Direct Chemisorption Site Selectivity for Molecular Halogens on the Si(111)-(7 × 7) Surface

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Direct chemisorption site preferences within the Si(111)-(7 × 7) unit cell are examined for F_2, Cl_2, and Br_2. Abstractive chemisorption, which produces a single chemisorbed halide atom, always prefers center adatom adsorption, indicating that the site with the lowest electron density is the more reactive. Dissociative chemisorption, which produces a pair of chemisorbed halide atoms, shows an extreme preference for the closest neighboring pair of center adatoms. The notion of a stepwise direct chemisorption mechanism is upheld by these results.

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Adsorption site preferences can elucidate the nature of the chemisorption mechanism involved. By correlating chemisorption site selectivity with the occupancy and surrounding structure of each possible dangling bond, we hope to discern the electronic and steric factors which govern the chemisorption process, including the relative electrophilicity or nucleophilicity of the adsorbate and surface. In this Letter, the adsorption site preferences for abstractive and dissociative chemisorption of molecular halogens on the Si(111)-(7 × 7) surface are examined in order to gain a better understanding of these direct chemisorption mechanisms.

Abstractive and dissociative chemisorption are expected to have the same initial adsorption step: the chemisorption of one halogen atom of the molecule to a surface silicon dangling bond [1]. This creates a short lived "molecular chemisorbate" species with a lifetime much less than a picosecond. From this complex, the reaction can proceed in two directions as the halogen-halogen bond is lost for the formation of a silicon-halogen bond. In abstractive chemisorption, the terminal halogen atom is repulsed from the newly formed silicon halide and ejected into the gas phase [2]. In dissociative chemisorption, the incident translational energy or momentum of the molecule is sufficient to carry the second halogen atom past the newly formed silicon halide and onto a neighboring dangling bond.

The structure of the Si(111)-(7 × 7) unit cell is known and shown elsewhere [3–6]. It has been shown that the adatom dangling bonds contain approximately 0.5 electron while the rest of the atom dangling bond contains approximately 1.5 to 2 electrons [5–10]. The center adatom electron occupancy is considerably less than that of the corner adatom due to adatom to rest atom charge transfer [10].

In the low coverage regime, the adatoms are the exclusive adsorption sites for molecular chlorine [11–15]. In a previous publication [16], we proposed that the presence of isolated single chlorinated adatoms on the Si(111)-(7 × 7) surface was due to dissociative chemisorption of Cl_2 onto an adatom–rest-atom pair. However, the scan-

ning tunneling microscopy (STM) work of Boland and Villarrubia [14] and several photoelectron spectroscopy studies [11–13,15] show that the rest atoms do not serve as adsorption sites for molecular chlorine in the low coverage regime. Instead, the recent work of Li *et al.* [2] and Carter *et al.* [1] definitively show that F_2 abstrac-
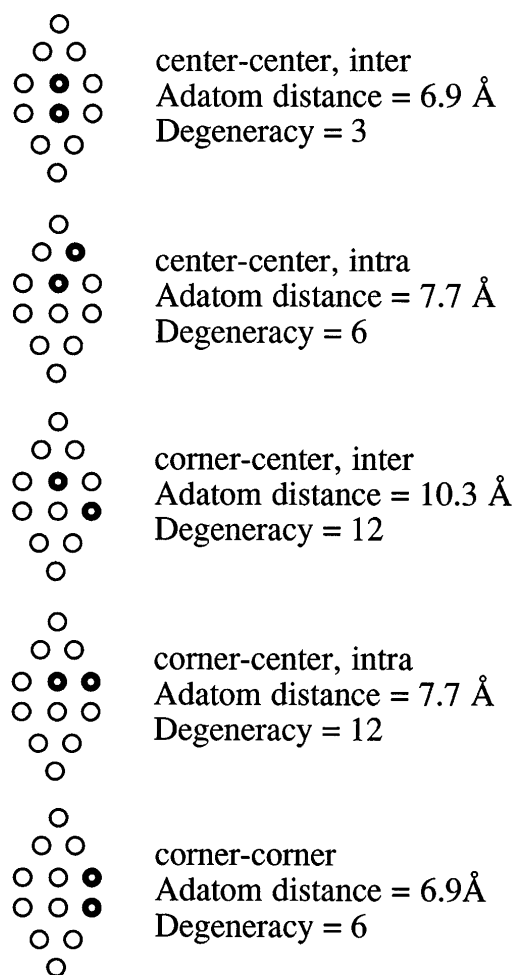

