

## Barrierless Dimer Breaking at Semiconductor Surfaces by Chlorine Atoms

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The interaction of chlorine with semiconductor surfaces is investigated using the first-principles pseudopotential method. We determine the adsorption geometries of Cl atoms on both GaAs(001) and Si(001) dimerized surfaces in the high-coverage limit. It is found that Cl atoms can break Ga dimers at Ga-terminated GaAs surfaces without any potential barrier. The Cl adsorption simultaneously weakens the Ga-As back bonds at the surface, which contributes to the etching process. The effect of Cl adsorption on the bonding character of semiconductor surfaces is elucidated.

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The interaction of adsorbates with semiconductor surfaces has been one of the main subjects in surface science for many years. Halogens are the most electronegative and reactive atoms, and the question of how halogens react with semiconductor surfaces is of fundamental interest. This reaction also plays an essential role in such technologically important processes in semiconductor device fabrication as reactive-ion etching. Experiments show that the chemical reaction can noticeably enhance the etching rate compared with physical sputtering [1]. Recently, layer-by-layer etching techniques making good use of the chemical reaction have been proposed for future atomically controlled device fabrication [2]. Knowledge of the reaction between halogens and semiconductor surfaces is absolutely necessary to understanding the etching mechanism.

The surface structures induced by the adsorption of halogen have recently come under intense investigation [3–7]. Semiconductor surfaces exhibit various reconstructions due to the presence of dangling bonds (DBs) on the bulk-terminated surfaces. The (001)-oriented surfaces, such as Si(001) and GaAs(001), for example, form reconstructions in which dimers are formed between neighboring surface atoms. How the adsorption of halogen modifies the surface reconstruction is of great importance since it is the first step in the reaction between halogens and surfaces. For Cl-adsorbed Si(001) surfaces, it was experimentally suggested that Cl atoms bond to Si dimer atoms without breaking the dimer bonds [3]. Experimental data available so far, however, are not sufficient to provide an understanding of the halogen-induced surface reconstruction. There have been reported a few theoretical studies, based on *ab initio* methods, which considered halogen adsorption only on *ideal* semiconductor surfaces: F-adsorbed Si(111)-(1 × 1) [5, 6] and Cl-adsorbed GaAs(001)-(1 × 1) [7]. The effect of the halogen adsorption on reconstructed surfaces has not yet been theoretically investigated.

In this Letter we report on the adsorption of Cl atoms on reconstructed semiconductor surfaces using state-of-

the-art theoretical techniques. GaAs(001)-(2 × 1) and Si(001)-(2 × 1) reconstructed surfaces having surface dimers were considered, and the surface structures modified by Cl adsorption were determined in the high-coverage limit. We found that the Cl atoms break Ga dimers on the GaAs surface without any potential barrier, but do not break Si dimers on the Si surface. This is the first report on the barrierless breaking of dimers on semiconductor surfaces as far as we know. We also investigated whether the Cl adsorption can weaken back bonds at the surface, and discussed the mechanism underlying the etching process.

We calculated total energy using the local density functional approach. The total energy functional was minimized with respect to both the plane-wave coefficients of the occupied orbitals and the ionic degrees of freedom by using the conjugate-gradient technique [8]. In computing the total energy, we employed the Wigner form of the exchange-correlation energy and *ab initio* norm-conserving pseudopotentials. Separable pseudopotentials were used for the Si, Ga, and As atoms [9, 10] and a non-separable BHS-type pseudopotential was used for the Cl atom [7, 11]. The pseudo wave functions were expanded in terms of a plane-wave basis set corresponding to a kinetic-energy cutoff of 7.29 Ry. Four special *k* points were employed to sample the primitive surface Brillouin zone. Repeated slab geometry was used to simulate the semiconductor surfaces. The unit supercell contains six atomic layers and one layer of hypothetical hydrogen was used as the surface termination [7]. It was found that an energy cutoff of 7.29 Ry and a supercell containing six atomic layers are sufficient to achieve the convergence of energy differences within 0.2 eV. The optimized geometry of the Si(001)-(2 × 1) dimerized surface determined by this method is in good agreement with that obtained by Yin and Cohen [12]. The details of this method have been described elsewhere [7, 10].

