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Theoretical study of Cl adsorption on the GaAs(110) surface

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The positions and energies of four candidate adsorption sites for Cl on GaAs(110) have been investigated using the *ab initio* pseudopotential plane-wave method. We obtain general agreement with recent experimental studies on the distribution and pattern formation of Cl adatoms. An analysis of adatom height based on valence charge density agrees quantitatively with reported scanning tunneling microscopy values. For the four adatom sites considered, the relaxation of the first GaAs surface layer was similar to or less than the relaxation of the bare surface. In the case of the lowest energy site, the relaxation is nearly healed due to a change in character of the surface bonding. This is in contrast to conclusions based on core photoemission results and simple charge-transfer arguments.

I. INTRODUCTION

Understanding halogen adsorption on semiconductor surfaces is important as semiconductor device fabrication moves toward smaller scales. As a result of the smaller scales, dry-etch processes become more important and need to be refined continually. In the past decade, experimental interest in the surface science aspect of etching reactions[1] has been strong and should continue to be important.

A system that has been the subject of some recent studies is Cl_2-GaAs with focus on the (100) (Refs. 2–10) and (110) (Refs. 10–23) surfaces. For the GaAs(110) surface, early studies[11–14] favored bonding to the As surface atoms only. It was believed[14] that the surface relaxation prevented Cl bonding to the surface Ga atoms. More recently, an increasing number of studies[15,19–23] report evidence of bonding to both As and Ga surface atoms.

Although there are many experimental studies reported, there have been few theoretical studies of this system. Margaritondo *et al.*[11,12] carried out tight-binding calculations of the surface density of states and band structure of the Cl-GaAs(110) system for several Ga-bonded and As-bonded adatom geometries. When these tight-binding results were compared to their angle-integrated photoemission and angle-resolved photoemission data, they concluded that the Cl atoms are bound to the As substrate atoms only. They also find better agreement between theory and experiment when the surface Ga and As atoms are relaxed, similar to the clean GaAs(110) surface, rather than near their bulk positions.

Recently, the evolution of adsorbate pattern formation on the surface as a function of temperature was studied via scanning tunneling microscopy[20] (STM) and a corresponding study of the core level energy distribution curves were presented.[22] From the STM images, it appeared that Cl adatoms preferentially occupied high-symmetry sites closer to Ga surface atoms ("*A*" sites) rather than the site atop surface As atoms ("*B*" sites) at low coverages, with *B*-type sites occurring once *A*-site islands were formed. Core spectra indicated that at low coverage the Cl bonded with Ga surface atoms and as the Ga atoms lost charge, neighboring As atoms gained charge.[22] Based on simple charge-transfer arguments used to explain the relaxation of the bare (110) surface, this charge transfer would be accompanied by a relaxation of the surface layer beyond that found for the bare surface. Bonding with As surface atoms occurred only as Cl coverage increased.

Following these experimental reports, Khoo and Ong[23] carried out semiempirical molecular orbital method calculations for Cl, Cl_2, and 0.16 ML Cl on GaAs(110). Their results agree well with Refs. 20 and 22. They found that for isolated Cl adatoms, bonding to As atoms is preferred whereas for a small island (four adatoms), configurations with mostly Ga bonding rather than equal Ga and As bonding are energetically preferred. For the case of a small island, relaxation beyond that for the bare 1×1 surface was found.

An explanation based on first-principles calculations for the preferred adatoms sites, surface reconstruction, and surface bonding would be useful[24] in understanding these recent experiments and in reconciling conflicting conclusions of previous studies.

We present here an *ab initio* study of four adsorption sites *A*, *B*, *C*, and *D* as depicted in Fig. 1. Sites *A* and *B* are seen experimentally[20] for Cl. In addition, the *C* site is observed for Br,[20] which behaves similarly to Cl in other respects. The hypothetical *D* site is included for completeness as it is the fourth high-symmetry site of the 1×1 GaAs(110) surface unit cell. A schematic drawing of the GaAs(110) surface and the four different sites considered for Cl adatoms is shown at the bottom of Fig. 1. Our goal in this study is to understand better the behavior of Cl adatoms on the (110) surface, the formations seen in STM images, and the effect of Cl adatoms on the bonding of the GaAs(110) surface.

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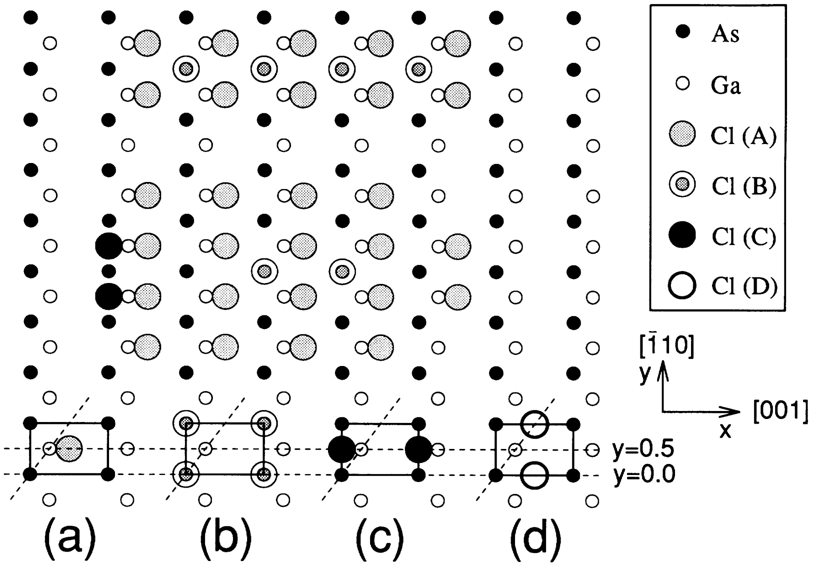

FIG. 1. The (110) surface of GaAs is shown with adsorbed Cl adatoms on the experimentally observed (Ref. 20) *A*, *B*, and *C* sites. An *A*-site–*B*-site chain is depicted in the top of the figure. A representative island of mostly *A* sites with a few *B* and *C* sites is shown in the center of the figure. Unit cells used in our calculations for the *A*, *B*, *C*, and hypothetical *D* sites are shown at the bottom of the figure labeled as (a), (b), (c), and (d), respectively.

