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Surface structure and doping-induced etching of Si(100) by chlorine: First-principles study

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Surface-structure and doping effects on Si(100) surface etchings by Cl atoms and molecules have been studied based on first-principles calculations. The calculated results reveal that the desorption energy of $SiCl_2$ from the $p(1\times1)$ geometry is in excellent agreement with the experimental result, implying that a plausible surface-structure change in Cl adsorbed surfaces at high temperatures above 600 °C could trigger a spontaneous desorption. The calculated desorption energies for Cl adsorbed Si surface systems have been decreased by raising the Fermi level as observed in experiments. It is found to be mostly the effects of total energy reduction by dipole fields generated between virtual holes and ionized Cl atoms. [S0163-1829(96)07227-X]

I. INTRODUCTION

Halogens on semiconductors are of great interest not only for technological importance, but also from scientific viewpoints to understand systematic adsorption and desorption processes initiated by atoms or molecules. Molecular halogens are chemisorbed on the Si(100) surface exothermally and form a stable adsorbed structure on the Si(100) surface at low temperatures.[1] The halogen atoms are chemically bonded to dimer dangling bonds or bonded on bridge sites.[2] The adsorbed halogens spontaneously desorb or cause etching as volatile molecules, when the surface temperature is elevated up to 600 °C.[3–5] A flux of halogen atoms and molecules exposed to Si surfaces at elevated temperatures also yields a continuous etching of the Si surfaces.[6,7] There are still some ambiguities concerning the etch rate strongly dependent on surface structures. The etch rate by a flux of halogen molecules also depends on the doping levels in semiconductors.[7] A higher etch rate has been achieved on n-type Si rather than on p-type Si.[8]

The contradictions in halogen adsorption and desorption on semiconductors stimulated us to study the etching of the Si(100) surface by Cl to learn the principles inherent in overall aspects of semiconductor etching by halogens. Electron stimulated desorption ion angular distribution (ESDIAD) studies have implied possible geometries for Cl adsorbed structures on the Si(100) surface.[9,10] Those studies, including angle-resolved photoemission (ARPES) studies, suggest that adsorbed Cl atoms are chemically bonded to dimer dangling bonds.[9,11–13] Those structures are confirmed to undergo some reconstructions at high temperatures.[9] Cl molecular beam studies have shown that the volatile molecules desorbed from the Cl adsorbed Si(100) surface are $SiCl_2$ and SiCl rather than $SiCl_4$ at high temperatures.[3–5] Those findings imply that the spontaneous molecule desorption might be related to a possible structure change at high temperatures. Several theoretical studies have shown stable configurations for Cl adsorption on the Si(100) surface.[2,14,15] Based on this understanding, the present study is focused on the basic mechanism of etching occurring as volatile molecules from Cl adsorbed Si(100) surfaces. Then the study is also extended to doping effects on etching. n-type doping has been shown to enhance the Si etch rates by more than two orders of magnitude.[8] The present calculations start from those optimized geometries of Cl adsorbed structures and are extended to desorption pathways which may strongly depend on the surface structure. For understanding the effects of surface structure and doping, the present calculations are performed on the following subjects: desorption induced by activated Cl atoms, desorption of spontaneous or Cl_2 activated reactions, and the n-type doping dependence of desorption.

II. CALCULATION METHODS

The electronic-state calculations have been performed using self-consistent pseudopotential techniques within density-functional formalism in the local-density approximation. The norm-conserving pseudopotential is employed, following the method of Bachelet, Hamann, and Schlüter.[16] The Perdew-Zunger and Cerperley-Alder correlations were implemented.[17,18] Fictitious time derivatives of electronic wave functions are integrated to converge the electronic states on the basis of momentum-space formalism at each time step for ionic motions. The Si(100) surface is modeled as a repeated slab consisting of 10 Si layers and 16.3 Å of vacuum spacing. Inversion symmetry with respect to the middle of the slab is employed to increase the computational efficiency. A cutoff energy of 12 Ry has been employed at a single k point (Γ point) to converge the total energy sufficiently. The errors of the calculations due to the single k point have been checked by comparing the desorption energy of a Cl atom from the Cl adsorbed $c(4\times2)$ geometry with two and four k point sampling. The desorption energy was found to be reduced by 0.1 eV from one k point to two and four k points. It was found that the calculations have achieved convergence of the energy difference within 0.1 eV. The initial configurations of Cl adsorbed Si surfaces were first formed by optimizing atom positions in the supercell geometry.

