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Chemisorption of Cl on the Si(100)-2 × 1 surface

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We have investigated the chemisorption of Cl atoms on the Si(100)-2 × 1 surface using a semiempirical self-consistent molecular-orbital method. Cl atoms are found to saturate the dangling bonds of the surface Si symmetric dimer atoms in an off-normal direction in the equilibrium geometry. A low-energy diffusion path exists between these sites via a saddle point at the bridge-bonded site, consistent with the proposal of Boland based on scanning tunneling microscopy observations. The bridge-bonded site can also act as the attack site for further chemisorption of Cl on the dimer whose dangling bonds are already saturated by Cl atoms. This leads to bond lengthening and weakening of the Si-Si dimer bond and can contribute to subsequent bond breaking and redimerization yielding a mixture of monochloride and dichloride bonding configurations on the surface. The dichloride unit ($SiCl_2$), in turn, exhibits bond weakening of the Si backbonds and this finding provides strong evidence for the spontaneous etching phenomena observed for halogens on Si(100) by Chander, Li, Rioux, and Weaver.

I. INTRODUCTION

Halogenated and hydrogenated semiconductor surfaces have always been used as prototypes for the investigation of semiconductor-adsorbate interactions. One related area that has been receiving increasing interest in recent years is the dry etching of semiconductors using halogens, for which a variety of processing methods have been developed. The resulting body of observations and data, however, has not elucidated completely some of the phenomena at the atomic level and thus, has encouraged intense theoretical work to explain and interpret some of these phenomena.

One system that has been receiving due attention is the Cl/Si(100)-2 × 1 system. Although the bonding structure of Cl on the Si(100) surface has been studied extensively using a variety of surface-science techniques, conflicting results about this system exist in the literature. Photoemission and low-energy electron-energy-loss-spectroscopy studies suggest that two Cl atoms are bonded to two Si atoms giving rise to an off-normal Cl-Si bonding configuration involving a symmetric Si_2 dimer.[1-3] In contrast, a recent electron-stimulated-desorption ion angular distribution (ESDIAD) study of Cl chemisorption on the Si(100) surface yielded the existence of two different bonding structures for Cl on Si(100) depending on the temperature.[4] More recently, surface-extended and near-edge x-ray-absorption-spectroscopy measurements indicated that upon adsorption at 530 K, the Si-Cl bond is perpendicular to the (100) plane.[5] The Cl atom is postulated to chemisorb on a single Si atom in a buckled Si_2 dimer with a normally oriented Si-Cl bond. In contrast, however, recent *ab initio* calculations[6] of a monolayer of Cl on the Si(100) surface indicated that the Cl adlayer gives rise to Cl:Si(100)2 × 1. The Cl adatoms adsorb at the dangling-bond sites of the (2 × 1)-reconstructed substrate surface showing symmetric Si dimers. This is in good agreement with the proposed off-normal Si-Cl bonding to a symmetric Si_2 dimer model above.[1-4] In addition, spontaneous etching of Si(100) with Br_2 recently investigated with atomic-resolution scanning tunneling microscopy (STM) suggests the coordinated breaking of dimer bonds with redimerization, which produces rows of Si doubly bonded to Br adjacent to Si dimers singly bonded to Br.[7] The concerted desorption of the $SiBr_2$ units yields the missing row patterns. These observations tie in with the mixed-bonding configurations as suggested from studies of H-Si(100)2 × 1, where rows of Si atoms bonded to a couple of H atoms alternate with rows of dimerized Si bonded to a single H atom.[8] Also, Boland[9] observed that Cl atoms strongly chemisorbed at dangling-bond sites on the Si(100)-2 × 1 surface migrate between adjacent sites, facilitated by the presence of a metastable Cl bridge-bonded site. Thus, the picture for Cl adsorption on Si(100) is still controversial.

The aim of this paper is to establish how the Cl atom at the bridge-bonded site atop a dimer compares energetically with the Cl atom saturating the dangling bond of one of the surface dimers: we will extend the calculations to cases for the adsorption of two and three Cl atoms. We will demonstrate that both bonding structures are theoretically possible for Cl on Si(100), consistent with the findings of Cheng *et al.*,[4] with the configuration for Cl saturating the dangling-bond site the most stable. The calculated geometries and binding energy for the Cl atoms on Si(100) are also in good agreement with those from the recent *ab initio* calculations.[6] Since the bridge-bonded site is the next-lowest energy site for Cl adsorption on Si(100), it could also act as the intermediate site for Cl migration on Si(100),[9] as well as the nucleation site

