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Adsorption and abstraction reactions of HCl on a single Si(100) dangling bond

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On a Si(100)-(2×1) surface with abundant dangling bonds, reaction of HCl molecules at room temperature is dominated by exothermic dissociative adsorption of H and Cl on two adjacent dangling bonds. This coadsorption reaction is blocked for an isolated dangling bond, yet surprisingly endothermic H or Cl abstractive adsorption occurs, as observed by *in situ* scanning tunneling microscopy. On an isolated dimer dangling bond (DB) pair, coadsorption of H and Cl is common as expected, but adsorption of a pair of abstracted Cl or H from two HCl molecules also occurs. These results, complemented by theoretical calculations, indicate that dissociative adsorption and abstractive reaction of a multiatom gas molecule can be initiated at a single DB by forming an intermediate adsorption state.

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I. INTRODUCTION

Adsorption and subsequent reactions of gaseous molecules on solid surfaces occur in many natural physical, biological, and chemical systems. These processes are relevant to industrial applications such as chemical vapor deposition, surface etching, and heterogeneous catalysis. A comprehensive understanding of the underlying atomic processes and mechanisms is of great interest. When a polyatomic molecule impinges upon a surface, it may be reflected (unreactive scattering), bind to the surface as an intact molecule (molecular adsorption), fragment into adsorbed components (dissociative adsorption),[1–3] or fragment into adsorbed and reflected components (abstraction).[4–8] The last two processes are usually exothermic; chemical bond formation between surface atoms and radicals derived from the parent molecule drives the reactions toward a lower-energy state. However, a few previous studies have reported that endothermic chemisorption can occur under certain conditions.[9,10]

In dissociative chemisorption of a diatomic molecule AB, for example, the adsorption energy E_{ad} can often be estimated as the sum of the formation energy of two newly established adsorbate-surface bonds, E_{AS} and E_{BS}, less the energy needed to break the molecular bond E_{AB}. If E_{AB} is larger than E_{AS} or E_{BS}, the bond cleavage and the formation of two new bonds must take place simultaneously for exothermic chemisorption. In this scenario, two empty adsorption sites on the surface are required and their distance must be compatible with the molecular bond length of AB. Thus, this spontaneous dissociative adsorption cannot occur at an isolated empty site.[11] Furthermore, random dissociative adsorption generally cannot saturate a surface.[12] These constraints and consequences for spontaneous adsorption reactions have not been examined in detail experimentally owing to the generally complex outcome of surface reactions involving heterogeneous diatomic molecules. Herein, we report a combined experimental and theoretical study of the adsorption and subsequent reactions of the diatomic molecule HCl on Si(100)-(2×1). This is a simple model system, but the results are surprisingly rich and challenge the usual notions regarding how chemisorption proceeds.

The Si(100)-(2×1) surface is made up of dimers; each surface dimer atom has a chemically active dangling bond (DB). As both H and Cl are highly reactive radicals, the most probable reaction of HCl with Si(100), based on energetics, is dissociative adsorption involving the cleavage of the H-Cl bond and concurrent adsorption of the H and Cl to neighboring DBs. The final product is a mixture of H-Si and Cl-Si surface species as observed by photoemission and scanning tunneling microscopy (STM).[13] If the Si(100) surface is first mostly passivated by H adsorption, leaving only sparsely distributed single DBs that are isolated from one another, dissociative adsorption is blocked. We find, unexpectedly, these isolated active sites can still react to HCl, resulting in either H or Cl abstraction, which are both endothermic reactions. It is also curious that in the case of Cl abstraction, the Cl occupies either the original DB site or its dimer partner site, with equal probability. Reaction of HCl with isolated DB pairs (DBPs) results in mostly two-atom adsorption, as expected, but pairs of abstracted Cl atoms or H atoms derived from two HCl molecules are also observed with significant probabilities. All of these results point to a nontrivial reaction pathway involving long-lived intermediate states that can branch out into various final configurations. Prior studies using molecular beam scattering methods have revealed exthothermic halogen abstraction on Si surfaces for molecular halogens and xenon difluoride,[5–7] but the present study is the first case involving an endothermic reaction, and it can involve just one DB.