We investigated how Cl atoms adsorb on a Ga-terminated GaAs(001)-(2 × 1) surface, on which Ga dimers are formed and each Ga atom has a single DB

occupied by 0.5 electron. The Cl atoms are quietly deposited at a distance from the surface and then they are allowed to move according to the calculated Hellmann-Feynman forces on them. This procedure corresponds to the situation in which the incident Cl atom has no kinetic energy. We focused on the chemical reaction between the GaAs surface and the Cl atom, instead of the physical sputtering effect induced by the kinetic energy. The Cl atoms with large kinetic energy do uncontrollable damage on the GaAs surface and prevent a smooth and clean etching.

Now let us deposit one Cl atom per  $(2 \times 1)$  unit cell, which is defined as a Cl coverage of 0.5 monolayer,  $\theta = 0.5$ . The Cl atom approaches to within one Ga atom of the surface Ga dimer (denoted as  $\text{Ga}^1$ ) forming a bond with it, as shown in Fig. 1(a). The  $\text{Ga}^1$  atom moves upwards from the surface, whereas the other Ga atom (denoted as  $\text{Ga}^2$ ) moves downwards, leading to asymmetrization of the Ga dimer. Since the DB of the  $\text{Ga}^2$  atom shifts higher in energy as it moves downwards, a charge transfer of 0.5 electron occurs from the  $\text{Ga}^2$  atom to the  $\text{Ga}^1$ -Cl bond. As a result, the  $\text{Ga}^1$ -Cl bonding state is completely filled and the  $\text{Ga}^2$  DB is empty, which stabilizes this structure. The  $\text{Ga}^1$ -Cl bond length is cal-

culated to be  $2.06 \text{ \AA}$ , which is nearly equal to the experimental value of  $2.09 \text{ \AA}$  in a  $\text{Ga}_2\text{Cl}_6$  molecule. The calculated  $\text{Ga}^1$ -Cl adsorption energy of 5.0 eV is comparable to the experimental binding energy of 4.9 eV.

When one more Cl atom is deposited on this surface (corresponding to a Cl coverage of 1.0 monolayer), the Cl atom moves to form a bond with the  $\text{Ga}^2$  atom of the dimer. The resulting surface is a monochloride phase, in which the Cl atoms terminate the DBs of the Ga dimer without breaking the dimer [Fig. 1(b)]. The  $(2 \times 1)$  periodicity is maintained after this Cl adsorption. The monochloride structure corresponds to the hydrogen-chemisorbed  $\text{Si}(001)-(2 \times 1)$  surface [13]. A Cl-adsorbed  $(1 \times 1)$  surface with the Ga dimer broken, shown in Fig. 1(c), has a slightly lower energy than the monochloride surface. An activation energy is, however, required for the Cl atom to break the Ga dimer and achieve the  $(1 \times 1)$  phase.

Furthermore, we deposit one more Cl atom on the monochloride surface. The Ga dimer can be broken for the first time at this Cl 1.5-monolayer coverage. The resultant broken-dimer surface is shown in Fig. 1(d). The  $\text{Ga}^1$  atom is bonded with one Cl atom, forming a quasi-monochloride subunit, whereas the  $\text{Ga}^2$  atom is bonded with two Cl atoms corresponding to a dichloride structure. Since we move the deposited Cl atom according to the calculated forces, it could not break the Ga dimer if there was a potential barrier. The breaking of the Ga dimer by the Cl adsorption is, therefore, a barrierless and exothermic reaction.