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and subsequently, attack site for bond breaking, thus, providing strong evidence for the spontaneous etching of Si(100) with halogens.[7]

II. THEORETICAL METHOD

We use a well-established semiempirical self-consistent molecular-orbital method: the complete neglect of differential overlap (CNDO) method[10] to investigate the adsorption of Cl on the Si(100)-2×1 surface. Basically, it starts from the rigorous Hartree-Fock-Roothaan equations. Slater-type atomic orbitals are then chosen as the atomic basis set. The basic approximation is to systematically neglect those integrals that are expectd to be of small magnitude including those terms associated with the exchange and Coulomb integrals. Further approximations are also applied to preserve the rotational invariance of the wave functions.

The same order of approximations is then applied to the matrix elements of the Hamiltonian operator, and empirical parameters, like the orbital exponent, the electronegativity, and the bonding parameter are introduced. An iterative process is then performed to obtain self-consistent solutions, similar to Hartree-Fock solutions. The CNDO method can also be derived as a systematic approximation of the Hartree-Fock theory[11] or a systematic approximation of the density-functional theory.[12] It has been especially successful in defect studies where geometries, charge densities, and total energies are concerned.[13] Recently, it has been employed to study the adsorption properties of metals[14] and halogens,[15] and excitation processes of defect sites on semiconductor surfaces.[16] In the present work, the CNDO parameters for Si yield calculated values of their bulk properties in good agreement with experiment,[17] while the parameters for Cl are from Ong and Tay.[18] We implement the MOSES code[19] and calculations are performed on a 63-atom (100) surface cluster to depict the Si(100) surface. The details have been provided previously in Ref. 20.

III. SURFACE RECONSTRUCTION AND CALCULATIONS

Prior to investigating the adsorption of Cl atoms on the Si(100)-2×1 surface, various kinds of surface reconstructions were carried out as outlined in Ref. 20. We obtain the minimum-energy configuration for the 2×1 dimer structure on Si(100), whereby two adjacent atoms on the surface displace toward each other to form a third covalent bond; this pair of atoms constitutes a dimer. The calculated dimer bond length is greater than the bulk bond length by 1.92%. This value is comparable with the findings from low-energy ion-scattering-spectroscopy experiments, which determined the dimer bond length to be 2.4 ± 0.1 Å.[21]

Charge-transfer polarization is also treated in our self-consistent calculations and the minimum total energy found will also include terms that allow net charges on atoms and place these charge entities at the appropriate positions. The charge transfer obtained for the 2×1 reconstruction is about $0.15e$. Other surface relaxations such as the 4×1, 4×2, and 2×2, which have already been described in detail in Ref. 20, yield total energies per dimer reasonably close to each other. After obtaining the minimum-energy configuration for the Si(100)-2×1 surface, we introduce monatomic, diatomic, and triatomic Cl on the surface to investigate their adsorption properties and correlate to experimental findings.

IV. RESULTS AND DISCUSSION

We investigate the interactions of the isolated Cl atom, two and three Cl atoms with a pair of dimers on the Si(100)-2×1 surface where subsequent relaxations are taken into account for the Cl adsorbates and the pair of dimers involved. Initially, we map out the total-energy surface of the isolated Cl atom by moving the Cl atom along the five traverses, P, Q, R, S, and T as in Ref. 14, for Al on Si(100)-2×1. At each location along each traverse, the Cl atom is displaced perpendicularly to the surface to obtain the local minimum position. The