II. EXPERIMENTAL AND COMPUTATIONAL DETAILS

In our experiment, clean and H-terminated Si(100)-(2×1) surfaces were prepared by standard procedures.[11,14] The Si surfaces after saturation exposure of atomic hydrogen were mostly terminated by monohydrides, with the dimer structure intact. Various nanoscale patterns of bare DBs were formed by either under exposure of atomic hydrogen, mild thermal desorption at 700 K for 60 s,[14,15] or programmed STM tip-induced desorption of the H.[16] Exposure of HCl and STM imaging were performed at room temperature. The STM tip was retracted for hundreds of nanometers during HCl exposure. The HCl dosage used was 2400 L (exposure for 20 min at 2×10^{-6} Torr), which was sufficient to fully saturate all DBs.

Our density functional theory (DFT) calculations were based on the Vienna *ab initio* simulation program (VASP) using the projector-augmented wave method and the revised Perdew-Burke-Ernzerhof pseudopotential including spin polarization effects.[17–20] The Si substrate was modeled by a $4\times4\times8$ slab (15.44 Å×15.44 Å×24.64 Å), with its bottom surface terminated by hydrogen. A vacuum region of thickness 11.84 Å on top of the Si surface was included to form a supercell. The irreducible Brillouin zone was sampled with a $(4\times4\times1)$ Monkhorst-Pack mesh,[21] the energy cutoff was set at 400 eV, and the energy convergence was set at 10^{-4} eV. The bottom four Si layers were held frozen; all other atoms were fully relaxed with the residual atomic forces less than 0.02 eV/Å. The relaxation allows the system to evolve and find equilibrium as well as metastable or intermediate states.

III. RESULTS AND DISCUSSION

Prior STM studies of HCl, Cl_2, and atomic H reactions with Si(100)-(2×1) have established reference images for distinguishing bare, H-, and Cl-terminated DBs under various imaging conditions.[11,13,22] Upon HCl exposure, STM images show that a fully H-terminated Si(100)-(2×1) surface is inert to HCl exposure, but similar surfaces prepared with low-density isolated DBs show local reactions within three unit-cell distances around each DB. Figures 1(a) and 1(c) present examples of STM images before the HCl exposure. The rows are monohydride dimers, and the isolated DBs (labeled S) appear as bright spots, each biased on one side of the underlying dimer. Figures 1(b) and 1(d) are corresponding images after the exposure. In Fig. 1(b), two of the three original DB sites are now terminated by H and become indistinguishable from the rest of the H-terminated surface. The reactions correspond to H abstraction, leaving the companion Cl to scatter back into vacuum. The third DB becomes Cl terminated. A Cl-terminated site appears brighter than the surrounding H-terminated ones, but not quite as bright as the bare DBs. This event corresponds to Cl abstraction. Figure 1(d) also corresponds to a case of Cl abstraction, but the positions of the H and Cl are switched on the dimer of interest. The statistics of various final states based on 176 samples are listed in Table I. Abstraction of H dominates with a probability (percentage occurrence) of 73%. Abstraction of Cl has a probability of 26%, about equally divided between the two channels (normal position and switched position at 14 and 12%, respectively). There are also two events (1%) recorded where the DB becomes terminated by H, and the released Cl radical moves to a nearby site to replace the H there. These rare events will be ignored in our analysis below.