II. CALCULATIONAL METHOD

The *ab initio* pseudopotential method[25] within the local density approximation[26] is used to calculate the structural and electronic properties of the bare GaAs(110) surface and systems which include the four different Cl-GaAs(110) adsorption sites. Troullier-Martins pseudopotentials[27] are used to represent the electron-ion interaction. The exchange and correlation potential employed was that of Ceperley and Alder[28] as parametrized by Perdew and Zunger.[29] Partial core corrections[30] are included in order to model the core-valence exchange and correlation potentials. Wave functions, potentials, and charge densities are expanded in a plane-wave basis with a cutoff of 16 Ry (about 4000 plane waves). Brillouin zone sums are carried out using 16 special **k** points[31] in the irreducible zone.

We use a seven-layer GaAs slab within a supercell to model the surface with Cl adatoms on top and bottom of the slab in order to preserve inversion symmetry. The length of the unit cell perpendicular to the surface is chosen large enough so that the neighboring slabs have negligible interaction (in this case there is 7–8 Å of vacuum between slabs).

In order to compare the different sites, we choose a unit cell equal to the bare surface unit cell (1×1 geometry). These unit cells for the *A*, *B*, *C*, and *D* sites are shown schematically in Figs. 1(a), (b), (c), and (d), respectively. Since each 1×1 surface cell contains a Cl adatom, all of our calculations correspond to uniform coverage of one Cl adatom per Ga-As surface pair or a Cl adatom density of 4.45×10^{14} cm^{-2}. The energy for each cell contains the interaction energy of the Cl adatom with adatoms in neighboring cells. Interactions between nearest-neighbor Cl atoms should be small compared with the interaction with the surface Ga and As atoms, however, since the distance between Cl adatoms is about 4 Å, which is almost twice as large as the Cl-Cl molecular bond length. In any case, this interaction will be present in each of the four calculations and cancels when we consider the relative energies of the sites.

Within the 1×1 cells, the Cl adatoms and the first surface layer of GaAs atoms are allowed to relax while the remaining five layers of the GaAs slab are held fixed. Calculations of the forces on the unrelaxed atoms show that the individual force components are less than 0.02 Ry/a.u. with the largest values occurring for atoms in the second GaAs layer. As a figure of merit for our calculation, we calculate a bond rotation angle of 30.4° for the bare surface. This value is in excellent agreement with previous experimental and theoretical values[32] which range from 27.4° to 31.6°.

III. RESULTS AND DISCUSSION

Shown in the center of Fig. 1 is a representative island of Cl adatoms as observed[20] via STM. An *A*-site–*B*-site chain is shown in the top of the figure. These chains are more common than *A*-site islands for Cl deposited at high temperatures as well as for annealed samples. For condensation at room temperature, however, islands of *A*-site adatoms predominate. These islands are decorated with *B*-site adatoms which appear almost twice as high as the *A*-site features. Occasionally *C*-site adatoms are found in pairs at the edge of the island where the edge and *C*-site pair are aligned along the [$\bar{1}$10] direction, at least in the case of Br adsorption,[20] which is similar to Cl adsorption in other respects. The fourth symmetry site *D* is not observed experimentally.

A. Site energies

Calculated energies and nuclear heights for the Cl atoms in the observed *A*, *B*, and *C* sites and hypothetical *D* site are given in Table I. Measured STM heights[20] for the adsorbed atoms are shown for comparison. We do not expect quantitative agreement between the measured STM heights and calculated nuclear heights, however, since STM images reflect the surface charge distribution and not the atomic positions. This will be discussed in detail in Sec. III B. Also note that a true *B* or *C* site is found within or adjacent to an island of *A* adatoms

TABLE I. Site energies, calculated nuclear heights, and experimental STM-image heights, of adsorption sites A, B, C, and D for Cl on GaAs(110) are shown. Energies are given in eV relative to the energy for site A. Site labels are shown in Fig. 1. Calculated nuclear heights are given in angstroms relative to the height of As surface atoms in a bare 1×1 cell. Experimental (STM) values for the adsorbed Cl atom height from Ref. 20 are cited for positive sample bias. As discussed in the text, STM heights reflect the charge density due to states near the Fermi energy and not the nuclear positions.

	A site	B site	C site	D site
E-E_A (eV)	0	1.24	1.51	0.55
z_{nuclear} (Å)	1.36	2.18	1.75	0.59
z_{STM} (Å)	0.7–0.8	1.5–1.7		

and, as a result, the nuclear positions calculated in the presence of A sites would most likely be higher than the values reported here.

The lowest energy symmetry site is the A site, centered within the rectangle formed by four As surface atoms. Of the adatom sites included in this study, the A site is the site nearest to the surface Ga atoms. At low temperatures, this should be the observed site unless there are kinetic barriers to diffusion of a physisorbed atom into an "available" site. Since A-site islands are the dominant feature seen in lower-temperature deposited Cl_2 and our calculations correspond to the $T \to 0$ limit, it is not surprising that we find it to be the energy-preferred site.

The next lowest energy site in is the D site, located between neighboring As atoms along the longer ([001]) edge of the rectangle. This site has the lowest nuclear height above the plane of the As surface atoms. While the nuclear height of the A site is 1.36 Å, the D site lies only 0.59 Å higher than surface As atoms.

