

## Large Island Formation versus Single-Site Adsorption for Cl<sub>2</sub> Chemisorption onto Si(111)-(7×7) Surfaces

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(Received 10 December 1993)

Scanning tunneling microscopy and molecular beam techniques are used to investigate adsorbate structure as a function of reactant translation energy. When a Si(111)-(7×7) surface is dosed with a monoenergetic Cl<sub>2</sub> beam of translational energy less than 0.11 eV, the dominant adsorbate structure is SiCl islands. Conversely, for 0.44 eV Cl<sub>2</sub> dosing, only single-site center-atom preferred chemisorption is present. It is proposed that center-atom preferred reaction results from direct activated chemisorption and island formation results from precursor mediated chemisorption.

PACS numbers: 68.35.Fx, 34.50.Lf, 81.60.Cp, 82.65.My

Adsorbate structures for a given gas-surface system can show great diversity due to inequivalent sites within the surface unit cell, surface defects and/or steps, and multiple chemisorption mechanisms. By combining monoenergetic molecular beam dosing with scanning tunneling microscopy (STM) [1], we have directly observed the effect of variation in chemisorption mechanism upon local adsorbate structure for Cl<sub>2</sub>/Si(111). For gas-metal surface chemistry, adsorption often proceeds via a mobile-precursor mechanism at low incident translational energies and a direct activated mechanism at higher incident translational energies [2,3], and different adsorption mechanisms can result in very different adsorbate structures [4,5]. In precursor mediated chemisorption, the molecule physisorbs to the surface and then subsequently chemisorbs by either migrating to a surface site with a lower chemisorption barrier or by using the thermal energy of the surface to overcome the barrier to chemisorption. In contrast, for direct activated chemisorption, the molecule uses only its incident kinetic energy to overcome the barrier to chemisorption. To understand the fundamentals of halogen-semiconductor surface chemistry, one must also determine the adsorbate structures from each of the chemisorption mechanisms.

In this Letter, we have studied the adsorption mechanism of Cl<sub>2</sub> onto the Si(111)-(7×7) surface. At low incident Cl<sub>2</sub> energies, where precursor mediated chemisorption is dominant, SiCl island formation is observed indicating that Cl<sub>2</sub> has dissociated on the surface to form silicon monochlorides that are located in giant two-dimensional islands. Island formation can occur due to the mobility of the Cl<sub>2</sub> in its physisorption state prior to dissociation to form SiCl. However, for high translational energy Cl<sub>2</sub> dosing of Si(111)-(7×7), direct activated chemisorption is dominant and only single-site adsorption is observed by STM. In single-site adsorption, the SiCl is observed to be at nearly randomly located sites and no large islands of SiCl are observed.

Previous studies on Cl<sub>2</sub> chemisorption onto Si(111)-(7×7) have shown that Cl<sub>2</sub> dissociatively chemisorbs to form SiCl at low coverage and SiCl<sub>1-3</sub> at high coverage

[6-11]. The structural modifications induced by Cl<sub>2</sub> from an electrochemical source upon reaction with Si(111)-(7×7) have been carefully studied using scanning tunneling microscopy [12-14]. However, the adsorption mechanism of Cl<sub>2</sub> produced by an electrochemical source on the Si(111)-(7×7) surface is still not fully understood because the Cl<sub>2</sub> from an electrochemical source has an unknown velocity and vibrational distributions plus an unknown atomic Cl composition [15]. It has recently been shown that the sticking probability of Cl<sub>2</sub> onto the Si(111)-(7×7) surface is a strong function of surface temperature at incident translational energies less than 0.15 eV but independent of surface temperature at translational energies higher than 0.2 eV. This indicates that there is a precursor mediated chemisorption mechanism at low translational energy (< 0.15 eV) and only a direct activated mechanism at higher translational energy (> 0.2 eV) [16].

The experimental apparatus has a diffusion-pumped ultrahigh vacuum (UHV) chamber and a molecular beam source chamber. The commercial STM is mounted in the UHV chamber with base pressure of  $1.5 \times 10^{-10}$  torr. The Cl<sub>2</sub> beam of different translational energies was generated by expanding pure Cl<sub>2</sub> or mixtures of Cl<sub>2</sub> and He or Xe through a pulsed valve at 300 K. The rotational temperature of Cl<sub>2</sub> is expected to be below 10 K because rotational temperatures for N<sub>2</sub>, F<sub>2</sub>, and I<sub>2</sub> under similar experimental conditions normally drop below 10 K. The vibrational temperature is unknown. However, it is expected to be below 200 K and thus about 98% Cl<sub>2</sub> is in its ground vibrational state. The monoenergetic beam was passed through a skimmer before entering the UHV chamber. The clean Si(111)-(7×7) surface was prepared by heating an arsenic-doped (0.005  $\Omega$  cm) Si(111) wafer to  $1200 \pm 3^\circ\text{C}$  for 30 s, and then annealing at  $600 \pm 1^\circ\text{C}$  for 2 min. The sublimation defect (missing adatom) density of our clean Si(111)-(7×7) surface is less than 2%. All experiments were performed with a normal incidence Cl<sub>2</sub> beam and a 300 K surface temperature. The images shown are standard constant-current topography in which the bias voltage refers to the voltage on the tip.