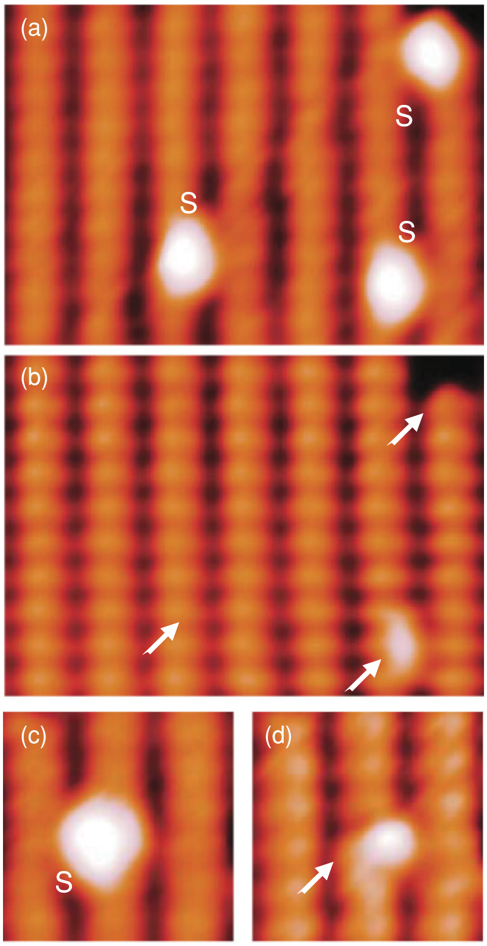

FIG. 1. (Color online) (a), (c) STM images ($V_s = -2.0$ V, $I_t = 0.3$ nA, $T = 300$ K) of a Si(100)-2×1:H surface after annealing at ~700 K for 120 s. Isolated single DBs are labeled by S. (b), (d) are corresponding images after saturation exposure to HCl. The S sites after reaction are indicated by arrows. Note that the abstracted Cl atom in (d) occupies the dimer partner site of the original DB. The distance between two dimer rows is 7.68 Å.

TABLE I. Reaction products and their probabilities (percentage occurrences) beginning with isolated single DBs (H–Si–Si–) and DBPs (–Si–Si–). The notations (g) and (a) denote the gas phase and an adsorbed species, respectively.

Initial states	Reactants	Products	Event counts/sample sizes	Probabilities
H–Si–Si– DB	+ HCl (g)	H-Si-Si-H + Cl (g)	128/176	(73 ± 4%)
		H-Si-Si-Cl + H (g)	22/176	(12 ± 3%)
		Cl-Si-Si-H + H (g)	24/176	(14 ± 3%)
		H-Si-Si-H + Cl (a)	2/176	Rare event
–Si–Si– DBP	+ HCl (g) + 2HCl (g)	H-Si-Si-Cl	31/37	(84 ± 6%)
		H-Si-Si-H + Cl_2 (g)	5/37	(13 ± 6%)
		Cl-Si-Si-Cl + H_2 (g)	1/37	Rare event