There are no D-site adatoms observed in STM images, however. It might be argued that due to the low height of the Cl(D) site the STM image contrast near a D site is not much different than the bare surface and, as a result, it is very hard to identify these adatoms. A more likely explanation is that the D site, 1.24 eV higher in energy than the A site, is a saddle point in the potential energy curve for Cl on the (110) surface. This explanation is supported by the shape[33] of the potential energy map calculated for a Cl atom on the GaAs(110) surface.[23] A single adatom in the D site would easily fall into the A-site position, and once there is a single A-site adatom on the surface it will act as a nucleus for an island of similar sites making D sites unstable.

Next highest in energy is the B site, followed by the C site only 0.27 eV higher. Based on the 1.24 eV energy difference between the A and B sites, there should not be any isolated B or C adatoms on a clean surface. The presence of B-site Cl adatoms within A-site islands simply reflects the onset of marblelike stacking. Once there is an A-site island, the surface charge density is dominated by Cl A-type adatoms and the next layer of Cl adatoms "fits" into the holes between the A sites. These holes correspond to the B-site position. Even with the A sites filled, B-site adatoms can get very close to the underlying As surface atoms because the distance between A- and B-type sites is almost twice the ionic Cl^- radius[34] and nearly 75% larger than the Cl_2 molecular bond length. Each of the other high-symmetry sites are at least 0.6 Å closer to the filled A sites, so the B site will be energetically favored over other second-layer adatom sites.

In comparing our calculation of site energies for uniform coverages of A, B, C, and D sites to the theoretical results of Ref. 23 we find several discrepancies. Whereas the A site is identified here as the lowest energy high-symmetry site, Khoo and Ong[23] find the global minimum in the potential energy surface for a single adsorbed Cl adatom to be the B site. In addition, the present study indicates that the D site also lies lower in energy than the B site. For a group of adsorbed Cl atoms, however, Ref. 23 finds a configuration containing mostly A sites with a few adjacent B sites to be energetically preferred over islands of equal numbers of A and B sites. The disagreement could be due to the neglect of the surface relaxation energy in the potential energy calculation for the single Cl adatom (the surface Ga and As atoms were fixed at their bare surface relaxed positions in this preliminary calculation). In the case of the group of adsorbed Cl atoms, however, further surface relaxation was included. As will be discussed in Sec. III C, the movement of the surface Ga and As atoms back toward their bulk positions is especially important in describing the A site and we propose that the potential energy surface minimum lies at A when surface relaxation in response to the Cl adatom is taken into account.

Based on the calculated energies of the four high-symmetry sites, we can infer the barriers to diffusion in the [001] and [$\bar{1}$10] directions. Since the D sites are close in energy to the A sites, we would expect diffusion to preferably occur along the [$\bar{1}$10] direction. The energy barrier in the [001] direction, around 1.25–1.50 eV, is low enough that local heating due to bond formation would enable diffusion to occur in that direction, also. As reported in Ref. 20, Br- and Cl-induced features are mobile, consistent with the magnitude of these energy differences.

One question we have not addressed in this study is why chain formation is preferred over uniform A-site coverage of the surface. Both Cl-Ga and Cl-As bond strengths are nearly twice that of the Cl-Cl bond strength.[35] The higher coordination of a second-layer B site as compared to the first-layer A site is a plausible explanation for chain formation, but calculations of the energy difference between an A-site–B-site pair and an A-site–A-site pair would quantitatively compare the interaction energies involved in island and chain formation. Low-coverage calculations[23] within a semiempirical molecular orbital method have been reported which give some insight into Cl adatom interactions, although further studies are needed to understand the competing interactions quantitatively.

B. Atom heights based on distribution of charge

In order to compare our calculations of adatom positions to the observed heights of Cl adatoms, we need to consider the distribution of charge near the surface atoms. There are cases in which STM images reflect electronic structure effects rather than the surface geometry[36,37] so one should be careful in the way adatom surface heights are calculated and in the interpretation of STM images as structural data.

In most cases the STM image is quite similar to the total charge density.[38] The total valence charge densities for the bare (110) surface and for uniform coverages of A, B, C, and D sites are shown in Figs. 2–6. Shown is the charge density in the y=0.0 and y=0.5 planes as labeled in Fig. 1. Since these figures correspond to a bias of the full valence bandwidth, corrugations based on them should not be expected to agree well with Ref. 20. In order to calculate a reasonable corrugation to compare to the STM observed heights, we follow standard models which relate STM current to partial sums over occupied valence band states.

A simple extension[39] of the expression derived by Tersoff and Hamann[38] within an s-wave model for the tip relates the STM tunneling current density $j(\mathbf{r})$ to the local density of states at the center of curvature of the tip.

$$j(\mathbf{r}, V) \propto \rho_{\mathrm{STM}}(\mathbf{r}, V), \tag{1}$$

where

$$\rho_{\mathrm{STM}}(\mathbf{r}, V) \equiv \int_{E_F-eV}^{E_F} \rho(\mathbf{r}, E)\, dE \tag{2}$$

and

$$\rho(\mathbf{r}, E) \equiv \sum_{n,\mathbf{k}} \mid \psi_{n,\mathbf{k}}(\mathbf{r}) \mid^2 \delta(E_{n,\mathbf{k}} - E). \tag{3}$$

Here E_F is the Fermi level and ψ are the eigenstates of the semi-infinite sample. According to this model, then, the constant-current STM image is simply a contour of constant $\rho(\mathbf{r}$,V).