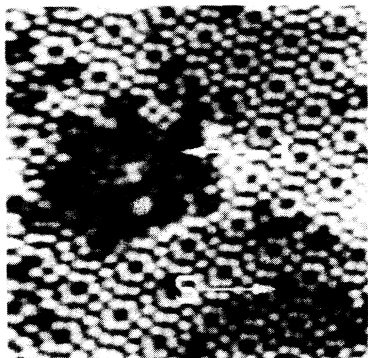


FIG. 1. STM topograph of a Si(111)-(7 $\times$ 7) surface exposed to a 0.05 eV Cl<sub>2</sub> beam (bias = -1.0 V). The scan size  $\sim$ 200 Å $\times$ 200 Å. The dark areas are SiCl adsorbates and bright sites represent unreacted adatoms. The image shows large island formation (marked by an *I*) and single-site reacted adatoms (marked by an *S*).

Figure 1 shows a STM topograph of the Si(111)-(7 $\times$ 7) surface dosed with a Cl<sub>2</sub> beam of 0.05 eV incident translational energy. The STM image was recorded at -1.0 V. The dark areas are reacted Si adatoms and bright sites represent unreacted adatoms. Reacted adatoms, SiCl, appear to be dark at low bias voltage because the adatom dangling-bond states are eliminated by Cl, and the Si-Cl derived  $\sigma^*$  empty state is far from the Fermi level [14]. It is clearly seen in Fig. 1 that a large island is formed (marked by an *I*) and there are some single-site reacted adatoms (marked by an *S*). In general, island formation reflects the strong interactions between mobile adsorbates and reacted sites and/or adsorbate-adsorbate interactions. Strongly bound SiCl is not expected to diffuse on the Si(111)-(7 $\times$ 7) surface at 300 K, and this is confirmed by experiments [7,12]. Thus SiCl island formation probably results from the mobility of physisorbed Cl<sub>2</sub>. A survey of the single-site reacted adatoms (from a large amount of STM images) shows about a 2:1 ( $1.9 \pm 0.2$ ) preference for center adatoms. Figure 2 is a large STM scan of Si(111)-(7 $\times$ 7) surface dosed with a Cl<sub>2</sub> beam of incident translational energy 0.11 eV. The depressions in Fig. 2 are SiCl islands. Figure 2 shows that the step edge (marked by an arrow) is not the preferred nucleation site. Clearly all islands are round and some islands are more than 100 Å from neighboring islands. It is known that the sticking probability under our experimental conditions is above 50% onto the clean surface but 0% onto the adsorbate covered portions of the surface [16]. Therefore, island growth by Cl<sub>2</sub> directly adsorbed on the perimeters of islands is very unlikely. In addition, it is known that SiCl is not mobile on Si(111)-(7 $\times$ 7) surfaces at 300 K [7,12]. Therefore, island growth probably occurs by Cl<sub>2</sub> physisorbing to the unreacted portions of the surface and migrating to the edges of the islands prior to dissociation. It is surprising

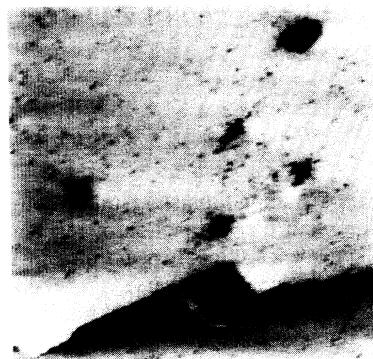


FIG. 2. A large STM scan of a Si(111)-(7 $\times$ 7) surface exposed to a 0.11 eV Cl<sub>2</sub> beam (bias = -1.0 V). The scan size  $\sim$ 1000 Å $\times$ 1000 Å. The arrow points to a step edge. The depressions in the three-dimensional rendering are SiCl islands. All islands are round-shaped and some islands are more than 100 Å apart.

that physisorbed Cl<sub>2</sub> molecules can migrate more than 100 Å prior to dissociation on surfaces with dangling bonds. We have estimated that the lifetime of physisorbed Cl<sub>2</sub> is about 800 ns using a simple 2D gas model [17].