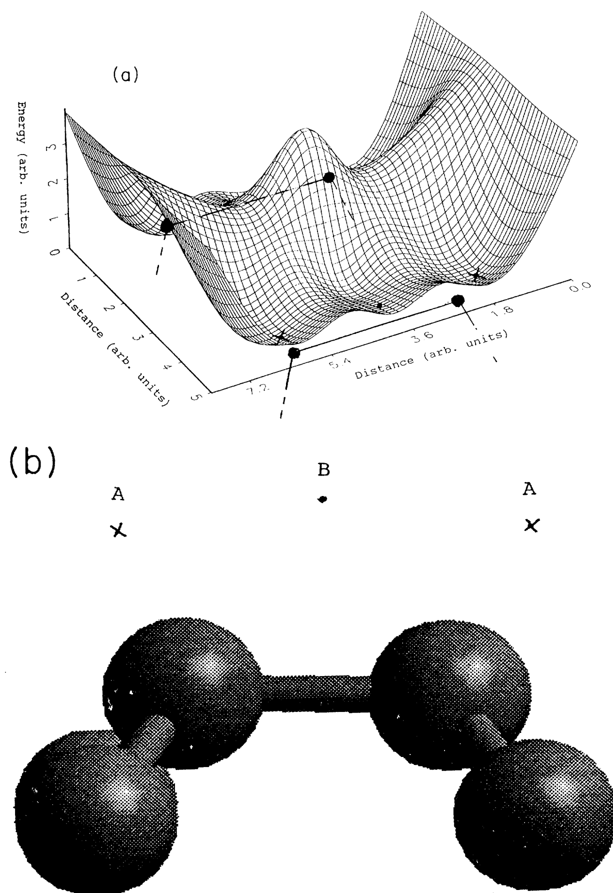

FIG. 1. (a) The calculated total-energy surface obtained for Cl on Si(100)-2×1 surface. There exists two low-energy paths for Cl to diffuse on the surface: the lower-energy path is atop the dimer bond where the Cl atom can migrate easily from the dangling-bond site (X) to another via the bridge-bonded site (●), and second, along the edge of and parallel to the dimer row. (b) The two lowest-energy sites (A and B) for the equilibrium configuration of Cl on Si(100)-2×1.

findings, when repeated throughout the whole surface, will yield the total-energy surface for an isolated Cl atom on Si(100)-2×1. For the cases where two and three Cl atoms are deposited near the vicinity of a dimer pair, the Cl atoms and the surface dimer atoms are also relaxed to obtain the minimum energy configuration. Figure 1(a) illustrates the total-energy surface obtained for Cl/Si(100). It appears that there are two low-energy paths: one between the dangling-bond site of a dimer atom and the bridge-bonded site atop of the dimer, i.e., above the dimer itself. The second one is along the edge of the dimer row, parallel to it on either side. The barrier to diffusion along this path (edge of the dimer row) is about 1.0 eV. Diffusion across dimer rows is unlikely due to the higher barrier. On the other hand, the first path would facilitate the migration of Cl atoms from one dangling-bond site to another via the intermediate bridge-bonded site as proposed by Boland based on his STM observations. An alternative diffusion path is for the Cl to move parallel to the dimer row although the activation energy is higher than for the path above. Based on these total-energy calculations, two lowest-energy sites, A and B, are identified as shown in Fig. 1(b). Site A refers to the dangling-bond site of one of the surface dimer atoms [marked with a cross "X" in Fig. 1(a)] while site B, which is 0.14 eV higher, refers to the bridge-bonded site above the dimer bond [marked with a small dark circle in Fig. 1(a)]. This finding agrees very well with the observations of Cheng *et al.*[4] from ESDIAD studies that there exists two

TABLE I. Comparison of calculated results (X) of bond lengths and binding energy for the Cl/Si(100) system with those of Kruger and Pollmann (Y) experimental data.

	X	Y	Experiment
Si-Si dimer without Cl (Å)	2.395		2.40[a]
Si-Si dimer site B (Å)	2.40		
Si-Cl bond (Å)	2.08		2.01[b]
Si-Si dimer with Cl at dangling-bond site A (Å)	2.44	2.40	
Inclination of Si-Cl bond from surface normal	19.3°	15°	25°±4°[c]
Si-Cl bond (Å)	2.11	2.05	2.01[b]
Si-Cl bond strength (eV)	4.02	4.14	4.34[d]

[a]Reference 21.
[b]The Si-Cl bond length in $SiCl_4$ is 2.01 Å (see Ref. 4).
[c]Reference 4.
[d]J. C. Bailar, H. J. Emeleus, Sir R. Nyholm, and A. F. Trotman-Dickenson, *Comprehensive Inorganic Chemistry* (Pergamon, Oxford, 1973), Vol. 1, p. 1259.

