption of SiCl₂. Investigations into the etch kinetics reveal that insertion occurs via a novel form of Cl₂ dissociative chemisorption that is mediated by dangling bond sites. Upon dissociation, one Cl atom adsorbs at the dangling bond while the other can insert.

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Si(100) is one of the most thoroughly studied surfaces, and it has served as the test bed for numerous theoretical and experimental advances. Studies that have focused on structural aspects of halogen-induced modifications have revealed a richness of atomic-scale processes with intriguing dependencies on halogen species, concentration, and temperature [1–4]. There is now agreement that the etching/roughening reactions are hindered on a halogen-saturated Si(100), and there has been the belief that uptake beyond one halogen adatom per dangling bond is not possible [2,3,5,6].

In this Letter, we demonstrate a new form of dissociative chemisorption for Cl₂ on Si(100) that allows Cl uptake beyond 1 monolayer (ML). The supersaturated surface then follows a novel etching pathway, studied here with scanning tunneling microscopy (STM). Supersaturation can be achieved by exposing a saturated surface to a flux of Cl₂ at elevated temperature. The mechanism by which Cl inserts is particularly intriguing because it requires a Si dangling bond to activate Cl₂ dissociation, with one atom tying up the dangling bond and the other inserting into a Si-Si dimer bond or backbond with ~10% probability. The dangling bond sites that mediate insertion are produced by phonon-activated electron-stimulated desorption (PAESD) of Cl [7,8], and the PAESD rate limits the uptake and subsequent etching reactions. Studies of the dependence of etch rate on time, flux, and temperature reveal the kinetics and establish the insertion mechanism.

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 Ωcm, and oriented within 0.15° of (100). Clean Si(100)-(2 × 1) was prepared by standard thermal annealing procedures [9]. A solid-state electrochemical cell made from AgCl doped with 5 wt% CdCl₂ provided a constant Cl₂ flux that could be controlled through the applied voltage. Immediately after cleaning, the surface was exposed to Cl₂ at ~300 K and then annealed at 700 K for 5 min to obtain a saturated Si(100)-(2 × 1) surface with very low defect density. Supersaturation etching (SSE) was achieved by exposing

this surface to Cl₂ at 750–825 K. The flux was varied from $3\text{--}40 \times 10^{-3}$ ML/s, where 1 ML corresponds to the atom density of Si(100). The extent of etching was determined by counting the Si dimer vacancies in 4–10 STM images each spanning 100×100 nm², taken away from steps on large A-type terraces. Since it has been shown experimentally that dimer vacancies are nearly frozen on a Cl-saturated surface [10], the vacancy defects could not diffuse to annihilate at steps during SSE (Cl coverage ≥ 1).

Heating Si(100) with a Cl coverage of 1 ML or less results in a combination of etching and roughening reactions [2,3,5,6]. These start when a Si dimer with two terminally bonded Cl atoms, 2SiCl, undergoes an isomerization reaction to form SiCl₂ + Si. The so-called Si bystander can move onto the terrace to produce a single Si vacancy. Etching occurs if the SiCl₂ unit desorbs. Alternatively, roughening occurs if the SiCl₂ unit transfers its Cl adatoms to a neighboring Cl-free site, and the now-bare Si atom transfers to the terrace. Both reactions produce Si dimer vacancies that grow into dimer vacancy lines and pits, together with regrowth islands that form from the excess Si adatoms on the terrace. The inset of Fig. 1 shows the consequences of heating a Cl-saturated surface at 800 K for 25 min. In striking contrast, the main image of Fig. 1 shows what happens when an equivalent surface was heated to 800 K while being exposed to a Cl₂ flux of 6×10^{-3} ML/s for 40 min. It reveals dimer vacancy lines that have occasionally branched, but remarkably there is no regrowth of the sort seen in the inset.

The conventional reactions require Cl-free dimers to which the Si bystander can move [2,3,5,6]. For a saturated surface, the required bare dimer sites are generated by desorption of atomic Cl via PAESD, as demonstrated by Trenhaile *et al.* [7,8]. Such bare dimers are readily evident in STM images [8]. Examination of the surface in Fig. 1 shows that there are no Cl-free dimers, implying that the Cl₂ flux was sufficient to replenish the Cl lost via PAESD and preventing the surface from undergoing the conventional reactions. Thus, we conclude that the etching seen in Fig. 1 results from a new type of surface mechanism, termed SSE.