It has been shown that reacted sites (SiCl species) appear to be darker than unreacted sites in constant-current STM topographs at low bias voltage and brighter at higher bias voltage on Si(111)-(7 $\times$ 7) surface [14]. This gives us a unique way to determine the features inside the islands. Figure 3 shows two STM images of the same area at bias voltages -1.0 and -2.2 V, respectively. The small darker island in Fig. 3(a) appears brighter in Fig. 3(b). Theoretical calculations predict that the Si-Cl derived  $\sigma^*$  empty state is about 4 eV above the Fermi



FIG. 3. STM topographs of a single area on a Si(111)-(7 $\times$ 7) surface exposed to a 0.05 eV Cl<sub>2</sub> beam as a function of tip-surface bias voltage. (a) Bias is -1.0 V. (b) Bias is -2.2 V. The scan size  $\sim$ 150 Å $\times$ 150 Å. In (a) the dark areas are SiCl adsorbates and bright sites represent unreacted adatoms. In (b) the SiCl adsorbates are brighter than the unreacted atoms outside the island and the sites inside the island that remain completely dark (marked by arrows) are most probably sublimation defects.

level but disperses strongly over the Brillouin zone [18]. Therefore, the reacted areas appear brighter at high bias voltage because electrons start tunneling into the tail of this  $\sigma^*$  state. Figure 3(b) shows that the  $(7\times 7)$ -like structure is preserved inside the island. However, some sites inside the island remain completely dark (marked by an arrow), and these dark sites are probably sublimation defects.

At present, we cannot definitively identify the initial nucleation centers for physisorbed  $\text{Cl}_2$  on the surface. However, we speculate that sublimation defects are probably the nucleation centers since each sublimation defect results in the formation of dangling bonds on three adjacent rest atoms; these highly reactive dangling bonds are likely to induce dissociation of  $\text{Cl}_2$  [19]. Island growth probably results from two factors: first there may be a strong interaction between physisorbed  $\text{Cl}_2$  and reacted sites at the perimeter of the islands. Second, the physisorbed  $\text{Cl}_2$  should have lower dissociation barrier at adatoms just outside the island because Si adatoms just outside the island should have an increased electron density of unsaturated dangling bonds due to reverse charge transfer from adjacent reacted rest atoms [1]. The detailed interaction of physisorbed  $\text{Cl}_2$  and steps is unknown. However, it is likely that each Si adatom on step edges is still triply bonded and has one dangling bond since  $7\times 7$  reconstructions at step edges are well preserved [20]. Therefore, except for small distortions at step edges, it is possible that adatoms at step edges have similar electron density to those on terraces. Equivalent electron densities at step and terrace sites would explain the absence of  $\text{Cl}_2$  nucleation at steps.

Upon further increasing incident translational energy, we observe very different structures of adsorbates on the surface. Figure 4 shows large and small area STM topographs of the  $\text{Si}(111)-(7\times 7)$  surface dosed with a  $\text{Cl}_2$

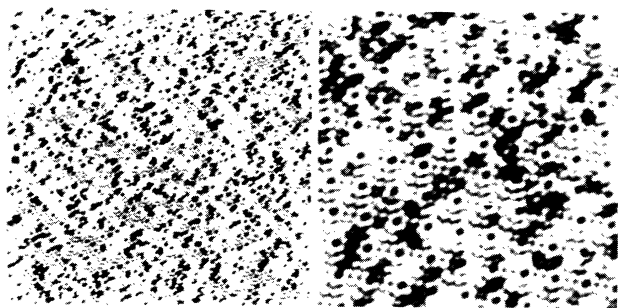


FIG. 4. STM topographs of a  $\text{Si}(111)-(7\times 7)$  surface exposed to a 0.44 eV  $\text{Cl}_2$  beam (bias = -1.0 V). (a) The scan size  $\sim 600 \text{ \AA} \times 600 \text{ \AA}$ . (b) The scan size  $\sim 250 \text{ \AA} \times 250 \text{ \AA}$ . The dark areas (marked by an arrow) are SiCl adsorbates and bright sites represent unreacted adatoms. There is no island formation and only center-adatom preferred reaction is observed. The ratio of the number of reacted center adatoms to that of reacted corner adatoms is about 2:1 at low coverage.

beam of incident translational energy 0.44 eV. Both STM images were recorded at -1.0 V. In Fig. 4, the dark areas (for example, marked by an arrow) are SiCl adsorbates and bright sites represent unreacted adatoms. The striking feature of the images shown in Fig. 4 is that there is no island formation and only center-adatom preferred reaction is present on the surface. After carefully examining many STM images, we have found that the ratio of the number of reacted center adatoms to that of reacted corner adatoms is about 2:1 ( $2.0 \pm 0.3$ ) at low coverage. This behavior is very similar to that observed for the reaction of  $\text{H}_2\text{O}$  with  $\text{Si}(111)-(7\times 7)$  [1].