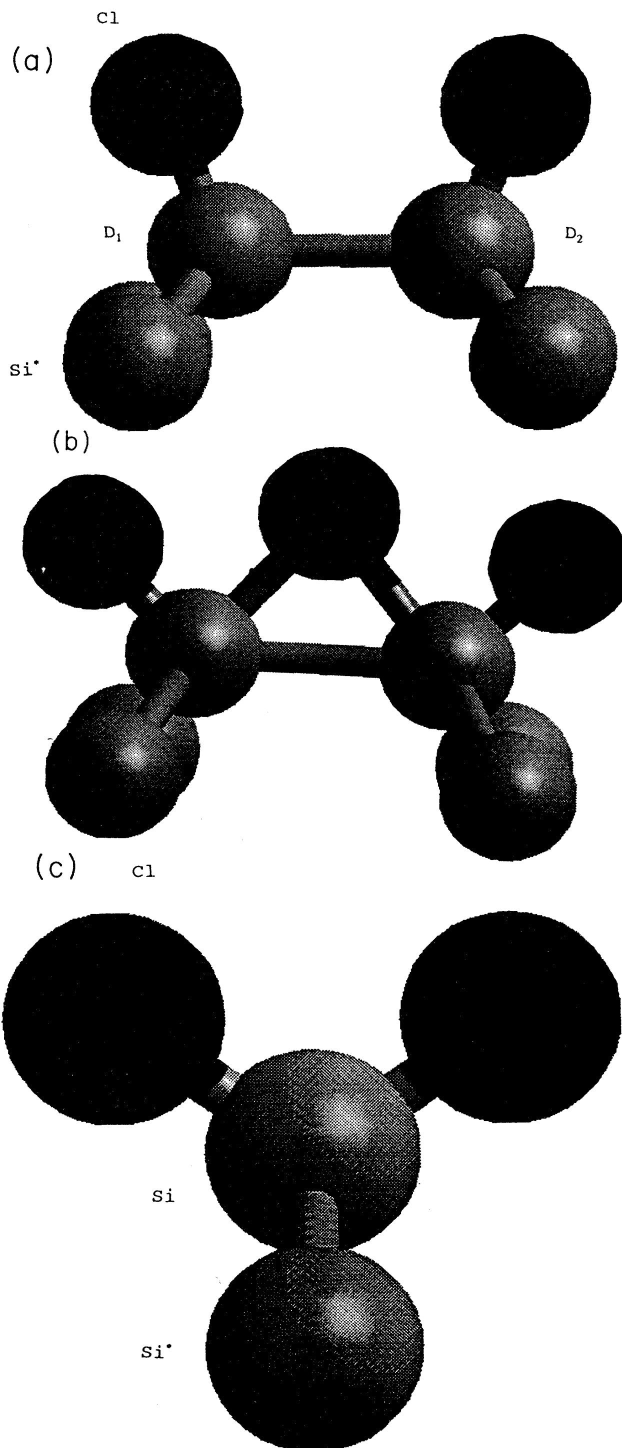

FIG. 2. (a) Geometry of the monochloride phase of Cl/Si(100) whereby the Cl atoms saturate the dangling bonds of the surface Si dimer atoms (D_1 and D_2). Details of the geometry are in the text. The Si atoms just below the surface are designated Si*. (b) Geometry for three Cl atoms chemisorbed on a dimer bond. Bond weakening is evident from the lengthening of the dimer bond as well as the backbonds of the surface Si dimer atoms. (c) Structure of the $SiCl_2$ unit on the Si(100) surface. The Si-Si* backbonds are weakened due to the chemisorption of the Cl atoms on the surface Si atom.

different bonding structures for Cl on Si(100): the off-normal Si-Cl bonding geometry, corresponding to site A in our calculations, is the lower-energy configuration for Cl chemisorbed on the Si(100) surface; the bridge-bonded structure for Cl on Si(100), corresponding to geometry B in our calculations, is the higher-energy structure. Our results are also compatible with the STM findings of Boland[9] where he suggested that the bridge-bonded site is the metastable intermediate site facilitating the migration of Cl atoms from one dangling-bond site (site A) to another as well as those from the *ab initio* calculations by Kruger and Pollmann.[6] Hence, our results are in contrast to those of Purdie *et al.*[5] who identified a normally oriented Si-Cl bond geometry with the Cl atom chemisorbed on a buckled dimer to be their equilibrium configuration for Cl on Si(100). [Guo, Sterratt, and Williams[22] also recently identified bonding forms for Cl on Si(100) which are multiple, with relative contributions dependent on both substrate temperature and Cl gas coverage, with the Cl atoms adsorbed on the symmetric dimer a stable form.] For Cl at the dangling-bond site (A), the dimer bond length is relaxed by about 1.9%; for Cl at the bridge-bonded site (B), the dimer bond length is shorter than for Cl at site A (refer to Table I for comparison with *ab initio* calculations and experiment), although it is comparable to the value on the clean surface. Hence, the isolated Cl atom at the bridge-bonded site does not appear to break the surface Si-Si dimer bond.