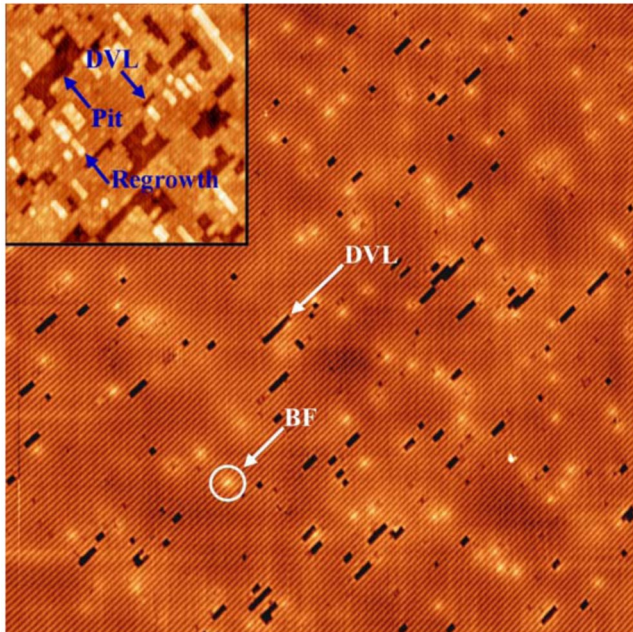


FIG. 1 (color online). STM images of Si(100)-(2 × 1) acquired at room temperature. The dimer rows run from the lower left to the upper right. The inset shows the consequences of conventional etching/roughening for a Cl-saturated surface heated to 800 K for 25 min with dimer vacancy lines (DVLs), pits, and Si island regrowth features. (38 × 38 nm²; -3.0 V sample bias) The main image represents an equivalent surface that was heated to 800 K while being exposed to a Cl₂ flux of $\sim 6 \times 10^{-3}$ ML/s for 40 min. Etching has produced DVLs that have occasionally branched, but there is no evidence of regrowth. Bright features like within the circle (BF) represents moieties related to inserted Cl (100 × 100 nm²; -1.4 V sample bias).

Images equivalent to that of Fig. 1 were obtained for samples exposed to fluxes of $(3.2\text{--}6) \times 10^{-3}$ ML/s during equivalent 800 K–40 min cycles. The results show that the extent of SSE increases linearly with flux, emphasizing that the impinging Cl₂ must produce extra inserted Cl, denoted Cl(i), to etch the surface. Therefore, SSE should involve steps associated with Cl₂ dissociation and insertion to produce Cl(i), diffusion of the Cl(i) moieties and their pairing up to form a new type of volatile precursor, and finally desorption of SiCl₂. Each Cl(i) forms one potentially volatile SiCl₂ unit. Insertion of one Cl(i) into the dimer bond produces a Si₂Cl₃ unit with bridge-bonded Cl while two will produce a 2SiCl₂ unit. It is this latter structure that we associate with etching since its desorption will create a dimer vacancy without leaving residual Si for regrowth.

Figure 1 also shows bright features (BFs) scattered on the post-SSE surface that were not present on the starting Cl-saturated surface. On surfaces prepared such that BFs were present, together with Cl-free dimers, a mild anneal to ~ 700 K reduces the concentration of both. Therefore, we associate these BFs with moieties related to extra inserted Cl on the surface.

To investigate the SSE kinetics and determine whether insertion or desorption is the rate limiting step, we moni-

tored the amount of material removed as a function of time at 825 K with a Cl₂ flux of 1×10^{-2} ML/s. (We assume that Cl(i) diffusion is thermally activated with a much lower barrier than dissociation/insertion and desorption [11]). Figure 2 shows that the amount of etching increased linearly with time, demonstrating that the rate remained constant as the surface evolved. If desorption were faster than insertion, then the etch rate would simply reflect the insertion rate, which should be constant for a given temperature and flux, consistent with Fig. 2. On the other hand, if desorption were slower than insertion, then there would be an accumulation of Cl(i), and the desorption rate would increase. This should continue until the increasing desorption rate equaled the insertion rate and a steady-state is reached with the Cl(i) concentration and the etch rate remaining constant. Figure 2 shows that this is not the case as there is no period for which the rate increases before becoming constant. We conclude that SSE is rate-limited by the Cl insertion step.