Since etchings of Si surfaces occur more rapidly at high temperatures, one can propose that desorption of volatile molecules occurs through the bond breakings with the smallest binding energies. This idea is supported by the fact that volatile molecules in the case of Si etching by Cl molecules are mostly $SiCl_2$ and SiCl rather than $SiCl_4$ in spite of an earlier belief that a Cl atom has to break a Si-Si bond and

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induces the desorption of $SiCl_4$ molecules. A similar phenomenon has also been found in Si etching by oxygen, where SiO molecules desorb from the oxidized Si surfaces above 600 °C.[19] In the present study, therefore, the desorption of Cl atoms and volatile molecules was investigated by searching for the minimum-energy-barrier pathways.[20] Thermal desorption was presumed to occur as an adiabatic process. Since there are some degrees of freedom in atomic motions, the present calculations do not include all possible trajectories in atomic motions. The desorption studies have been carried out for a restricted set of configurations in the direction perpendicular to the surfaces. A specific atom or a center of mass of a desorbing molecule was moved to pass through the saddle point on the potential energy surfaces to find the pathways with the minimum barrier energies.

Thermally activated bond breakings occur at weaker bonds. Those bond strengths are strongly dependent on the energetic balance in atom-atom bond configurations on surfaces. The binding energy between a Cl atom and a Si atom is 3.72 eV, which is almost twice as much as the binding energy of 1.83 eV between two Si atoms.[21] This energetic balance could be slightly distorted by deformations of surface structures. In the present calculations, therefore, we paid attention to effects of possible structure changes on desorption. Two types of Si(100) surfaces, $c(4\times2)$ and $p(1\times1)$, are prepared as a substrate for etching and desorption calculations. The $c(4\times2)$ surface has been found to be the lowest energy configuration on Si(100) surfaces.[22] There is affirmative evidence that the transition from a $p(2\times1)$ to a $p(1\times1)$ surface occurs on Ge(100) surfaces at about 600 °C,[23] although there is no actual confirmation of the rearrangement from the $p(2\times1)$ to the $p(1\times1)$ geometry on Si(100) surfaces by elevating temperatures. Frequent flippings and transitions from (7×7) to (1×1) have been observed on Si(111) surfaces at high temperatures above 830 °C. Here, etchings at high temperatures are assumed as desorptions from the $p(1\times1)$ surfaces. All calculations have been carried out using a (4×2) unit cell employing the $c(4\times2)$ or the $p(1\times1)$ surface geometry.

III. RESULTS

A. Desorption induced by an activated Cl atom

Cl atoms impinging on the Si surface cause etchings as is known from plasma assisted etching experiments. If one Cl atom has a sufficient kinetic energy to break Si-Si backbonds, the incident Cl atom could be repelled together with surface Si atoms as a volatile molecule from the Si surface. Since there are infinitely many pathways for Cl collisions with the Si atoms on surfaces, this reaction is modeled by a simple desorption process from the Cl chemisorbed Si surfaces. Figures 1(a) and 2(a) show (011) cross-sectional views of one-Cl-atom chemisorbed Si(100) surfaces with $c(4\times2)$ and $p(1\times1)$ geometries, respectively. The geometries of Cl and Si atoms are optimized in these structures. In the case of desorption of one Cl atom from chemisorbed Si(100) surfaces, the Cl atom is moved toward the vertical direction from the optimized geometries as shown in Fig. 1(a) and Fig. 2(a). The final configurations for these cases are shown in Fig. 1(b) and Fig. 2(b). In both cases, solely the Cl atom is found to simply desorb. The desorption energies are 4.1 and 4.5 eV, respectively. In the case of Fig. 2(a), the top Si atom is bonded only to two substrate Si atoms in contrast to the top Si atom bonding to three Si atoms in Fig. 1(a). The Si-Cl binding energy is almost equal to the sum of binding energies of the two substrate Si atoms in the case of Fig. 2(a). The desorption of a SiCl or a $SiCl_2$ molecule does not, however, occur because of the energetically unfavored geometry of Cl atoms on the Si surface in this case.