We have calculated $\rho(\mathbf{r}$,V) [see Eq. (2)] for biases of 2 and 4 eV for the bare surface and surfaces with A-, B-, C-, and D-type Cl adatoms. The resulting charge densities for the y=0.0 and y=0.5 planes were plotted as for the sum over all occupied states shown in Figs. 2–6. They look similar to the total valence charge distributions in shape, but with a much lower magnitude of $\rho(r)$,

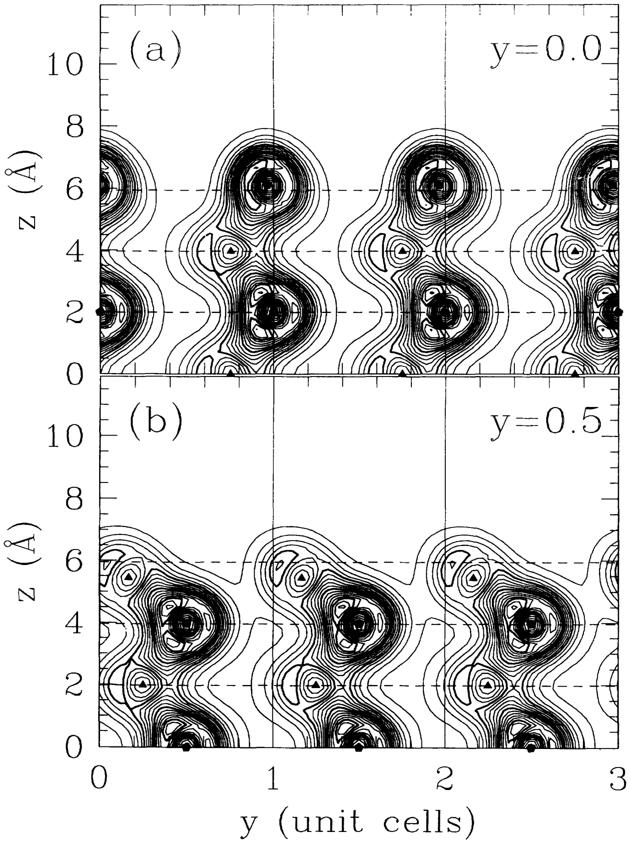

FIG. 2. Charge density for the 1 × 1 GaAs slab in the (a) y = 0.0 and (b) y = 0.5 [$\bar{1}$10] planes (see Fig. 1). Contours are shown for 20,40,. . . ,340 electrons/unit cell (1 e/cell is 2.8×10^{-4} e/a.u.^{3} for Figs. 2–6). Heavier contours correspond to 100, 200, and 300 e/cell. Dashed lines correspond to planes through the Ga and As unrelaxed bulk positions.

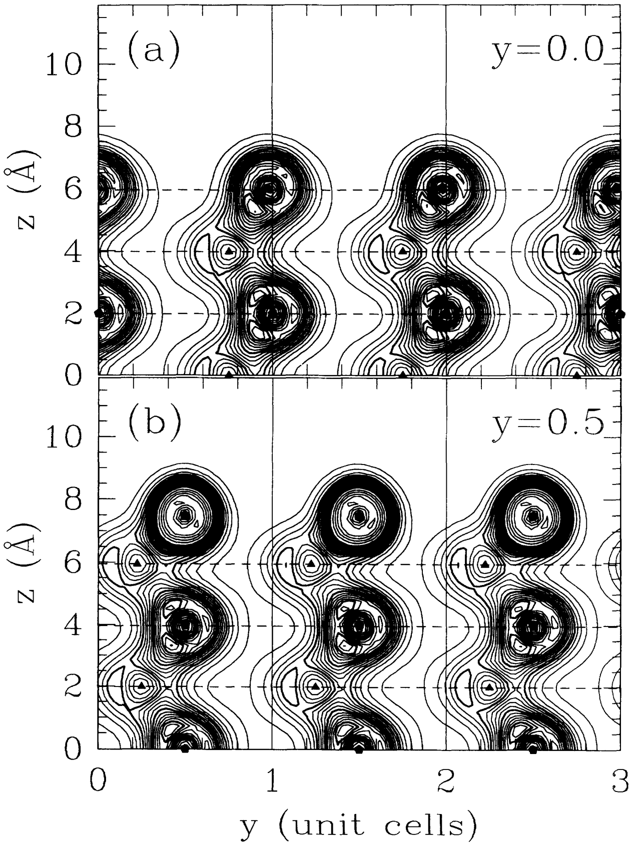

FIG. 3. Charge density for the 1 × 1 GaAs slab with one Cl atom per cell on the A site in the (a) y = 0.0 and (b) y = 0.5 [$\bar{1}$10] planes (see Fig. 1). Contours are shown for (a) 20,40,. . . ,340 and (b) 20,40,. . . ,380,400,500,. . . ,900 electrons/unit cell. Heavier contours correspond to 100, 200, and 300 e/cell. Dashed lines correspond to planes through the Ga and As unrelaxed bulk positions.

as expected. Contours for very low charge density were plotted since the STM tip will sample charge lying far from the surface (in terms of Figs. 2–6, these contours fell around $z \simeq 8$–10 Å).

Since the constant-current STM image corresponds to a $z(x,y)$ map of constant ρ for a given bias V, we are interested in the "height" of the charge density contours above an adatom compared to the height of the As atoms on the bare surface. An estimate for the adatom height relative to the bare surface is then just the difference of $z_{\rm Cl}(\rho = x)$ and $z_{\rm GaAs}(\rho = x)$, which are read off from charge density plots in planes through Cl adatoms and As atoms on the bare surface, respectively. These numbers vary about 0.05 Å for different contours x, where x=0.1–0.5(1–5) e/cell for a bias of 2(4) eV. For the STM tip far from the surface, we are interested in z_ρ for the smallest contour, i.e., farthest from the surface. Because the difference between $z_{\rm Cl}$ and $z_{\rm GaAs}$ decreases slightly for decreasing value of ρ contour, our estimate of the adatom height should be seen as an upper bound on the expected value. This estimate is shown as z_ρ in Table II.