To learn more about the insertion mechanism, we studied the dependence of etch rate on flux in the range 750–825 K, when the flux was always sufficient to replenish the Cl lost by PAESD. Figure 3 shows that the etch rate at 800 K initially increases with flux but then plateaus at $\sim 6.51 \times 10^{-6}$ ML/s. The same trend is observed at 825 K. The figure also shows a plateau region for 750 and 775 K. Thus, the etch rate has a distinct flux-independent regime at all temperatures studied. This is interesting as it implies that a simple picture of Cl₂ dissociation and insertion at saturated terrace dimer sites does not apply—if it did, the insertion rate and hence the etch rate would increase monotonically with flux.

The flux-independent regime indicates that insertion is mediated by special surface sites. We know that heating a Cl-saturated surface produces dangling bonds (DBs) by the PAESD process. These DBs should be able to induce Cl₂ dissociation [6,12], thus potentially linking them to the insertion process. At a DB, the incoming Cl₂ molecule can dissociate with one Cl atom tying up the DB. The second atom can then either be scattered into the gas phase

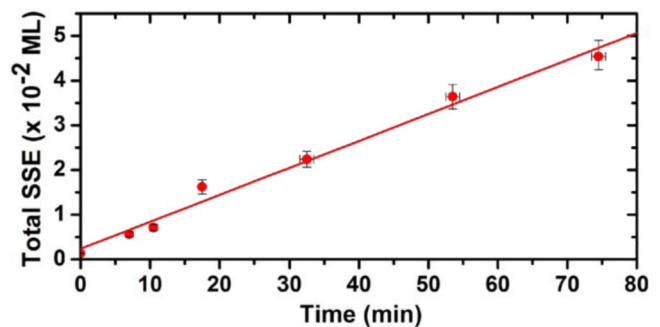


FIG. 2 (color online). Amount of etching at several time intervals during progressive SSE at 825 K for a flux of 1×10^{-2} ML/s. The straightline fit shows that the etch rate remained constant.

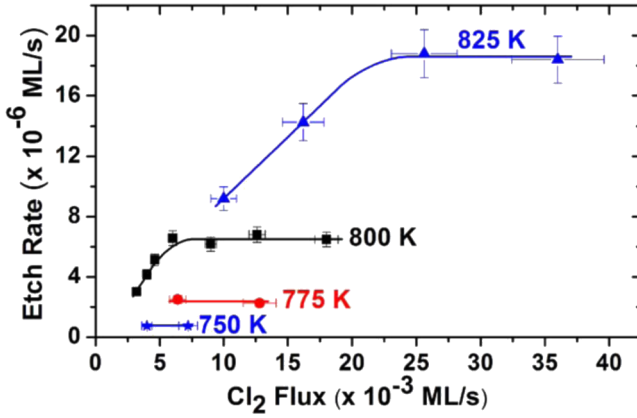


FIG. 3 (color online). Etch rates for SSE in the range of 750–825 K as a function of incident Cl_2 flux. At 800 K, the etch rate initially increases with flux but then plateaus at $\sim 6.51 \times 10^{-6}$ ML/s. The solid line is a guide for the eye. The same trend is observed for 825 K. For 750 and 775 K, the plateau region in etch rate is shown. Thus, the etch rate has a distinct flux-independent regime at all temperatures studied.

or it can be adsorbed on the surface by inserting into a Si-Si dimer bond or backbond [6,12,13].