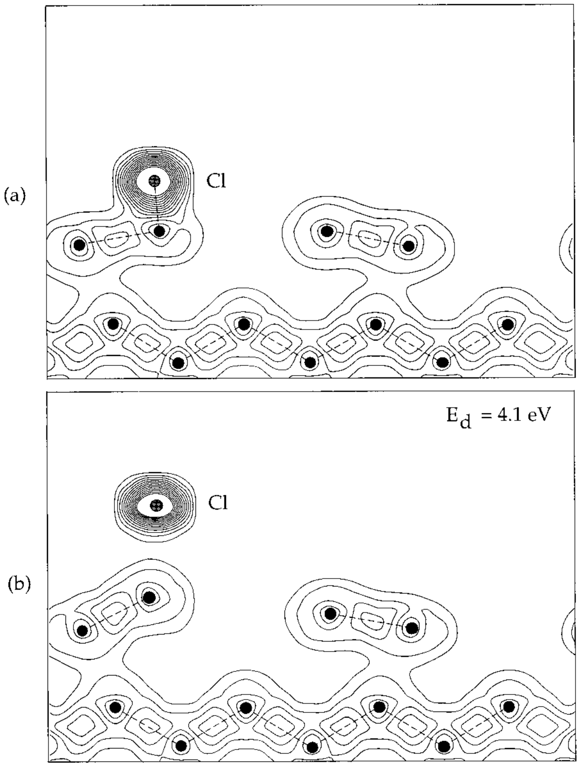

FIG. 1. (011) cross-sectional views of (a) the initial configuration for Cl adsorbed Si(100)-$c(4\times2)$ surface and (b) the final configuration for Cl desorption from Si(100)-$c(4\times2)$ surface. Cl and Si atoms are represented by shaded and filled circles, respectively. Valence-charge densities are given by equicontour plots.

Figures 3(a) and 4(a) show the (011) cross-sectional view of the two-Cl-atom chemisorbed Si(100) surfaces with $c(4\times2)$ and $p(1\times1)$ geometries, respectively. There is another stable geometry on the $c(4\times2)$ surface, where one dimer is terminated by two Cl atoms as shown in Fig. 5. The total energy of this geometry is calculated to be 1.5 eV higher than that of Fig. 3(a), where the Cl atoms are almost forming a molecular structure. Since both Si atoms in the dimer are bonded tightly to three Si atoms, a thermal activation of single Cl atoms does not cause desorption as $SiCl_x$, but mostly results in desorption of one Cl atom as confirmed in the present subsection. We have neglected the desorption in this case. Both Cl atoms in Figs. 3(a) and 4(a) are bonded to one of the Si atoms on the surface. The geometries of Cl and Si atoms are also optimized in these structures. Both geometries could be possible intermediate configurations for spontaneous desorption, to be described in the following subsection. The desorption process is started by moving one of two Cl atoms along the vertical direction from the Si surface chemisorbed with two Cl atoms. The final configurations after the minimum-barrier desorption processes for these cases