FIG. 1. The five possible arrangements of nearest neighboring adatom pairs on the Si(111)-(7 × 7) unit cell. Also listed are the distances between adatoms and the degeneracy of each pair.

tive chemisorption produces isolated single reacted sites on Si(100)-(2 × 1). We have assumed that the adatoms are the exclusive chemisorption sites for F_2, Cl_2, and Br_2 based on the parallels in reactivity [17]. Dissociative chemisorption will produce pairs of adsorbates, and there will be the five distinct arrangements on the Si(111)-(7 × 7) lattice, as shown in Fig. 1. Also shown in Fig. 1 are the distances between adatoms and the degeneracy of each pairwise adsorption site. The degeneracy is the number of possible pairs per unit area.

The experiments were performed in a two stainless steel UHV chamber with a base pressure of 1.0×10^{-10} Torr. The apparatus and sample preparation have been described in detail elsewhere [17,18]. The main features of the apparatus are a single stage differentially pumped molecular beam source (base pressure $\sim 1 \times 10^{-8}$ Torr) and a UHV STM (Park Scientific Instr., model SU2-210). Clean Si(111)-(7 × 7) samples at room temperature were exposed to a supersonic molecular beam of a halogen-carrier gas mixture at normal incidence. The resulting adsorbates were analyzed in empty state STM images for site selectivity (center or corner adatom) as well as adsorbate size (number of nearest neighboring halogenated adatoms).

Abstractive chemisorption is a direct chemisorption process which produces a single chemisorbed halogen atom (single reacted site) on the surface and ejects one halogen atom into the gas phase. The ratio of center adatom adsorption events to corner adatom adsorption events for single site adsorption as well as for all adsorbate sizes are listed in Table I. A complete analysis of halogen adsorbate size distributions can be found elsewhere [19]. For all three F_2 translational energies and the 0.11 and 0.44 eV Cl_2 data, the initial adatom vacancies are included in the data; therefore, the observed ratio of center to corner adatom adsorption events partially reflects the ratio of initial center to corner adatom vacancies. The average defect density (0.5%) and average center to corner adatom vacancy ratio (2.5:1) were used to correct the center to corner reactivity ratio. This gives the bracketed ratios shown in Table I. For the 0.11 and 0.44 eV Cl_2 data, consideration of initial defects does not change the observed single site center to corner adatom reactivity ratio. Table I clearly shows that in all cases center adatom adsorption is preferred (center adatom events/corner adatom events >1).

Dissociative chemisorption is a direct chemisorption process which produces a nearest neighboring pair of chemisorbed atoms. Representative empty state STM images of high translational Cl_2 and Br_2 chemisorbates are shown in Fig. 2. Figure 3 shows the relative number of each type of pair for the adsorption of molecular chlorine and bromine at low and high incident translational energy. The relative numbers of pairs have been normalized taking into account the degeneracy of each type of pair. At 0.03 eV incident translational energy, it has been shown that the adsorption of molecular fluorine occurs exclusively via abstractive chemisorption [17]. Therefore, the fluorine distributions are not useful in determining dissociative chemisorption site selectivity. For high translational energy chlorine and bromine, which adsorb primarily via dissociative chemisorption [17], there is a strong preference for the center-center interpair [see Fig. 3(b)]. This is only one of the two closest neighboring pair of adatoms (see Fig. 1). At lower translational energy, the Cl_2 and Br_2 data show a preference for the center-center, interpair as well as a lesser preference for the corner-corner adatom pair. These are the two closest neighboring pairs of adatoms, both spaced 6.9 Å apart.