We then perform the calculations for the following geometries, illustrated in Fig. 2, to see how the Cl atoms chemisorbed at the dangling-bond sites of the dimer atoms affect the dimer-bond length, in the absence [Fig. 2(a)] and presence [Fig. 2(b)] of a third Cl atom at the bridge-bonded site. The calculations take into account the relaxation of the Cl atoms and the surface dimer atoms, D_1 and D_2 illustrated in Fig. 2, which depicts the calculated geometries and bond distances for Cl adsorption at both sites A and B. In the equilibrium configurations (absence of third Cl atom), for two Cl atoms, each adsorbed at the dangling-bond site of the surface dimer atoms, the dimer bond length is 2.44 Å, 1.9% larger than the value on the clean surface. The Si-Cl bond makes an angle of 19.3° with the surface normal, quite close to the experimental value of 25°±4°.[4] The calculated Si-Si bond length between a Si dimer atom and a Si atom in the second layer just below the surface (Si* in Fig. 2) is 2.36 Å.

On the other hand, for three Cl atoms, where two of the Cl atoms saturate the dangling bonds of the surface dimer atoms, the introduction of the third Cl atom at the bridge-bonded site leads to appreciable changes in the equilibrium geometry on the surface [see Fig. 2(b)]. First, the dimer bond length extends to 2.56 Å (an increase of almost 6.9% over the value of the clean surface), suggesting an induced bond weakening of the surface dimer bond upon further adsorption of Cl atom at the bridge-bonded site after the dangling bonds of the dimer atoms have initially been saturated by Cl atoms. Second, the adsorbate-adsorbate repulsion is evident as the angle of inclination to the surface normal made by the Si-Cl bonds at the respective dangling-bond sites increases to almost 49° from 20° once the third Cl atom is introduced in between at site B. Third, there is also a lengthening of the bond between the surface dimer Si atom and Si*, the second-layer Si atom bonded to the surface atom. This bond length increases to 2.40 Å, about 2% larger than the bulk bond length. Therefore, the backbonds of the Si surface dimer atoms appear to be under strain due to the deposition of another Cl atom at the bridge-bonded site after saturation of their dangling bonds by Cl atoms initially.

All these suggest a prelude to the spontaneous etching phenomena observed recently by Chander *et al.*[7] whereby they also suggested that a coordinated breaking of the dimer bonds due to halogen adsorbates is followed by redimerization, which may eventually yield a mixed-bonding configurations [reminiscent of the H-Si(100)2×1 system] where rows of Si atoms doubly bonded to Cl (Br) may alternate with rows of dimerized Si singly bonded to Cl (Br). The concerted desorption of the $SiCl_2$ ($SiBr_2$) units will then result in the missing row patterns observed experimentally. To investigate further, an additional set of calculations is performed with two Cl atoms attached to a surface Si atom to mimic a $SiCl_2$ unit on the Si(100) surface [see Fig. 2(c)]. Our calculations indicate that the backbonds of the Si atom involved in this dichloride phase are weakened as there is an increase in the bond length from 2.36 to 2.43 Å. In addition, examination of the coefficients of the basis functions belonging to these bonding orbitals indicate some hole localization on these backbonds associated with the Si atom with two Cl atoms attached, leading to the bond lengthening. Although we are not able to simulate the bond breaking as observed for the spontaneous etching of $SiBr_2$ units, the results of the above calculations do provide strong evidence for the bond-weakening effect of the halogen adsorbates, which may subsequently lead to the spontaneous etching as observed experimentally.[7] It appears that the chemisorption of Cl (or Br) on the Si(100) surfaces reduces the Si-Si backbond strength, probably due to localization of a hole on the Si-Si bond because of the large electron affinity of a halogen atom. Examination of the lowest unoccupied orbital and the reduction in charge of the Si-Si backbond provides support for this assumption. We speculate that the breaking of the dimer bonds should not proceed until all the dangling bonds of the dimer atoms have been saturated by the halogen atoms.

V. CONCLUSION

In summary, we have shown that Cl atoms can easily migrate atop the dimer row from one dangling-bond site to another via an intermediate bridge-bonded site, compatible with the STM observations of Boland.[9] In addition, the bridge-bonded site can also act as the nucleation site for further adsorption of a Cl atom. Thus, subsequent chemisorption of halogen atoms may then lead to

the loosening of the dimer bonds and backbonds especially if further chemisorption takes place at the bridge-bonded site, which is also favored energetically as it is the second lowest-energy bonding site after the dangling-bond site. The accompanying breakage of the bonds is then followed by redimerization as mentioned above.[7]

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