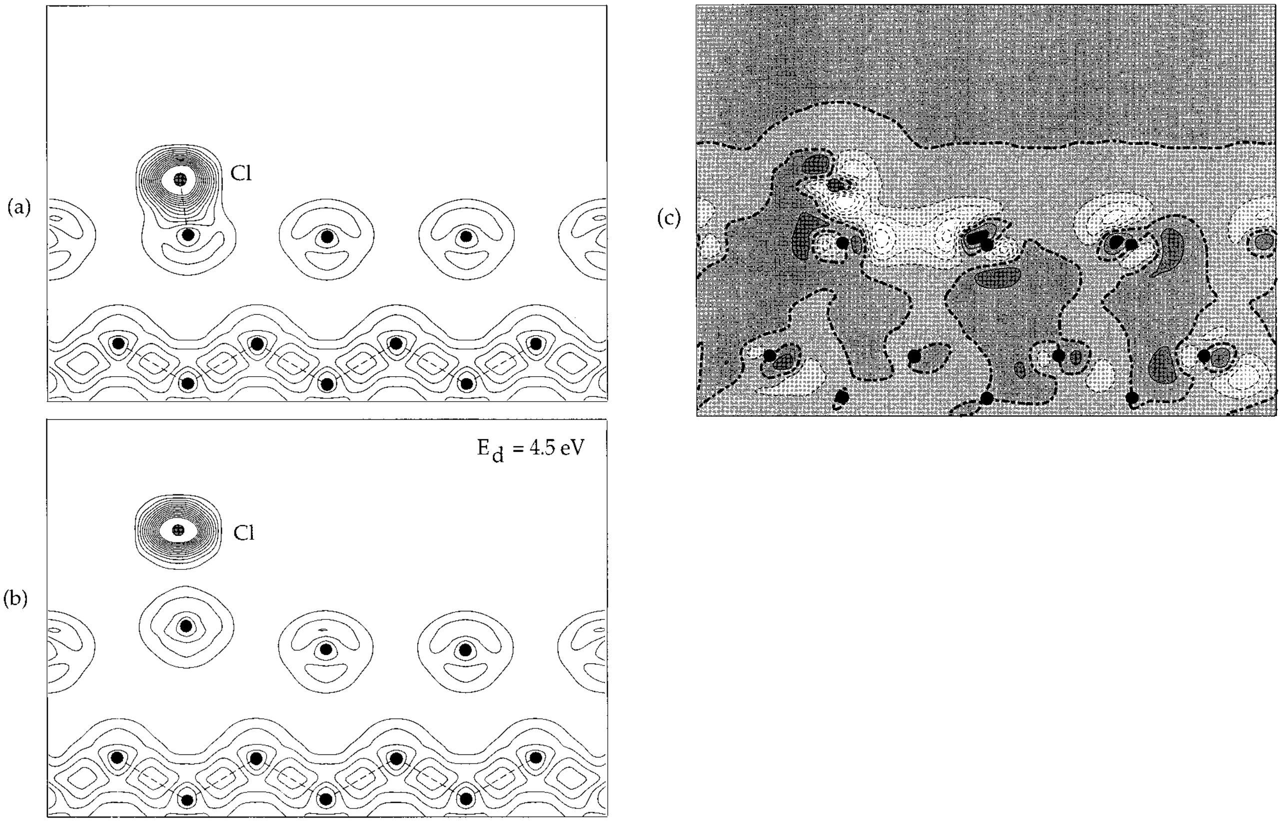

FIG. 2. (011) cross-sectional views of (a) the initial configuration for Cl adsorbed Si(100)-$p(1\times1)$ surface and (b) the final configuration for Cl desorption from Si(100)-$c(1\times1)$ surface. Cl and Si atoms are represented by shaded and filled circles, respectively. Valence-charge densities are given by equicontour plots. (c) Equicontour plots of difference in valence-charge densities between the undoped and the excess-electron cases on (011) cross section for Cl atom adsorbed Si(100)-$p(1\times1)$ surface, corresponding to (a). Solid lines show charge surplus regions, while dotted lines show charge deficit regions in the undoped cases compared with the excess-electron cases. Thick dash-dotted lines represent the 0 value.

are shown in Fig. 3(b) and Fig. 4(b). The Cl atom alone desorbs in the case of the $c(4\times2)$ surface, while it desorbs as a $SiCl_2$ molecule in the case of the $p(1\times1)$ surface. The difference of the two-Cl-atom chemisorbed surface geometry shown in Fig. 4(a) from the one-Cl-atom chemisorbed surface geometry as shown in Fig. 2(a) can be attributed to strong sp^3 bond formation by two upper Cl atoms and two lower Si atoms bonding to one Si atom. This favors the Si-Cl bond rather than the Si-Si backbonds, as is indicated by a slight bond energy dominance of one Si-Cl bond over two Si-Si bonds. The desorption energies for Fig. 3(b) and 4(b) are 6.8 and 6.5 eV, respectively. Those energies are relatively higher as compared to those of spontaneous desorption, which will be described in the following subsection. This is mostly due to large surface deformation accompanying the desorption.

B. Spontaneous desorption or Cl_2 activated reaction

Major volatile molecules for spontaneous desorption are primary $SiCl_2$ and secondarily SiCl as indicated by several experimental results.[3–5] Our study is mainly concentrated on desorption of major $SiCl_2$ molecules. The desorption of $SiCl_2$ is likely to break the backbonds more easily than in the case of SiCl desorption.

For one-monolayer-Cl saturated Si(100) surfaces, the $p(2\times1)$ surface geometry with each dimer dangling bond terminated by a Cl atom is the most plausible configuration realized at low temperatures. The existence has been confirmed by several ESDIAD and ARPES studies[9,11–13] and is supported by theoretical work,[14,15] although there still remains another possibility for the lowest energy configuration.[10] The geometry of Cl adsorbed on bridge sites could be the lowest energy configuration.[2] Since a $SiCl_2$ molecule has been found to desorb from Cl adsorbed Si surfaces, we have explored this mechanism starting from the $c(4\times2)$ surface geometry of one dimer terminated with two Cl atoms as shown in Fig. 5. Desorption of $SiCl_2$ requires formation of $SiCl_2$ prior to desorption:

$$2\,\mathrm{SiCl(ads)} \rightarrow \mathrm{Si(ads)} + \mathrm{SiCl_2(ads)} \qquad (1)$$

$$\rightarrow \mathrm{Si(ads)} + \mathrm{SiCl_2(gas)}. \qquad (2)$$

Here, we have to postulate an intermediate configuration for spontaneous $SiCl_2$ desorption. One of the most plausible geometries is obtained by moving one of the two Cl atoms closer to the other Cl atom. This corresponds to the case where a Cl molecule is chemisorbed at one of two Si atoms in a dimer as shown in the cross-sectional view of Fig. 3(a). The pathway for spontaneous desorption is explored by moving the center of the Cl mass along the vertical direction in the geometry shown in Fig. 3(a). The final configuration is shown in Fig. 3(c). This trajectory also corresponds to the