We will first discuss the selectivity for abstraction. In the limit of zero coverage, the adatoms are the exclusive direct chemisorption sites for molecular halogens on the Si(111)-(7 × 7) surface. The adatom dangling bonds have a much lower electron occupancy than the rest atom dangling bonds, indicating that molecular halogen reacts with the surface as a nucleophile; the halogen preferentially chemisorbs at the sites with the lowest electron density. This is somewhat counterintuitive considering the

TABLE I. The ratios of center adatom to corner adatom adsorption events for abstractive chemisorption (single sites) and for all adsorbates. The percentage of abstractive chemisorption relative to the total direct chemisorption probability is also listed. The standard deviation is between separate scans in one experiment, while (a) denotes the standard deviation is between separate experiments. The percent adatom coverages range from 1.8% to 5.5%.

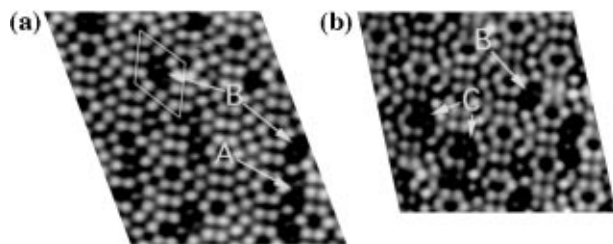| Halogen	Translational energy (eV)	Center-corner single site	Center-corner all adorbates	% Abstractive chemisorption
Fluorine	0.03	{1.2} 1.4 ± 0.2[a]	1.5 ± 0.1[a]	100 ± 5
	0.09	{1.6} 1.7 ± 0.3	1.5 ± 0.1	90 ± 5
	0.27	{1.2} 1.4 ± 0.2[a]	1.4 ± 0.08[a]	75 ± 5
Chlorine	0.05	2.8 ± 0.2	1.9 ± 0.1	65 ± 5
	0.11	2.6 ± 0.2	1.9 ± 0.2	65 ± 5
	0.44	2.3 ± 0.3	2.0 ± 0.3	30 ± 5
Bromine	0.2	2.3 ± 0.8	2.2 ± 0.6	65 ± 5
	0.5	2.0 ± 0.5	3.6 ± 1.1	30 ± 5

FIG. 2. Representative empty state STM image of the Si(111)-(7 × 7) surface dosed with (a) 0.44 eV Cl_2 and (b) 0.5 eV Br_2. The "A" denotes center-center, intra-adatom pairs, "B" denotes center-center interpairs, and "C" denotes corner-corner adatom pairs. In both cases, the center-center interadatom pair is preferred.

high electronegativity of the halogen atoms, but the situation is quite different for the halogen molecule. The highest occupied molecular orbital of the halogen diatomic is the degenerate set of two π^* states, both of which are doubly occupied. The interaction of this filled π^* state with the roughly quarter filled (~0.5 electron) nonbonding dangling bond state will be an attractive one; electron donation from the π^* state to the newly formed (π^*–dangling bond) state will form a net attraction between the molecule and the surface [20]. Furthermore, this model also provides an explanation for the relative reactivity of the center and corner adatoms: Since the center adatom dangling bonds have less electron density than the corner adatom dangling bonds [10], the center adatoms are more reactive.

Another explanation of the relative adatom reactivity lies in the structure of the 7 × 7 unit cell [4]. Adsorption of a halogen onto an adatom may induce strain on the silicon dimers in the third atomic layer of the 7 × 7 reconstruction [10,18]. The corner adatom resides above two such dimers while the center adatom lies above one, therefore adsorption on the corner adatom is unfavorable due to the relatively larger strain induced. This explanation is not as complete as the former because it does not address the nonreactivity of the rest atom dangling bonds which are relatively far from these silicon dimers. However, the structural argument cannot be completely ruled out and may play a role in governing the relative reactivity of the adatoms.