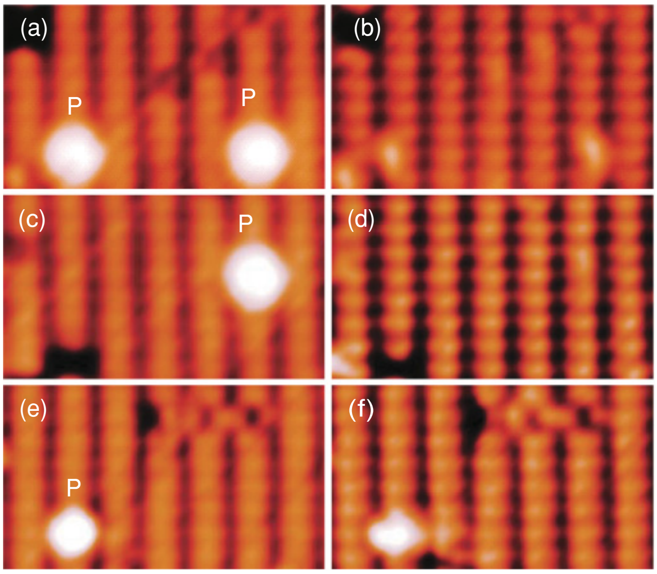

FIG. 2. (Color online) (a), (c), (e) STM images ($V_s = -2.0$ V, $I_t = 0.3$ nA, $T_s = 300$ K) of a Si(100)-2×1:H surface after annealing at ~700 K for 60 s. DBPs are labeled by P. (b), (d), (f) are corresponding images after exposure to HCl, showing the results of dissociative adsorption at two DBPs, a pair of H abstractions at a DBP, and a pair of Cl abstractions at a DBP, respectively.

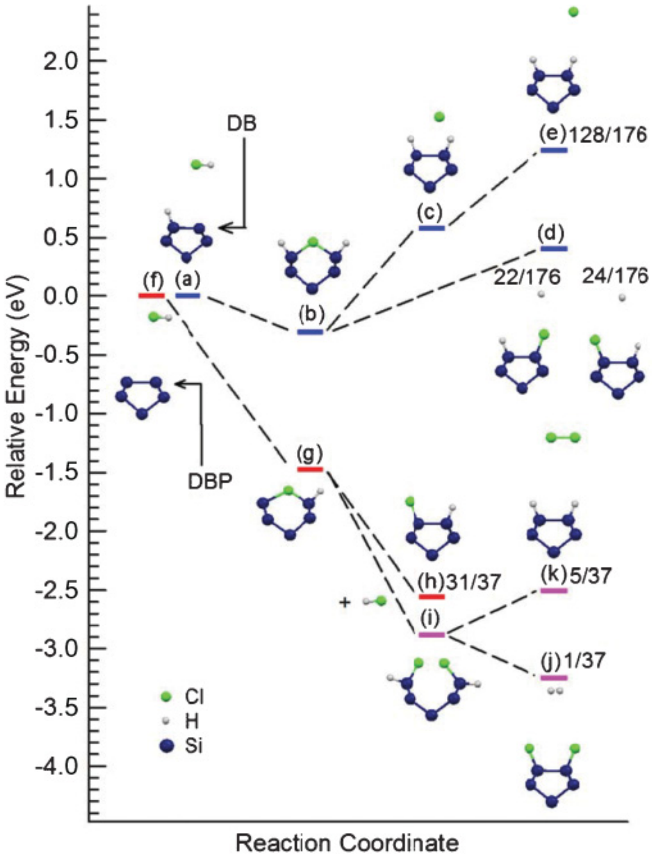

FIG. 3. (Color online) Reaction coordinate diagram for HCl adsorption on a single DB (a) and a DBP (f). Various intermediate states (b), (c), (g), (i), and final states (d), (e), (h), (j), (k) are indicated. The ratios of the event counts and sample sizes obtained from STM are indicated. The limited numbers of final and intermediate state configurations calculated herein are suggested by STM observation before and after the HCl adsorption.

Figure 2 presents similar results for isolated DBPs (labeled P). Figures 2(a) and 2(b) are before and after pictures involving two pairs, where dissociative adsorption at each pair results in H and Cl termination of the two DBs. Figures 2(c) and 2(d) illustrate a case where the DBs in a pair become both terminated by H; likewise, Figs. 2(e) and 2(f) illustrate a case for Cl pair termination. Table I presents the statistics based on 37 samples. This data set is relatively small owing to difficulties in preparing well-isolated DBPs. Consequently, the statistical error bars, presented in Table I, are relatively large for this set. The probabilities for dissociative adsorption, H pair adsorption, and Cl pair adsorption are $84 \pm 6\%$, $13 \pm 6\%$, and $3 \pm 3\%$, respectively. Dissociative adsorption dominates. The last two processes, with a combined probability of $16 \pm 6\%$, must involve two separate adsorption events in order to account for the addition of a pair of atoms of the same kind.