The surface dimers cannot be broken when Cl atoms are quietly deposited on the As-terminated  $\text{GaAs}(001)-(2 \times 1)$  surface or the  $\text{Si}(001)-(2 \times 1)$  surface. For the  $\text{GaAs}(001)\text{-As}(2 \times 1)$  surface, a broken-dimer structure like Fig. 1(d) is unstable against redimerization. The adsorption of three Cl atoms per  $(2 \times 1)$  unit cell results in a surface consisting of a monochloride structure plus one adsorbed Cl atom. For the  $\text{Si}(001)-(2 \times 1)$  surface, the monochloride phase is resistant to the deposited Cl atom breaking the Si dimer, although the total energy is lowered when the Cl atom can take the configuration of the broken-dimer structure. The Cl atoms cannot further adsorb on the monochloride surface.

To demonstrate the differences in dimer breaking by Cl atoms, we calculated the total energies of the Cl adsorption on the monochloride phase of the  $\text{GaAs}(001)\text{-Ga}(2 \times 1)$  and  $\text{Si}(001)-(2 \times 1)$  surfaces when the Cl atom approaches from above the middle of the dimer (Fig. 2). It was found that the Cl atom can break the Ga dimer without any potential barrier, whereas the breaking of the Si dimer has a barrier. Dimer breaking by Cl atoms can be explained in terms of the reduction in the bonding charge of the dimer, which is induced by the large electronegativity of the Cl atom. On the monochloride  $\text{GaAs}(001)\text{-Ga}(2 \times 1)$  surface, the Ga-Cl bond captures 0.5 electron from the Ga dimer to fill the Ga-Cl bonding

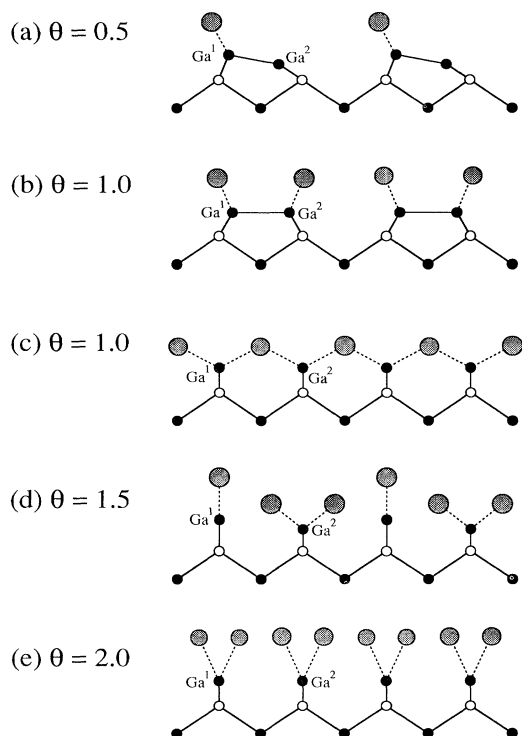


FIG. 1. Atomic structures of Ga-terminated  $\text{GaAs}(001)-(2 \times 1)$  surfaces with Cl atoms adsorbed. The Cl-atom coverage,  $\theta$ , is defined as the number of Cl atoms per  $(1 \times 1)$  unit cell. The solid, open, and dotted circles respectively describe the Ga, As, and Cl atoms.

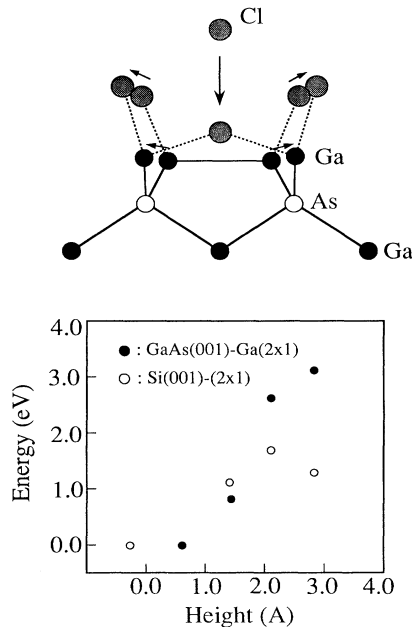


FIG. 2. Calculated total energy of the Cl adsorption on the monochloride phase of the GaAs(001)-Ga( $2 \times 1$ ) and Si(001)-( $2 \times 1$ ) surfaces. The adsorbed Cl atom approaches from above the middle of the surface dimer.

state completely. The reduction in the bond charge of the Ga dimer elongates its length by 0.53 Å. The Ga dimer, therefore, becomes weakened and ready to be broken by further Cl adsorption. On the other hand, the Si-Cl bonding state initially has two electrons without capturing any electrons from the Si dimer. Since the bond charge of the Si dimer is not reduced, the dimer length is not elongated, which means that the dimer is not weakened. Thus, the Cl atom requires an activation energy of 0.5 eV to break the Si dimer.