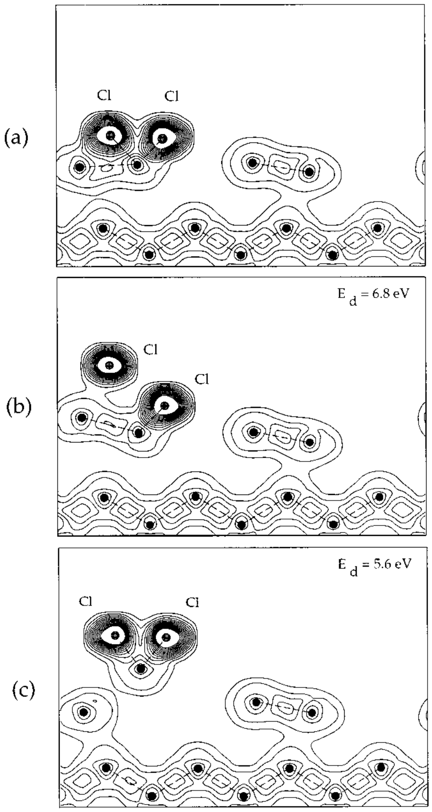

FIG. 3. (011) cross-sectional views of (a) the initial configuration for Cl adsorbed Si(100)-$c(4\times2)$ surface, (b) the final configuration for Cl-atom-induced desorption, and (c) the final configuration for Cl_2-molecule-induced desorption from Si(100)-$c(4\times2)$ surface. Cl and Si atoms are represented by shaded and filled circles, respectively. Valence-charge densities are given by equicontour plots.

desorption of a $SiCl_2$ molecule induced by a collision with one Cl_2 molecule. The desorption energy is 5.6 eV. This energy is still high for spontaneous desorption, but is reduced to 4.1 eV by the initial energy gain of 1.5 eV if the desorption could occur smoothly from the initial to the final configuration via the intermediate configuration.

For the spontaneous desorption at high temperatures, the desorption is started from the $p(1\times1)$ geometry with two Cl atoms chemisorbed on one Si atom on the surface as shown in Fig. 4(a). This geometry could be derived from the intermediate configuration of Fig. 3(a) by the $c(4\times2)$ to $p(1\times1)$ surface transition. It could also be derived from the configuration where two Cl atoms are adsorbed on bridge sites. The desorption pathway is searched by moving the center of the Cl mass along the vertical direction in this case. The final configuration for this motion is shown in Fig. 4(c). This trajectory also corresponds to the desorption of a $SiCl_2$ molecule induced by a collision with one Cl_2 molecule at high temperatures. The desorption energy is 3.2 eV, which is lower than the sum of two Si-Si atom binding energies (3.66 eV) and agrees well with the experimentally obtained desorption energy of 3.2 eV.[24]

C. *n*-type doping dependence of desorption

It has been reported in experimental work that doping has significant influence on the etch rates of Si surfaces. The reaction probabilities of etching can be enhanced by more than one order of magnitude when *n*-type dopant impurities are heavily concentrated. To explore the effect of raising the Fermi level by *n*-type doping of semiconductors, desorption of Cl and $SiCl_2$ is calculated for the Cl adsorbed Si surface system by adding electrons. Background charges are added for excess electrons to neutralize the total system. The calculated results are summarized in Table I together with those calculated without excess electrons in the previous subsection. In both cases of Cl and $SiCl_2$ desorption, desorption energies are reduced by the presence of excess electrons. In the case of Cl desorption from the $p(1\times1)$ geometry, the desorption energy is dramatically reduced from 4.5 eV to 3.7 eV as compared with 0.3 or 0.3 eV energy reduction in Cl desorption from $c(4\times2)$ geometry and $SiCl_2$ desorption from $p(1\times1)$ geometry.

To understand the desorption energy reduction by the presence of excess electrons, the differences of valence electron densities between the undoped and the excess-electron cases are drawn as contour maps. For implementing excess electrons, one electron is added for the one-Cl-atom adsorbed case, while two electrons are added for the two-Cl-atom adsorbed case. Figures 2(c) and 4(d) show the differences of valence electron densities when a Cl atom or two Cl atoms are adsorbed on the Si(100)-$p(1\times1)$ surface, respectively. Solid lines show charge surplus regions, while dotted lines show charge deficit regions in the undoped cases as compared to the excess-electron cases. Thick dash-dotted lines represent the 0 value. As can clearly be seen in both figures, we can confirm that there are charge deficit regions just below the Cl atoms on Si substrates in Fig. 2(c) and on surface dangling bonds in Fig. 4(d) for the undoped cases as compared to the excess-electron cases. In both cases, the electrons are adsorbed by Cl atoms because of the strong electronegativity of Cl. The charge deficit regions in the undoped cases, therefore, can be viewed as virtual holes compensating electron charges absorbed by Cl atoms. The electronic charge configurations of these structures in undoped Si and *n*-type doped Si are schematically summarized in Figs. 6 and 7, respectively. In both figures, (a) and (b) correspond to the initial configuration before desorption and the final configuration after desorption, respectively. The hole is located far from the Cl^- ion in Fig. 7(a), reducing the interaction energy between the hole and the Cl^- ion as is evident in Fig. 6(a). By comparing Fig. 6(a) with 7(a), we can understand that the total system of Cl adsorbed on undoped Si shows a lower energy because of dipole fields generated between virtual holes and Cl^- ions. The final configurations shown by Figs. 6(b) and 7(b) indicate that the undoped cases after desorption also stay in a lower energy state than the excess-electron cases.