For a detailed understanding of these results at the atomic level, we have performed density functional calculations to determine the intermediate states and the relevant energy levels. The results are summarized in Fig. 3. Various initial atomic configurations have been considered. HCl with either the H or Cl end pointing toward an isolated dangle bond [see Fig. 3(a)] leads to no chemical bonding after relaxation. This is expected based on the tabulated bond energies: 4.5, 3.3, and 4.0 eV for HCl, Si-H, and Si-Cl, respectively.[23] Other initial configurations involving a stretched Si-Si bond leads to, after relaxation, an intermediate state at -0.31 eV [Fig. 3(b)]. This state, referred to as I_S below, involves a bridge-bonded Cl. For H abstraction, the next step is the formation of a monohydride dimer, with the Cl still attached nearby [Fig. 3(c)]. Finally, the Cl desorbs, leaving behind the abstracted H [Fig. 3(e)]. Another path forward for I_S is Cl abstraction [Fig. 3(d)]. Note that Fig. 3(b) is a symmetric configuration with respect to the two Si atoms in the dimer; thus, the abstracted Cl can occupy either of the two bonds of the dimer. This is indeed the case, as observed experimentally, that the abstracted Cl occupies either site with equal probability within experimental error. This is strong evidence for the existence of a symmetric intermediate state I_S. A similar bridge-bonded-Cl configuration, stable at room temperature, has been observed experimentally for Si(100) after supersaturation exposure of Cl_2 at 800 K,[24] and calculations indicate that the dimer-bond breaking on a monochloride surface has a relatively low barrier of 0.5 eV.[25]

For HCl interaction with an isolated DBP [Fig. 3(f)], the usual picture of dissociative adsorption involves a single step of reaction [from Fig. 3(f) to 3(h)]. Calculations show, instead, that the reaction involves an intermediate state as indicated in Fig. 3(g). This state, referred to as I_P below, is very similar to I_S shown in Fig. 3(b) and also involves a bridge-bonded Cl. This two-step process comes about because of the substantial mismatch in bond length between HCl (1.3 Å) and the Si-Si dimer bond (2.4 Å). As a HCl molecule approaches a DB, the interaction causes both the H-Cl bond and the Si-Si dimer bond to weaken and stretch, leading to I_P formation before the H and Cl move further apart to form separate bonds with the two Si atoms. During the lifetime of I_P, it is possible for a second HCl molecule to adsorb on the other Si DB [Fig. 3(i)]. Afterwards, the system can evolve into a monohydride dimer, releasing a Cl_2 molecule into vacuum [Fig. 3(k)], or it can evolve into a monochloride dimer, releasing a H_2 molecule into vacuum [Fig. 3(j)]. For exposure of HCl at 2×10^{-6} Torr, each surface site is bombarded by HCl molecules, once per second on average. The intermediate state I_P must have a very long (up to subsecond) lifetime for two separate molecules to have a chance to react at the same dimer. This is not necessarily surprising in view of the stable bridged-bonded-Cl configuration on a Cl saturated surface as mentioned above.[24] This long lifetime may be related to a substantial barrier for transformation into the final state [Fig. 3(h)], which requires breakage of the bridge bond. In principle, higher HCl flux and/or low sample temperature can increase the low reaction probabilities for the final state [Figs. 3(j) and 3(k)]. To this end, further future experimental investigations are needed to quantify the life timeof I_P.

For similar reasons, the intermediate state I_S shown in Fig. 3(b) is likely to have a long lifetime. Its transition to the final states is endothermic. To the best of our knowledge, endothermic abstraction has never been reported before. The transition can be regarded as thermal desorption from I_S, which is aided by the entropy factor, but is suppressed by the thermal Boltzmann factor. The energy differences between the pairs of Figs. 3(b) and 3(c), Figs. 3(b) and 3(d), and Figs. 3(c) and 3(e), are 0.88, 0.71, and 0.84 eV, respectively. These energy barriers allow thermal excitations at room temperature at a rate of roughly 0.01 s^{-1}, assuming an attempt frequency of 10^{-12} s^{-1}.[26] A long lifetime of the intermediate state allows the system to make many attempts to overcome the energy barrier. In any case, there are no lower-energy states for this intermediate state to decay into. The only other option is for the H and Cl to recombine and desorb, resulting in a nonreactive scattering event. But then, another HCl molecule can come in to reinitiate the process.