We found that Cl atoms can break Ga dimers on the GaAs surface without any potential barrier at the Cl coverage  $\theta = 1.5$ . The barrierless dimer breaking is also expected to occur in the range  $0.5 < \theta < 1.5$ , where monochloride Ga dimers [Fig. 1(b)] exist, from *ab initio* pseudopotential calculations for ( $4 \times 1$ ) unit cells. Actually, *ab initio* calculations of ( $4 \times 1$ ) surfaces including two monochloride Ga dimers have shown that a Cl atom deposited further can break one of the two monochloride Ga dimers without any potential barrier, which situation corresponds to  $\theta = 1.25$ . Detailed discussions will be described elsewhere [14].

When the incident Cl atom has enough kinetic energy to overcome potential barriers, but not enough to destroy the semiconductor network, the Cl-adsorbed surface may take a thermodynamically stable structure. To determine the thermodynamic stabilities of the Cl-adsorbed surfaces with different Cl coverages, we must calculate

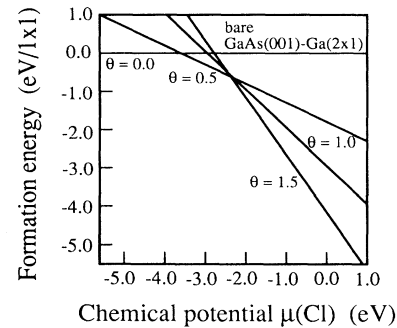


FIG. 3. Calculated surface formation energy for the Cl-adsorbed Ga-terminated GaAs(001)-( $2 \times 1$ ) surfaces. The horizontal line at 0.0 eV is the surface energy of the bare GaAs(001)-Ga( $2 \times 1$ ) surface. The origin of the Cl chemical potential is taken to be half of the total energy of a  $\text{Cl}_2$  molecule.

their formation energies, which depend on the Cl chemical potential  $\mu_{\text{Cl}}$ . At zero temperature, the formation energy  $\Omega$  may be written as

$$\Omega = E - n_{\text{Cl}}\mu_{\text{Cl}}, \quad (1)$$

where  $E$  is the total energy and  $n_{\text{Cl}}$  is the number of adsorbed Cl atoms.

In Fig. 3 we present the calculated formation energies for the Cl-adsorbed Ga-terminated GaAs(001)-( $2 \times 1$ ) surfaces as a function of Cl chemical potential. In this figure,  $\mu_{\text{Cl}}$  is measured relative to half of the total energy of a  $\text{Cl}_2$  molecule. Thus,  $\mu_{\text{Cl}} = 0$  is the chemical potential at which  $\text{Cl}_2$  molecules can be formed from a reservoir of Cl with no cost in energy. For  $\mu_{\text{Cl}} \leq -3.6$  eV, the bare Ga-terminated ( $2 \times 1$ ) surface has a lower energy than any of the Cl-adsorbed surfaces.