IV. DISCUSSION

A. Possible desorption by incident Cl atom activation

The present results imply that etching of Si surfaces activated by impinging Cl atoms can be achieved only on Cl adsorbed $p(1\times1)$ surfaces with a relatively high desorption energy of 6.5 eV. In comparison to the present calculations, measurements of Si etching by Cl atoms have reported that the activation energy of Si(100) surface etching by Cl atoms

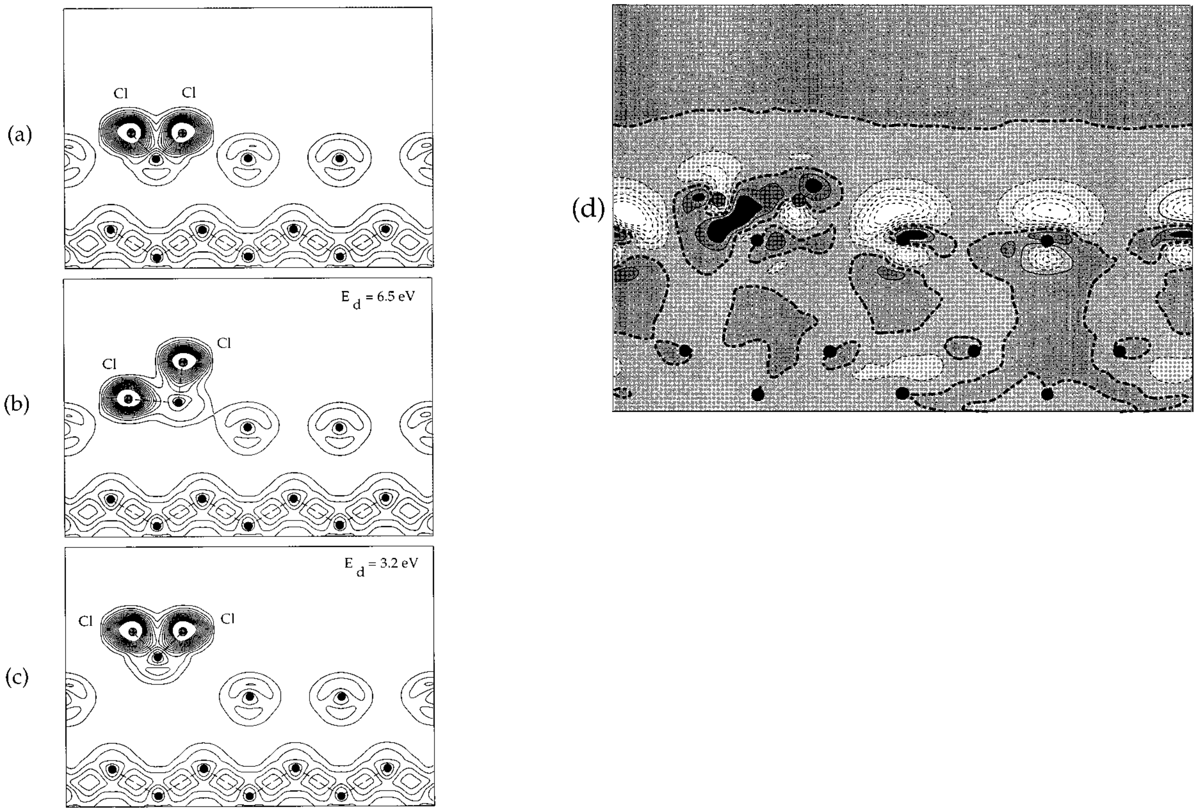

FIG. 4. (011) cross-sectional views of (a) the initial configuration for Cl adsorbed Si(100)-$p(1\times1)$ surface, (b) the final configuration for Cl-atom-induced desorption, and (c) the final configuration for Cl_2-molecule-induced desorption from Si(100)-$c(1\times1)$ surface. Cl and Si atoms are represented by shaded and filled circles, respectively. Valence-charge densities are given by equicontour plots. (d) Equicontour plots of difference in valence-charge densities between the undoped and the excess-electron cases on (011) cross section for two-Cl-atom adsorbed Si(100)-$p(1\times1)$ surface, corresponding to (a). Solid lines show charge surplus regions, while dotted lines show charge deficit regions in the undoped cases compared with the excess-electron cases. Thick dash-dotted lines represent the 0 value. Cl and Si atoms are represented by shaded and filled circles, respectively.

is as extremely small as 0.18 eV.[8] The direct impact energy of hyperthermal Cl atoms to induce desorption is about 1 eV.[25] These differences suggest that etching by Cl atoms occurs with a higher Cl coverage on Si surfaces, breaking backbonds under Si atoms on surfaces and forming volatile $SiCl_4$ molecules. These molecules easily evaporate with a lower activation energy. The etching processes described in the present calculations have not been realized in the actual stages of Si etching by Cl atoms. This implies that etching induced by Cl atom collisions cannot be achieved in so far as the incident energies of Cl atoms are not well regulated to induce stable Cl adsorption on Si surfaces.