The agreement between calculated and measured charge density height is best for a bias of 2 eV. Observed STM heights[20] were reported for an experimental bias of 1.5–3 eV, so better agreement is expected for the 2 eV calculation rather than the 4 eV calculation. True B- and C-site adatoms are surrounded by or adjacent to an A-site island, however. Therefore, the calculated z_ρ would be slightly higher for these sites if neighboring A adatoms were included. This perturbation is expected to be small for the B site since the distance between A- and B-type sites is almost 3.5 Å compared to the Cl_2 bond length

TABLE II. Estimated site heights based on charge density contours for states near the Fermi level are compared to experimental STM-observed (Ref. 20) Cl heights. Two theoretical estimates are given for states between the Fermi level E_F and (E_F-Δ) for Δ=2 eV and for Δ=4 eV. The reported sample bias used in the study of Ref. 20 was between 1.5 and 3 eV.

Atom heights	A site	B site	C site	D site
z_ρ (Å) Δ=4 eV	1.10	1.75	1.55	0.40
z_ρ (Å) Δ=2 eV	0.8–0.9	1.6	1.3	0.05
$z_{\rm STM}$ (Å)	0.7–0.8	1.5–1.7		

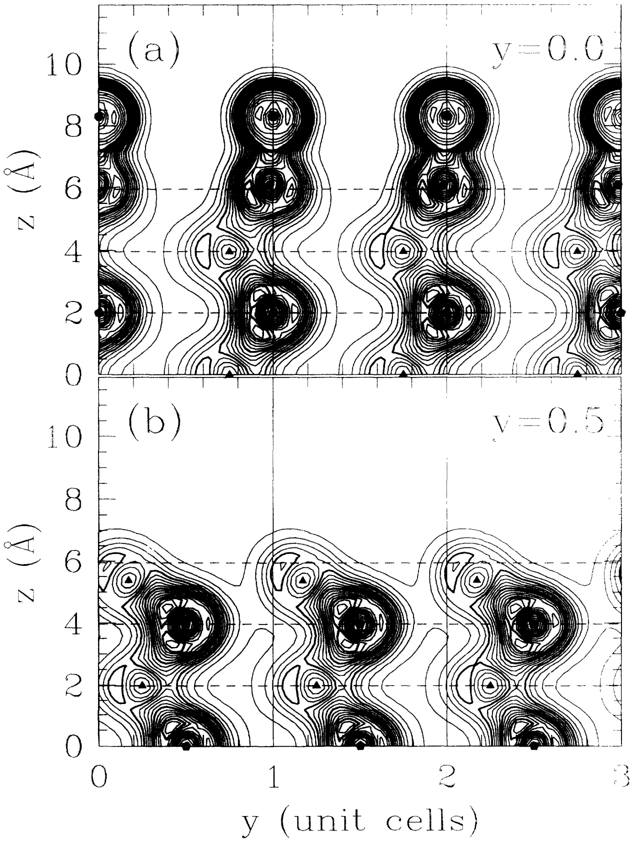

FIG. 4. Charge density for the 1 × 1 GaAs slab with one Cl atom per cell on the B site in the (a) y = 0.0 and (b) y = 0.5 [$\bar{1}$10] planes (see Fig. 1). Contours are shown for (a) 20,40,...,380,400,500,...,900 and (b) 20,40,...,340 electrons/unit cell. Heavier contours correspond to 100, 200, and 300 e/cell. Dashed lines correspond to planes through the Ga and As unrelaxed bulk positions.

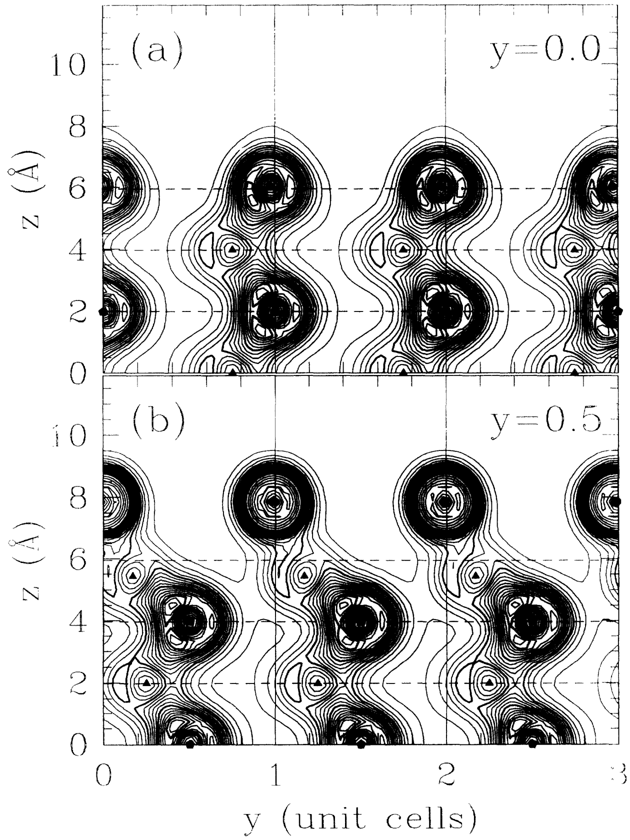

FIG. 5. Charge density for the 1 × 1 GaAs slab with one Cl atom per cell on the C site in the (a) y = 0.0 and (b) y = 0.5 [$\bar{1}$10] planes (see Fig. 1). Contours are shown for (a) 20,40,...,340 and (b) 20,40,...,380,400,500,...,900 electrons/unit cell. Heavier contours correspond to 100, 200, and 300 e/cell. Dashed lines correspond to planes through the Ga and As unrelaxed bulk positions.