The flux-dependent regime of Fig. 3 reflects the fact that at lower flux values, not all of the DBs created by PAESD see impinging Cl_2 molecules. These unreacted DBs are eliminated by capturing mobile $\text{Cl}(i)$, which converts to a terminally bonded Cl , $\text{Cl}(a)$ [14]. As the Cl_2 flux is increased, more DBs interact with impinging Cl_2 , and the insertion rate increases. This also reduces the conversion of the active etchant $\text{Cl}(i)$ to $\text{Cl}(a)$. The net result is an increase in the etch rate which continues until the flux is sufficiently high that all of the newly created DBs react with the incoming Cl_2 , representing the onset of the flux-independent regime.

Based on the above model, the insertion process in the flux-independent regime should be rate-limited by the creation of DB sites. The insertion rate, R_I , can be written as

$$R_I = \sigma R_{\text{PAESD}} \quad (1)$$

where R_{PAESD} is the rate of creation of DBs via PAESD and σ is the probability that atomic Cl produced from Cl_2 dissociation leads to insertion [15]. Because of faster desorption rate, the total amount of $\text{Cl}(i)$ is small, and the Cl surface coverage is always near unity. From Refs. [7,8]

$$R_{\text{PAESD}} = \nu_{\text{PAESD}} \exp(-E_{\text{PAESD}}/k_B T) \quad (2)$$

where ν_{PAESD} and E_{PAESD} are the prefactor and the activation energy for the PAESD-controlled DB creation. SSE is rate-limited by insertion, and with SiCl_2 as the desorbing species, each $\text{Cl}(i)$ leads to the loss of one Si atom. Thus, the measured etch rate equals the insertion rate. From Eqs. (1) and (2), the SSE etch rate can then be written as

$$R_{\text{SSE}} = R_I = [\sigma \nu_{\text{PAESD}}] \exp(-E_{\text{PAESD}}/k_B T) \quad (3)$$

$$\ln(R_{\text{SSE}}) = \ln[\sigma \nu_{\text{PAESD}}] - E_{\text{PAESD}}/k_B T. \quad (4)$$

Figure 4 shows an Arrhenius plot using the etch rates measured in the flux-independent regime of Fig. 3. From a straightline fit to Eq. (4), we find that $[\sigma \nu_{\text{PAESD}}] = 1 \times 10^{9.0 \pm 0.2} \text{ s}^{-1}$ and $E_{\text{PAESD}} = 2.27 \pm 0.04 \text{ eV}$. This value of E_{PAESD} , obtained from SSE rate measurements, is in excellent agreement with that of $2.26 \pm 0.05 \text{ eV}$ determined directly from PAESD rate measurements on Cl -saturated $\text{Si}(100)$. The PAESD experiments were done in the temperature range of 700–800 K following the same protocol as Trenhaile *et al.* [8]. From these, we deduced a value of $1 \times 10^{10.0 \pm 0.3} \text{ s}^{-1}$ for ν_{PAESD} [16] which gives a value for σ of $0.1 \times 10^{\pm 0.4}$. Physically, this means that there is ~ 1 insertion event for every 10 Cl_2 dissociation events at DBs. The agreement between E_{PAESD} and a physically meaningful value of σ (< 1) serve to confirm the insertion mechanism.

These results point to a new mechanism of Cl_2 dissociative chemisorption, as depicted in Fig. 5(a). Recent studies of O_2 and F_2 interaction with $\text{Si}(100)$ also reported dissociative chemisorption mediated by DBs [12,17,18]. In contrast to Cl_2 , however, the DB merely acts as a catalyst for O_2 dissociation. Following dissociation, both O atoms chemisorb into lower energy adsorption sites, either at the dimer bond or the backbond, leaving the DB intact. This can be attributed to the divalent nature of O; for monovalent Cl, the lowest energy adsorption site is the DB [14]. For the chemically alike F_2 , the DB plays a similar role in dissociation; however, the authors considered adsorption of the second F atom only at another DB site. They argued that it could not adsorb on a saturated dimer. Our findings show that such adsorption is possible with a probability of $\sim 10\%$ (for Cl), opening up a new reaction channel. This discovery should stimulate further investigations into halogen chemisorption on $\text{Si}(100)$ and similar systems.