B. Surface-structure effects on the desorption mechanism

For spontaneous or Cl_2 molecule activated desorption on Si surfaces, the calculated activation energy on the $p(1\times1)$ surface is in excellent agreement with the experimental value of 3.2 eV. The desorption energy of 4.1 eV on the $p(2\times1)$ surface is too high to account for the experimental results. The agreement for desorption from the $p(1\times1)$ surface implies that $SiCl_x$ desorption occurs on the $p(1\times1)$ surface at high temperatures. The abrupt increase in

TABLE I. Excessive electronic charge dependence of Cl and $SiCl_2$ desorption energies from Si (1×1) and (4×2) surfaces. All values are in eV.

Extra electron	Cl from (1×1)	Cl from (4×2)	$SiCl_2$ from (1×1)
0	4.5	4.1	3.2
1	3.7	3.8	2.9
2			2.8

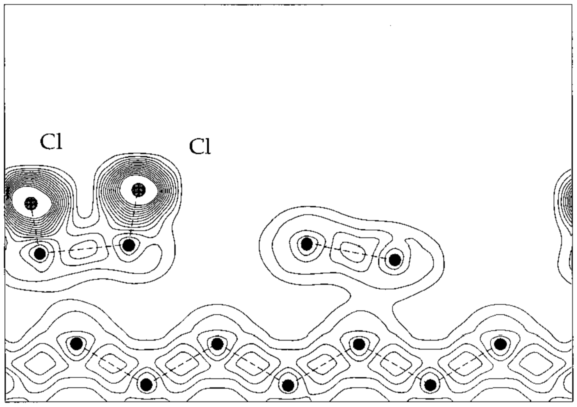

FIG. 5. (011) cross-sectional view of one dimer terminated by Cl atoms on Si(001)-$c(4\times2)$ surface. Cl and Si atoms are represented by shaded and filled circles, respectively. Valence-charge densities are given by equicontour plots.

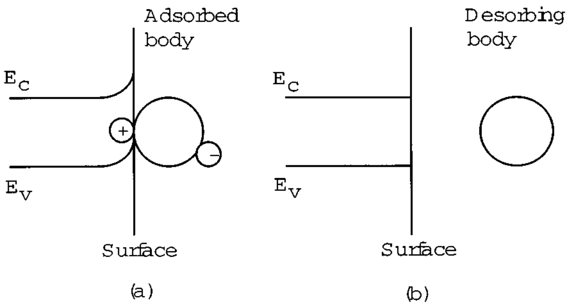

FIG. 6. Electronic charge configurations (a) for adsorbed state and (b) for desorbed state from undoped Si(100)-$p(1\times1)$.

$SiCl_x$ desorption from the Cl adsorbed surfaces found in desorption measurements by elevating the substrate temperatures above 600°C (Refs. 4 and 5) also supports the idea that the Cl adsorbed Si(100) surface shows the $p(1\times1)$ geometry at high temperatures rather than the $p(2\times1)$ geometry. The temperature dependence of desorption rates can be well explained by the geometry change in Cl adsorbed surface structures from the $p(2\times1)$ to the $p(1\times1)$. We have not, however, found any evidence for the $p(1\times1)$ surface geometry of Cl adsorbed Si(100) surfaces to our knowledge, although the $p(1\times1)$ surface geometry of Ge(100) surfaces above 600 °C has been observed by experiment. Here, the following notion could be proposed for high temperature phases of Si(100) surface structures. The geometry changes may have arisen from the nature of Si surface structures.

An abrupt increase in spontaneous desorption of $GaCl_x$ and $AsCl_x$ from the Cl adsorbed GaAs surfaces has been also observed at about 400 °C, where the same type of temperature dependence in desorption spectra is obtained.[26] The arguments discussed in the present study may be applicable to explain these experimental results, as well.