Of the three halogens studied, molecular chlorine shows the highest site selectivity for abstractive chemisorption, followed by bromine and then fluorine. Relative to F_2 and Br_2, Cl_2 shows a lower level of abstraction relative to the total direct chemisorption probability [17]. This is most likely due to the fact that Cl_2 has the highest bond strength of the three diatomics. It seems reasonable that Cl_2, having the lowest abstraction probability, also has the greatest site selectivity.

According to Carter *et al.* [1], the abstractive and dissociative chemisorption mechanisms have the same initial adsorption step: the chemisorption of one halogen
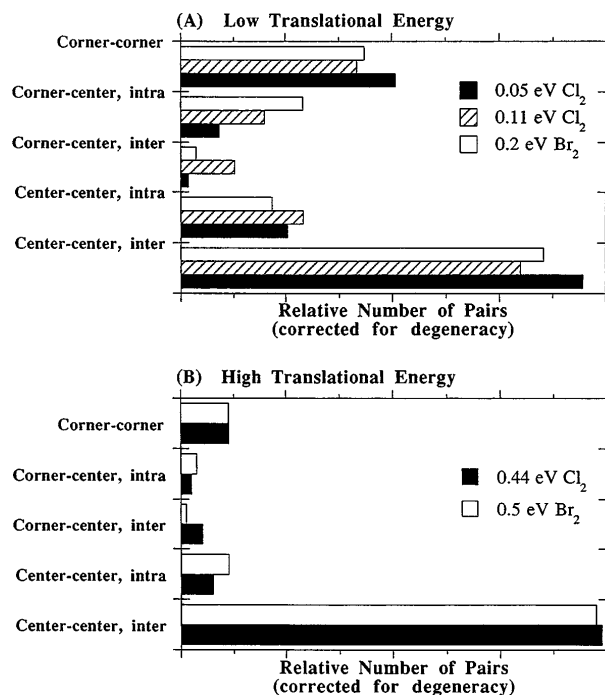

FIG. 3. The relative number of each type of adatom pair is plotted for Cl_2 and Br_2 chemisorption at low (a) and high (b) translational energy. The data have been normalized for the degeneracy of each type of pair. Data were obtained from the same database as the single site selectivities.

atom of the molecule to a surface silicon dangling bond to create a short lived molecular chemisorbate species. Both mechanisms proceed from the short lived molecular chemisorbed species, therefore the site selectivity of abstractive chemisorption should be reflected in the site selectivity of dissociative chemisorption.

At high translational energy, where dissociative chemisorption is the dominant adsorption process for molecular chlorine and bromine, there is an extreme preference for the center-center, interpairwise adsorption site. This selectivity is consistent with the direct chemisorption mechanisms. The center adatom is the preferred initial adsorption site as is evident from the selectivity of abstractive chemisorption. For dissociative chemisorption, the terminal halogen atom of the short lived molecular chemisorbate must access a neighboring site, and the data show that the closest adatom is the most probable site. While the closest center adatom is not the exclusive adsorption site for the terminal halogen atom, it has the highest cross section for chemisorption. The center-center interpair is the closest spaced set of center adatoms at 6.9 Å compared to the second closest set (center-center intrapair) which is at 7.7 Å. At lower translational energies, molecular chlorine and bromine also show a secondary pairwise adsorption preference for the corner-corner pair of adatoms. This would indicate that the distance between adsorption sites, as well as

the reactivity of the initial adsorption site, influences dissociative chemisorption site selectivity.