The existence of two readily distinguishable adsorbate structures on the  $\text{Si}(111)-(7\times 7)$  surface at very different incident translational energies suggests that there are two adsorption channels. At high incident translational energies, direct activated chemisorption is the only adsorption channel. At low incident translational energies, precursor mediated chemisorption is dominant. The recent sticking measurements of  $\text{Cl}_2$  on  $\text{Si}(111)-(7\times 7)$  have shown that there is a precursor mediated chemisorption mechanism at incident translational energies less than 0.15 eV and a direct activated chemisorption mechanism with a barrier of 0.05 eV [16]. This is consistent with our observations that for incident translational energies less than 0.11 eV two adsorption mechanisms coexist, as shown in Fig. 1, island formation and single-site reaction.

If chemisorption is direct and dissociative, one would expect that the reaction takes place very uniformly on the surface. However, the adsorbate structure from 0.44 eV  $\text{Cl}_2$  dosing in Fig. 4(b) shows that the reaction is not completely uniform over the surface; instead some unit cells are close to 100% reacted, but some are intact. The sticking measurements have shown that only a single site is needed for  $\text{Cl}_2$  chemisorption onto the  $\text{Si}(111)-(7\times 7)$  surface [16]. One possible explanation consistent with this result is that there is an activated molecular chemisorption state with a very low barrier to dissociation. For direct activated chemisorption,  $\text{Cl}_2$  first adsorbs in this molecular chemisorption state for a very short time (much shorter than that of physisorbed  $\text{Cl}_2$ ), then dissociates to form two SiCl species. It is possible that there is a strong attraction between molecularly chemisorbed  $\text{Cl}_2$  and nearby reacted sites which results in the observed nonuniform adsorbate structure in Fig. 4(b) instead of the large island in Fig. 1. We note that molecularly chemisorbed  $\text{Cl}_2$  is expected to have a very low mobility compared to physisorbed  $\text{Cl}_2$  due to the difference in bonding energy to the surface. A similar activated molecular chemisorption state is known to exist for  $\text{O}_2$  chemisorption on Pt(111) and  $\text{N}_2$  on Fe(111); for these systems there are three adsorption states: physisorption, molecular chemisorption, and dissociative chemisorption [21,22]. Very recent molecular dynamics calculations also show that a molecular chemisorption state exists when  $\text{Cl}_2$  molecules with 1 eV incident energy interact with  $\text{Si}(111)-(2\times 1)$  surfaces [23]. The direct activated

chemisorption results in about a 2:1 reactivity ratio of center to corner adatoms at all translational energies. This can be envisioned by a concerted reaction mechanism in which dissociation of chemisorbed  $\text{Cl}_2$  ties up two dangling bonds with one Cl attached to the adatom and the other to the rest atom. For Si(111)-(7 $\times$ 7), center adatoms have two rest-atom neighbors while corner adatoms have only one; this provides a reasonable explanation for the center-adatom preferred reaction [1].

Another possible chemisorption mechanism is "hot" atom formation upon dissociation as shown for  $\text{O}_2$  chemisorption onto the Al(111) surface [24]. If this mechanism dominated, we would see that  $\text{Cl}_2$  dissociates instantaneously upon impinging the surface with one Cl attached to the Si adatom and the other Cl diffusing on the surface ("hot" Cl atom). This hot Cl atom would find a dangling bond adjacent to the reacted site and form SiCl. This process indeed can result in nonuniform reaction and single-site adsorption. However, it is inconsistent with the reactivity ratio of center to corner adatoms being about 2:1 because it is very unlikely that hot Cl atoms will react with specific Si atoms.

In sum, at low incident  $\text{Cl}_2$  energies where precursor mediated chemisorption is dominant, SiCl island formation is observed. Island growth probably occurs by  $\text{Cl}_2$  physisorbing to the unreacted portions of the surface and migrating to the edges of the islands prior to dissociation. For high translational energy  $\text{Cl}_2$  dosing of Si(111)-(7 $\times$ 7), direct activated molecular chemisorption is dominant, no island formation occurs, and only single-site adsorption is observed by STM. The direct activated chemisorption results in about a 2:1 reactivity ratio of center to corner adatoms at all translational energies. This can be envisioned by a concerted reaction mechanism in which dissociation of chemisorbed  $\text{Cl}_2$  ties up two dangling bonds with one Cl attached to the adatom and the other to the rest atom.