The surface with a Cl coverage of 0.5 monolayer [Fig. 1(a)] is stable in the range  $-3.6 \leq \mu_{\text{Cl}} \leq -2.4$  eV. When  $\mu_{\text{Cl}}$  exceeds  $-2.4$  eV, the broken-dimer surface [Fig. 1(d)] is the most stable structure. Neither the ( $2 \times 1$ ) monochloride surface [Fig. 1(b)] nor the ( $1 \times 1$ ) surface with Cl atoms adsorbed on the bridge sites [Fig. 1(c)] is a thermodynamically allowed phase. The dichloride structure shown in Fig. 1(e) is not allowed either. The saturation coverage of Cl atoms is, therefore, 1.5 monolayers for the Ga-terminated GaAs surface. For the As-terminated GaAs(001)-( $2 \times 1$ ) surfaces, a transition occurs from the bare surface directly to the surface with a Cl saturation coverage of 1.5 monolayers, skipping surfaces covered with 0.5 and 1.0 Cl monolayer. The saturated surface still has As dimers on it, as described above. As shown in Fig. 4, the Cl-saturated Si(001)-( $2 \times 1$ ) surface is the monochloride phase having a Cl coverage of 1.0 monolayer, which is consistent with experimental results [15]. In this way, the Cl-saturated phase of each semiconductor surface is coincident with the final structure when Cl atoms are quietly adsorbed.

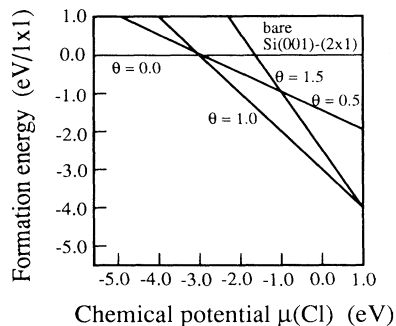


FIG. 4. Calculated surface formation energy for the Cl-adsorbed Si(001)-(2 × 1) surfaces. The horizontal line at 0.0 eV is the surface energy of the bare Si(001)-(2 × 1) surface.

On the Ga-terminated GaAs(001)-(2 × 1) surface, the adsorbed Cl atoms form strong Ga-Cl bonds and break the Ga dimers without a potential barrier. It is interesting to speculate whether the adsorption of Cl atoms can weaken the Ga-As back bonds, thus contributing to the etching of GaAs. When the Ga dimer is broken by the adsorption of three Cl atoms, the broken-dimer (2 × 1) surface is an ordered mixture of the quasimonochloride As-Ga<sup>1</sup>-Cl subunit and the dichloride As-Ga<sup>2</sup>-Cl<sub>2</sub> subunit, as shown in Fig. 1(d). It was found that the Ga<sup>1</sup>-As back bond of the former subunit is elongated by 0.22 Å, indicating that the bond is weakened, while the Ga<sup>2</sup>-As back bond of the latter is not elongated. A (1 × 1) surface which consists only of the quasimonochloride subunits, however, does not exhibit the elongation of the Ga<sup>1</sup>-As back bond. In the broken-dimer (2 × 1) surface, substantial charge transfer occurs from the quasimonochloride subunit to the dichloride one due to the large electronegativity of the Cl atom. As a result, the reduction in the number of bonding charges elongates and weakens the Ga<sup>1</sup>-As back bond. This weakening of the Ga-As back bond is, therefore, caused by the charge transfer between the two different subunits on the broken-dimer surface. The back bonds are not weakened on the As-terminated GaAs(001)-(2 × 1) or the Si(001)-(2 × 1) surfaces, since the Cl adsorption cannot break the surface dimers. It was experimentally found that GaCl is the main Cl-containing species produced in the thermal desorption from GaAs(001) with low Cl coverages [16]. The weakening of the Ga<sup>1</sup>-As back bond is consistent with the observed thermal desorption of GaCl species.

It has been shown in our previous work [7] that Cl atoms have the possibility to break the GaAs crystal through two reaction processes: the exchange between Cl and As atoms and the insertion of Cl atoms into Ga-As bonds. The weakening of the Ga-As back bond induced

by the Cl adsorption can lower the activation barriers for these reactions and contribute to the GaAs etching. Actually, the Cl adsorption is shown to significantly enhance the etching rate of GaAs(001) surface by recent experiments [2].

In summary, we investigated the interaction of Cl atoms with semiconductor surfaces using the first-principles pseudopotential method and explained the effect of Cl adsorption on the bonding character of surfaces. It was found that Cl atoms can break Ga dimers at the GaAs surface without any potential barrier and simultaneously weaken the Ga-As back bond at the surface. These interactions play an essential role in the GaAs etching processes.

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