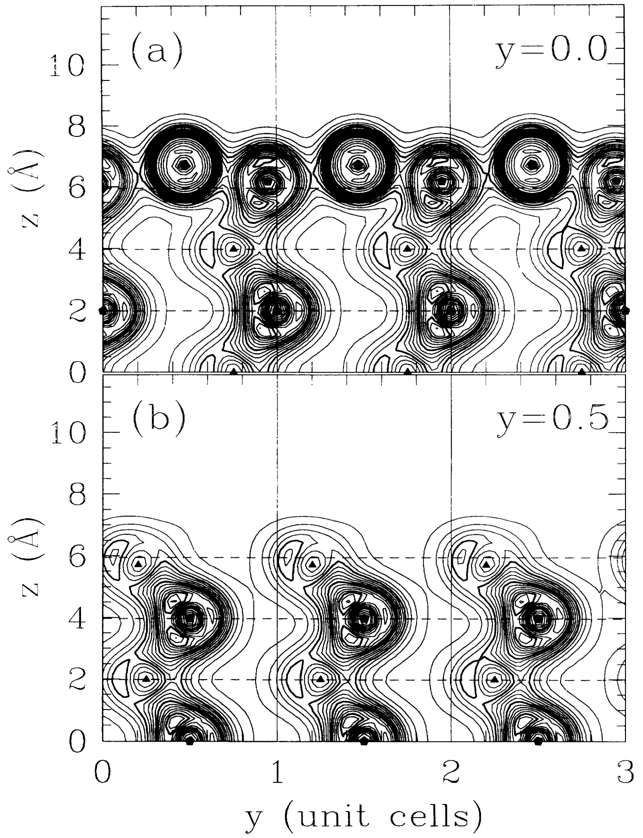

FIG. 6. Charge density for the 1 × 1 GaAs slab with one Cl atom per cell on the D site in the (a) y = 0.0 and (b) y = 0.5 [$\bar{1}$10] planes (see Fig. 1). Contours are shown for (a) 20,40,. . . ,380,400,500,. . . ,900 and (b) 20,40,. . . ,340 electrons/unit cell. Heavier contours correspond to 100, 200, and 300 e/cell. Dashed lines correspond to planes through the Ga and As unrelaxed bulk positions.

of 1.99 Å. The effect on the C-site height will be larger, however, since it is only 2 Å from the A site.

Note that the heights calculated in this way scale differently with bias for the four adsorption sites. This is simply a reflection of variation in character of the wave functions as a function of energy.

C. Bonding properties and surface relaxation

Changes in the bonding properties and estimates of charge transfer between the bare surface and the four surfaces with adatoms can be understood by comparing Figs. 2–6. The largest qualitative difference between the bare surface and the four uniformly covered surfaces is for the A site shown in Fig. 3. Whereas the Ga atoms on the bare surface have peaks in the charge density directed out of the surface plane, for the surface covered with A sites the bonding of the surface Ga atoms looks very similar to the bonding for bulk Ga atoms. For both the bulk Ga atoms and the Ga atoms beneath Cl(A) adatoms, the peak in $\rho(r)$ lies in a plane parallel to the surface plane [see Fig. 3(b)].

There is a slight decrease in the size of the ρ=120 e/cell contour from the bare surface Ga to the Ga under the A site, but the overall variation in this contour for sites A–D [see Figs. 2(b)–6(b)] is very small—the peak $\rho(r)$ values range from 121 to 126 e/cell in the y = 0.5 plane. In the plane containing both the Ga and As surface atoms (denoted by the diagonal line in Fig. 1), however, the peak near the Ga surface atom is noticeably smaller for the A-covered surface than for the bare surface or the B-, C-, or D-covered surfaces. Thus, although the full three-dimensional distribution of charge should be considered in order to definitively compare the sites, it appears that the Cl A-type adatom shifts charge away from the Ga surface atom whereas the B-, C-, and D-site adatoms do not have as large an effect.

Accompanying the decrease in charge density near the Ga atom below an A-site Cl is a moderate increase in charge around the As atom. The B-type site also produces a comparable increase in charge around the As atom, especially in the plane through the As-Ga bond.

For the B-, C-, and D-site covered surfaces, the Ga atom environment is very similar to that of the bare surface. Even for the C site, the shape of the charge density in the y=0.5 plane is basically a sum of the bare surface $\rho(r)$ and that of the Cl adatom. In other words, the C-type Cl adatom does not interact strongly with the surface Ga atom, even though it is as close to the Ga atom as the A site.

In general, variations in charge distribution around the As surface atoms are a little more pronounced than for the Ga atoms, although there are no remarkable changes as there is for the Ga beneath the Cl(A) site. In the case of the B site, there is more sharing of charge between the Cl and the underlying As atom than for the other three sites. Even so, the Cl(B) adatom alters the charge distribution near the As atom much less dramatically than the Cl(A) adatom alters the environment of the Ga surface atom [see Figs. 4(a) and 3(b)].

The core photoemission results of Ref. 22 give very specific information about the bonding properties of the different Cl adatom sites. Stepniak *et al.* find features identified as Ga^{1+}, As^{1+}, and As^{2+} peaks which result from Cl adsorption. In addition, an As^{*} feature was reported at lower bonding energy than the surface and bulk components (more negatively charged). The Ga^{1+} and As^{*} features are the strongest at low coverage, with the intensity of the As^{*} feature mirroring the intensity of the Ga^{1+} feature as a function of Cl coverage. Both the As^{*} and Ga^{1+} features were attributed to the growth of A-site islands. This is consistent with changes in the calculated bonding charge of the surface Ga and As atoms discussed above.

As coverage increases, the As^{1+} feature grows at the expense of the As^{*} feature. It appears that as Cl atoms bond directly to As surface atoms, the extra As charge indicated by the As^{*} feature is significantly modified. Differences between Figs. 2 and 4 support this interpretation.