The presence of the long-lived intermediate states I_P can result in additional effects. Figure 4(a) is a STM image taken from a H-terminated surface after a "dimer wire" was prepared by STM lithography to remove the H from a row of dimers. The image shows depressed (darker) regions surrounding the wire and defects, which are caused by tip-induced local band bending.[27,28] After HCl exposure, imaging by the same STM tip revealed a zigzag pattern for the wire [Fig. 4(b)]. This pattern can be attributed to mixed H- and Cl-terminated dimers, produced by dissociative adsorption, arranged in alternating orientations. The orientational correlation suggests the following picture. The intermediate state I_P and its symmetry equivalent state (with the H atom switched to the other Si atom) form a resonant pair. The lifetime is sufficiently long for this pair to sense the strain, electrostatic, or steric effects from the adsorption configuration of its neighbors and adopt the apparently more favored zigzag arrangement. The details will depend on the energy barriers involved in the reaction, which are not available from the present study. The same local zigzag patterns have been observed for clean Si(100)-(2×1) exposed to HCl.[13]

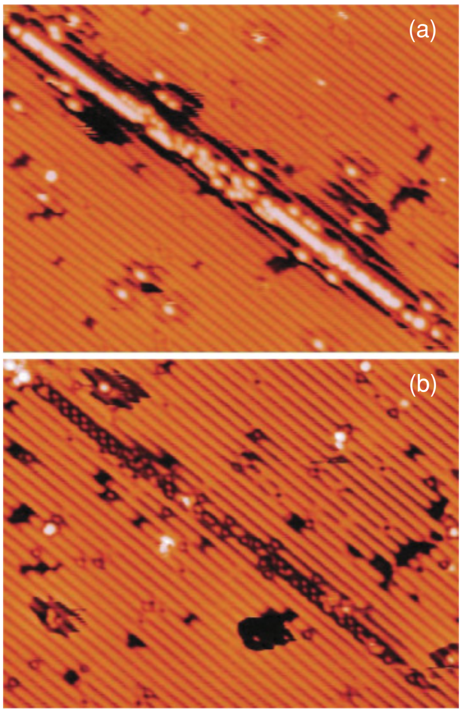

FIG. 4. (Color online) STM images ($V_s = -2.4$ V, $I_t = 0.23$ nA, $T = 300$ K) for (a) a DB wire produced by STM lithography and (b) the same area after HCl exposure.

IV. SUMMARY

In summary, our study of HCl adsorption on restricted configurations of DBs on Si(100) has yielded interesting and unexpected observations that shed light on the atomistics of chemisorption. Dissociative adsorption on pairs of dimer DBs is expected and observed to dominate. This reaction is blocked for isolated DBs. Instead, H or Cl abstraction takes place despite the endothermic nature of the processes. These reactions are mediated by a long-lived intermediate state involving a bridge-bonded Cl. Its symmetric configuration leads to a symmetric distribution of the final states for Cl abstraction. Adsorption on DBPs proceeds with a similar long-lived intermediate state, which allows two sequential HCl adsorption events to occur on the same DBP in addition to the dominant dissociative adsorption process. The long lifetime of the intermediate state also permits local ordering for HCl adsorption on neighboring DBPs. The work reported herein highlights the importance of intermediate states during chemisorption and the richness of reaction pathways for even relatively simple systems. Further measurements and calculations of the lifetime of intermediate states and various reaction barriers are necessary for comprehensive understandings of the atomistics of chemisorption.

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