The authors would like to thank J. J. Boland, D. M. Eigler, and W. H. Weinberg for helpful discussions and gratefully acknowledge support from the David and Lucille Packard Foundation (Grant No. 89-1618) and AFOSR (Grant No. 89-0390).

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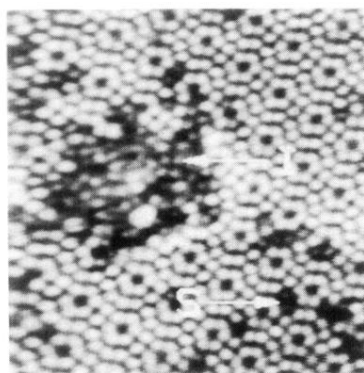


FIG. 1. STM topograph of a Si(111)-(7×7) surface exposed to a 0.05 eV Cl<sub>2</sub> beam (bias = -1.0 V). The scan size ~200 Å×200 Å. The dark areas are SiCl adsorbates and bright sites represent unreacted adatoms. The image shows large island formation (marked by an *I*) and single-site reacted adatoms (marked by an *S*).

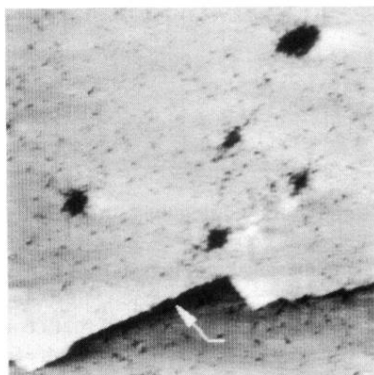


FIG. 2. A large STM scan of a Si(111)-(7 $\times$ 7) surface exposed to a 0.11 eV Cl<sub>2</sub> beam (bias = -1.0 V). The scan size  $\sim 1000 \text{ \AA} \times 1000 \text{ \AA}$ . The arrow points to a step edge. The depressions in the three-dimensional rendering are SiCl islands. All islands are round-shaped and some islands are more than 100  $\text{\AA}$  apart.

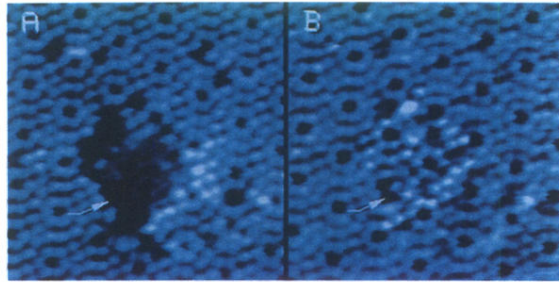


FIG. 3. STM topographs of a single area on a Si(111)-(7 $\times$ 7) surface exposed to a 0.05 eV Cl<sub>2</sub> beam as a function of tip-surface bias voltage. (a) Bias is -1.0 V. (b) Bias is -2.2 V. The scan size  $\sim$ 150 Å $\times$ 150 Å. In (a) the dark areas are SiCl adsorbates and bright sites represent unreacted adatoms. In (b) the SiCl adsorbates are brighter than the unreacted atoms outside the island and the sites inside the island that remain completely dark (marked by arrows) are most probably sublimation defects.

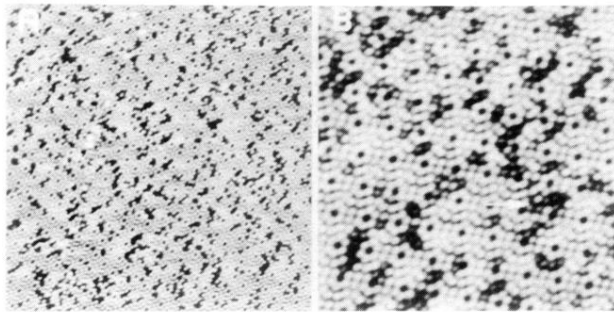


FIG. 4. STM topographs of a Si(111)-(7 $\times$ 7) surface exposed to a 0.44 eV Cl<sub>2</sub> beam (bias = -1.0 V). (a) The scan size  $\sim 600 \text{ \AA} \times 600 \text{ \AA}$ . (b) The scan size  $\sim 250 \text{ \AA} \times 250 \text{ \AA}$ . The dark areas (marked by an arrow) are SiCl adsorbates and bright sites represent unreacted adatoms. There is no island formation and only center-adatom preferred reaction is observed. The ratio of the number of reacted center adatoms to that of reacted corner adatoms is about 2:1 at low coverage.