Based on the Ga^{1+} feature, it was argued that the

TABLE III. Change in position of relaxed surface atoms compared with the bulk positions for the bare GaAs (110) surface and for the surface with Cl adatoms on the A, B, C, and D sites. The displacements δx and δy are in the [001] and [$\bar{1}$10] directions, respectively (see Fig. 1), and δz is perpendicular to the surface. By symmetry, δy is identically zero for both Ga and As atoms. Absolute displacements $|\delta \mathbf{r}|$ from the unrelaxed positions are also given.

Displacements	no Cl	A site	B site	C site	D site
$\delta x_{\rm As}$	-0.20	-0.13	-0.10	-0.16	-0.29
$\delta z_{\rm As}$	0.17	0.04	0.14	0.08	0.22
$\mid \delta \mathbf{r}_{\rm As} \mid$	0.26	0.14	0.17	0.18	0.36
$\delta x_{\rm Ga}$	-0.47	-0.15	-0.43	-0.45	-0.27
$\delta z_{\rm Ga}$	-0.51	-0.01	-0.58	-0.52	-0.24
$\mid \delta \mathbf{r}_{\rm Ga} \mid$	0.69	0.15	0.72	0.69	0.36

bonding of Cl to Ga surface sites enabled a more complete change in hybridization for the Ga from sp^3 to sp^2, beyond that for the bare surface. A corresponding shift in charge density from the Ga to As, then, would account for the As* peak which follows the Ga^{1+} peak. As a result of the change in bonding, the relaxation of the surface would increase relative to the bare surface. We do not see a significant overrelaxation for any of the adsorption sites, however. Rather, for the energetically preferred site we see a change in the direction of the unrelaxed bulk positions.

Differences in the surface relaxation of the bare and Cl-covered surfaces are given in Table III. Of the four adatom sites, we note that the A-site covered surface shows the least amount of relaxation. In the plots of the total valence charge density shown in Figs. 2–6, planes through the bulk Ga and As atoms positions are drawn as dashed lines.

In the case where a Cl(A) adatom is present, the relaxation of the bare surface has been healed. This can be understood in terms of the change in surface bonding between the bare and A-site covered surfaces. In a sense, the Cl adatom acts similarly to the missing next-layer As atom; i.e., the As and Ga surface atom positions are pulled back toward their unrelaxed values.

Relaxation for the B, C, and D sites remain significant, however. As seen in Figs. 2–6, this is a result of the fact that there is very little redistribution of Ga or As charge in response to the Cl adatom. Even for the As atom below the B-type site, the observed shift in $\rho(r)$ is not significant in the regions which affect the surface bonds.

Based on the fact that the Ga^{1+} and As* peaks indicate a net shift in charge from the Ga to the As surface atoms, a change in the bonding structure of the GaAs surface was inferred.[22] For the bare surface, the relaxation is often attributed to a similar charge transfer which occurs as the Ga electron density becomes sp^3-like while the As electron density becomes s^2p^3-like. These changes in hybridization are accompanied by changes in the bond angles and result in the surface relaxation of the bare (110) surface. In the case of the surface covered with Cl adatoms the same argument does not hold. The charge transfer happens in the presence of the Cl adatom which participates in the bonding of the surface. In fact, it participates in a way similar to the missing As bulk atom which would occupy the same site.

IV. CONCLUSIONS

Based on the site energies of four high-symmetry adsorption sites, the preference of low-temperature deposited Cl atoms to occupy A sites is understood. It is reasonable that the next layer of Cl atoms would occupy the B sites since the surface charge density is dominated by the Cl atoms once a layer of A sites has formed (marblelike stacking). Diffusion at room temperature is expected due to the relatively small barrier to movement between cells in the [$\bar{1}$10] direction. Although the calculated nuclear heights disagree with observed STM heights, a simple estimate based on the charge distribution due to states near E_f agrees well with the STM-reported values. A significant site-dependent variation in height with a change in bias was found. Finally, our results indicate that there is less relaxation of the top-layer substrate atoms under the A site than for the bare surface. This is due to the similarity in bonding of the surface Ga and As atoms under the A-site Cl to that of the bulk.

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[1] See H. F. Winters and J. W. Coburn, Surf. Sci. Rep. **14**, 161 (1992), and references therein. This review focuses on the most commonly studied system Si-F.

[2] M. Balooch, D. R. Olander, and W. J. Siekhaus, J. Vac. Sci. Technol. B **4**, 794 (1986).

[3] J. H. Ha, E. A. Ogryzlo, and S. Polyhronopoulos, J. Chem. Phys. **89**, 2844 (1988).

[4] S. M. Mokler and P. R. Watson, Solid State Commun. **70**, 415 (1989).

[5] S. M. Mokler, P. R. Watson, L. Ungier, and J. R. Arthur, J. Vac. Sci. Technol. B **8**, 1109 (1990).

[6] S. M. Mokler, P. R. Watson, L. Ungier, and J. R. Arthur, J. Vac. Sci. Technol. B **10**, 2371 (1992).

[7] G. C. Tyrrell, D. Marshall, J. Beckman, and R. B. Jackman, J. Phys. Condens. Matter **3**, S179 (1991).

[8] C. L. French, W. S. Balch, and J. S. Foord, J. Phys. Condens. Matter **3**, S351 (1991).

[9] A. Ludviksson, M. D. Xu, and R. M. Martin, Surf. Sci. **277**, 282 (1992).

[10] H. C. Flaum, D. J. D. Sullivan, and A. C. Kummel, J. Chem. Phys. **100**, 1634 (1994).

[11] G. Margaritondo, J. E. Rowe, C. M. Bertoni, C. Calandra, and F. Manghi, Phys. Rev. B **20**, 1538 (1979).

[12] G. Margaritondo, J. E. Rowe, C. M. Bertoni, C. Calandra, and F. Manghi, Phys. Rev. B **23**, 509 (1981).

[13] R. D. Schnell, D. Rieger, A. Bogen, K. Wandelt, and W. Steinmann, Solid State Commun. **53**, 205 (1985).