C. Dipole-field effects on the desorption mechanism

Cl adsorbed Si substrates without n-type dopant impurities generate a dipole field between negatively charged Cl ions and charge compensating virtual holes as shown in Fig. 6(a). This interaction adds an additional energy to the Cl adsorbed Si system. The total energy E_{tot} of the Cl adsorbed Si system can be described by

$$E_{\mathrm{tot}}=E_{\mathrm{Si}}+E_{\mathrm{Cl}}+E_{\mathrm{ads}}+E_{\mathrm{dpl}} \tag{3}$$

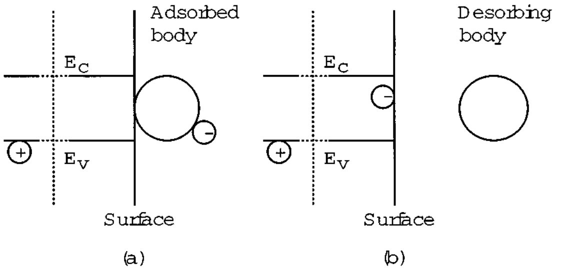

FIG. 7. Electronic charge configurations (a) for adsorbed state and (b) for desorbed state from n-type doped Si(100)-$p(1\times1)$.

where E_{Si} and E_{Cl} represent energies for Si surfaces and Cl atoms, while E_{ads} and E_{dpl} represent energy changes by chemisorption and dipole generation, respectively. Comparing Fig. 6(a) and 6(b), it becomes obvious that the value of E_{dpl} is negative. This negative value increases up to 0 eV by reducing the dipole field, when the substrate is n-type doped. As seen from the final configurations after desorption shown in Figs. 6(b) and 7(b), however, the excess-electron case stays in a higher energy state after desorption than in the undoped case. The consequent reduction in desorption energy in excess-electron cases means that dipole-field effects have a stronger influence than the energy of one electron located above the valence band after desorption. If holes are available to recombine with additional electrons on n-type doped Si substrates, the desorption energies may be further reduced. In the case of a Cl atom adsorbed on the $p(1\times1)$ surface, the desorption energy reduction is 0.8 eV, which is the largest among the postulated structures. This is because a strong dipole field can be generated between the adsorbed Cl^- ion and the virtual hole located on a closer dangling bond as seen in Fig. 2(c).

Etching rates of Si(100) surfaces have been observed to increase by more than two orders of magnitude at 400 K when the n-type dopant concentration is increased from 10^{15} to 10^{20} cm^{-3}.[8] In the present calculations, the increase in etch rates at 400 K by n-type doping is estimated from the desorption energy reduction by 0.3 eV to be more than three orders of magnitude. This estimation is not directly comparable to the experimental results because the present calculations for doped Si correspond to far more extreme cases for dopant concentration. If the experimentally obtained etch rate is extrapolated to the dopant concentration of 10^{22} cm^{-3}, the etch rate increases by more than three orders of magnitude. This tendency in experimentally obtained doping enhancement is almost completely described by the dipole-field effects proposed from the present calculations.

The reduction of desorption energy by dipole fields can be attributed to the charge transfer model proposed from the experimental work.[8] The charge transfer model suggests that adsorption and desorption are enhanced on n-type Si, where excess electrons can be easily transferred to adsorbed Cl atoms. This prevents further chemisorption of Cl atoms on the Si surface. Dipole fields between Cl atoms and Si surfaces well explain this phenomenon through microscopic energetics.

The general aspects of the surface structure and doping relevant to etching phenomena discussed here can be applicable not only to Si(100) but also to other Si surfaces, as well as to other semiconductor materials. n-type doping enhancement has also been found for Si(111) surfaces and polysilicons.

V. CONCLUSIONS

The present studies have been devoted to elucidating the surface structure and doping effects of Si(100) etching by Cl. Cl-atom-collision-induced etching is found to occur on $p(1\times1)$ geometries of Si(100) surfaces through volatile $SiCl_2$ molecules with a relatively high energy barrier of 6.5 eV. A comparison with experimental results on Cl-atom-induced etching implies that the etching mechanism is unlikely to have any influence on actual stages in so far as energies of incident atoms are not well regulated.

The surface-structure dependence of $SiCl_2$ desorption calculations reveals that the desorption energy of a $SiCl_2$ molecule from the two-Cl-atom adsorbed $p(1\times1)$ geometry on the Si(100) surface is in excellent agreement with the experimentally obtained value of 3.2 eV, rather than with that of the Cl adsorbed $p(2\times1)$ geometry. The temperature dependence of $SiCl_2$ desorption shows an abrupt increase at about 600 °C as reported by experimental work. It also supports $SiCl_2$ molecule desorption from the Cl adsorbed $p(1\times1)$ geometry, because it suggests that $p(1\times1)$ geometries may exist on Cl adsorbed Si(100) surfaces at high temperatures.

The desorption energies of Cl and $SiCl_2$ from Cl adsorbed Si(100)-$p(1\times1)$ surfaces are found to be reduced by 0.8 to 0.3 eV, when excess electrons are introduced to the initial configurations of Cl adsorbed Si surface systems. Dipole fields generated between adsorbed Cl^- ions and compensating virtual holes are reduced by adding electrons, leading to desorption energy reduction. This explains well the desorption enhancement by n-type doping in semiconductors found in previous experimental results.

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