Subsequent to insertion, the atomic events involving $\text{Cl}(i)$ in the SSE process can be envisioned as follows;

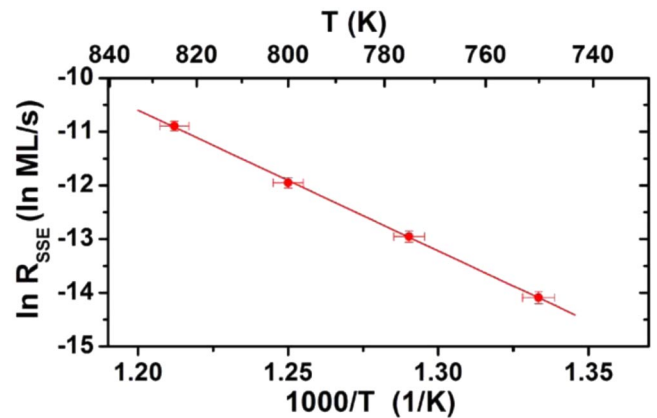


FIG. 4 (color online). Arrhenius plot using etch rates measured in the flux-independent regime of Fig. 3 giving the kinetic parameters for the SSE process. Straightline fit to Eq. (4) gives $[\sigma \nu_{\text{PAESD}}] = 1 \times 10^{9.0 \pm 0.2} \text{ s}^{-1}$ and $E_{\text{PAESD}} = 2.27 \pm 0.04 \text{ eV}$.

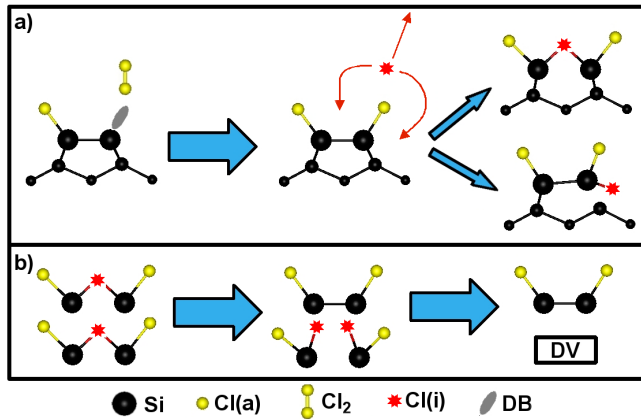


FIG. 5 (color online). (a) Schematics for insertion where the Cl_2 molecule dissociates at a DB, producing atomic Cl that could leave the surface or insert. (b) Two Cl(i) species in dimer bonds could diffuse to pair-up on the same dimer forming 2SiCl_2 , a favorable precursor for desorption, which creates a dimer vacancy, DV.

schematics for one of the possibilities is shown in Fig. 5(b). Pairing of two Cl(i) on a dimer should be favored over one per dimer [19] and hence the relatively facile diffusion should lead to formation of favorable precursors for desorption, such as 2SiCl_2 . Once paired, further diffusion would favor pairwise motion [20], conserving the volatile state. Etching then results from desorption of both SiCl_2 species to create a dimer vacancy without residual Si for regrowth. Once formed, the dimer vacancy would act as a capture site for Cl(i) moving along the dimer row. At these sites, desorption barriers for SiCl_2 are expected to be significantly lower due to gains in energy from rebonding of second layer Si [6], and desorption results in the growth of dimer vacancy lines, as observed in Fig. 1.

The SSE pathway provides an exciting opportunity to study the complementary nature of growth and “un-growth” and to control the etch morphology. Here, production of the active etchant Cl(i) from gas phase Cl_2 assumes the role of adatom deposition. Cl(i) diffusion and the ultimate desorption of SiCl_2 creates a stable nucleus, a dimer vacancy, which can grow into a vacancy line. As in the growth process, the Cl insertion rate can be independently controlled at a given temperature either by using atomic Cl to produce Cl(i) or by varying the DB creation rate via electron/photon-stimulated Cl desorption to override thermally activated PAESD [21,22]. In addition, ion bombardment can be used to produce a desired concentration and distribution of dimer vacancies [23] that would act as nuclei for directed growth of vacancy structures. Finally, switching from Cl to Br will allow for a different “adatom” to be deposited.

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