[14] R. D. Schnell, D. Rieger, A. Bogen, K. Wandelt, and W. Steinmann, Surf. Sci. **162**, 25 (1985).

[15] D. Troost, L. Koenders, L. Y. Fan, and W. Mönch, J. Vac. Sci. Technol. B **5**, 1119 (1987).

[16] L. A. DeLouise, J. Chem. Phys. **94**, 1528 (1991); Surf. Sci. **244**, L87 (1991); J. Vac. Sci. Technol. A **9**, 1732 (1991); J. Appl. Phys. **70**, 1718 (1991); Chem. Phys. Lett. **180**, 149 (1991); Vacuum **43**, 1083 (1992); J. Appl. Phys. **72**, 1608 (1992).

[17] V. Liberman, G. Haase, and R. M. Osgood, Jr., Chem. Phys. Lett. **176**, 379 (1991); J. Chem. Phys. **96**, 1590 (1992).

[18] G. Haase, V. Liberman, and R. M. Osgood, Jr., J. Vac. Sci. Technol. B **10**, 206 (1992).

[19] D. Troost, H. J. Clemens, L. Koenders, and W. Mönch, Surf. Sci. **286**, 97 (1993).

[20] J. C. Patrin and J. H. Weaver, Phys. Rev. B **48**, 17 913 (1993).

[21] D. K. Shuh, C. W. Lo, J. A. Yarmoff, A. Santoni, L. J. Terminello, and F. R. McFeely, Surf. Sci. **303**, 89 (1994).

[22] F. Stepniak, D. Rioux, and J. H. Weaver, Phys. Rev. B **50**, 1929 (1994).

[23] G. S. Khoo and C. K. Ong, Phys. Rev. B (to be published).

[24] A first-principles study of Cl on Si(111) and Ge(111), G. B. Bachelet and M. Schlüter, Phys. Rev. B **28**, 12 302 (1983), was instrumental in understanding preferred chemisorption sites for those surfaces.

[25] J. Ihm, A. Zunger, and M. L. Cohen, J. Phys. C **12**, 4401 (1979); M. L. Cohen, Phys. Scr. **T1**, 5 (1982); W. E. Pickett, Comput. Phys. Rep. **9**, 115 (1989).

[26] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964); W. Kohn and L. J. Sham, *ibid.* **140**, A1133 (1965).

[27] N. Troullier and J. L. Martins, Solid State Commun. **74**, 613 (1990); Phys. Rev. B **43**, 1993 (1991).

[28] D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980).

[29] J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

[30] S. G. Louie, S. Froyen, and M. L. Cohen, Phys. Rev. B **26**, 1738 (1982).

[31] D. J. Chadi and M. L. Cohen, Phys. Rev. B **8**, 5747 (1973).

[32] See values tabulated in J. Fritsch, P. Pavone, and U. Schröder, Phys. Rev. Lett. **71**, 4194 (1993).

[33] The present study disagrees with the ordering of the minima reported in Ref. 23, as discussed in the text, but the surface curvature should be correct.

[34] L. Pauling, *The Nature of the Chemical Bond*, 3rd ed. (Cornell University Press, Ithaca, 1960).

[35] *CRC Handbook of Chemistry and Physics*, 72nd ed. (CRC, Boca Raton, FL, 1991).

[36] J. Tersoff, Phys. Rev. Lett. **57**, 440 (1986).

[37] J. A. Stroscio, R. M. Feenstra, and A. P. Fein, Phys. Rev. Lett. **57**, 2579 (1986).

[38] J. Tersoff and D. R. Hamann, Phys. Rev. Lett. **50**, 1998 (1983); Phys. Rev. B **31**, 805 (1985).

[39] A. Selloni, P. Carnevali, E. Tosatti, and C. D. Chen, Phys. Rev. B **31**, 2602 (1985).

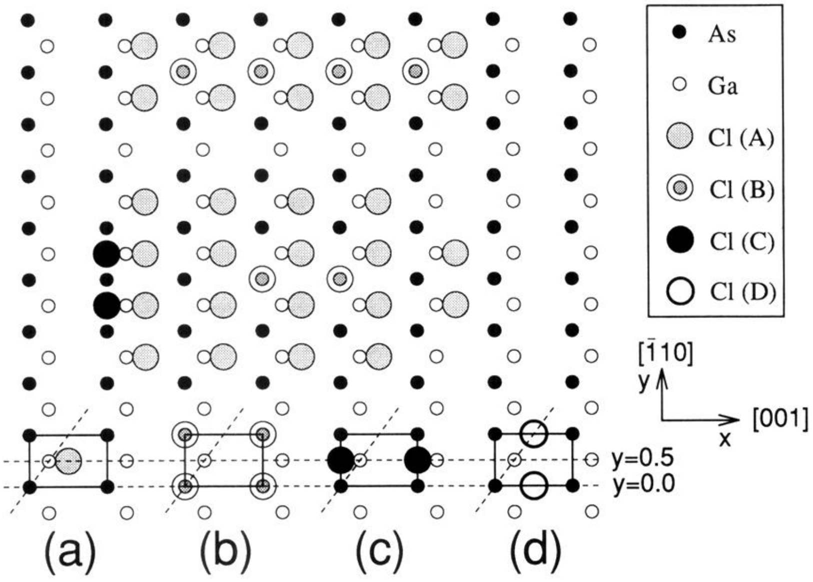

FIG. 1. The (110) surface of GaAs is shown with adsorbed Cl adatoms on the experimentally observed (Ref. 20) *A*, *B*, and *C* sites. An *A*-site–*B*-site chain is depicted in the top of the figure. A representative island of mostly *A* sites with a few *B* and *C* sites is shown in the center of the figure. Unit cells used in our calculations for the *A*, *B*, *C*, and hypothetical *D* sites are shown at the bottom of the figure labeled as (a), (b), (c), and (d), respectively.