In sum, abstractive chemisorption shows a preference for center adatom adsorption in all cases. The abstractive chemisorption of Cl_2 shows the strongest preference, followed by Br_2, while F_2 exhibits the least preference (see Table I). A cursory examination of the electronic structure of the Si(111)-(7×7) unit cell shows that the dangling bond site with the lowest occupancy, the center adatom, is the most reactive. Dissociative chemisorption shows a strong preference for one of the five possible pairwise adsorption sites within the 7×7 unit cell. For Cl_2 and Br_2 at high translational energy, where dissociation is the dominant direct chemisorption mechanism [17,19], the closest neighboring pair of center adatoms is preferred [see Fig. 3(b)].

The notion of a stepwise direct chemisorption mechanism is upheld by these results. Both abstractive and dissociative chemisorption proceed through the same initial adsorption step, therefore the site selectivity of abstraction should be reflected in the pairwise site selectivity of dissociation. This is the case: Absorption prefers the center adatom, and dissociation prefers a pair of center adatoms. For dissociative chemisorption, the terminal halogen atom of the short lived molecular chemisorbate complex must access a neighboring chemisorption site, therefore the closest dangling bond site should be preferred. Again, this is the case: Dissociative chemisorption prefers the closest neighboring pair of adatoms.

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[1] L. E. Carter, S. Khodabanedeh, P. C. Weakliem, and E. A. Carter, J. Chem. Phys. **100**, 2277 (1944).

[2] Y. L. Li, D. P. Pullman, J. J. Yang, A. A. Tsekouras, D. B. Gosalvez, K. B. Laughlin, Z. Zhang, M. T. Schulberg, D. J. Gladstone, M. McGonigal, and S. T. Ceyer, Phys. Rev. Lett. **74**, 2603 (1995).

[3] G. Binnig, H. Rohrer, C. Gerber, and E. Weibel, Phys. Rev. Lett. **50**, 120 (1983).

[4] K. Takayanagi, Y. Tanishiro, S. Takahashi, and M. Takahashi, Surf. Sci. **164**, 367 (1985).

[5] R. J. Hamers, R. M. Tromp, and J. E. Demuth, Phys. Rev. Lett. **56**, 1972 (1986).

[6] R. J. Hamers, R. M. Tromp, and J. E. Demuth, Surf. Sci. **181**, 346 (1987).

[7] J. E. Demuth, B. N. J. Persson, and A. J. Schell-Sorokin, Phys. Rev. Lett. **51**, 2214 (1983).

[8] J. E. Northrup, Phys. Rev. Lett. **57**, 154 (1986).

[9] R. M. Tromp, R. J. Hamers, and J. E. Demuth, Phys. Rev. B **34**, 1388 (1986).

[10] P. Avouris and R. Wolkow, Phys. Rev. B **39**, 5091 (1989).

[11] K. C. Pandey, T. Sakurai, and H. D. Hagstrum, Phys. Rev. B **16**, 3648 (1977).

[12] P. H. Citrin, J. E. Rowe, and P. Eisenberger, Phys. Rev. B **28**, 2299 (1983).

[13] G. Thornton, P. L. Wincott, R. McGrath, I. T. McGovern, F. M. Quinn, D. Norman, and D. Vvedensky, Surf. Sci. **211**, 959 (1989).

[14] J. J. Boland and J. S. Villarrubia, Phys. Rev. B **41**, 9865 (1990).

[15] D. Purdie, C. A. Muryn, N. S. Prakash, K. G. Purcell, P. L. Wincott, G. Thorton, and D. S.-L. Law, J. Phys. Condens. Matter **3**, 7751 (1991).

[16] C. Yan, J. A. Jensen, and A. C. Kummel, Phys. Rev. Lett. **72**, 4017 (1994).

[17] J. A. Jensen, C. Yan, and A. C. Kummel (to be published).

[18] C. Yan, J. A. Jensen, and A. C. Kummel, J. Chem. Phys. **102**, 3381 (1995).

[19] J. A. Jensen, C. Yan, and A. C. Kummel, Science **267**, 493 (1995).

[20] R. Hoffman, *Solids and Surfaces* (VCH Publishers, Inc., New York, 1988).