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Adsorption and diffusion of a Cl adatom on the GaAs(001)-$c(8\times2)$ ζ surface

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Using density-functional theory we investigate the adsorption and diffusion of Cl adatoms on the ζ structure of GaAs(001) that exhibits a large $c(8\times2)$ reconstruction. From the calculated potential-energy surface, we identify the adsorption sites and diffusion energy barriers of a single Cl adatom. The most favorable binding site is found to be the edge of the *in-surface* Ga dimer, lifting it *above the surface*. We also find that two Cl adatoms can bind at the same in-surface Ga dimer. The Cl diffusion is discussed and compared to experimental observations.

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I. INTRODUCTION

Dry etching of semiconductor surfaces with halogens (e.g., Cl_2, Br_2, and I_2) is an important step in device fabrication.[1–9] Nevertheless, the physical properties of halogens on semiconductor surfaces are not well understood, and this is particularly so for compound semiconductors, largely due to the diversity and complexity of their surface reconstructions.[1,2] For example, the pristine GaAs(001) surface, which is the substrate considered in the present study, is well known and understood to exhibit various surface reconstructions that are controlled by the thermodynamic conditions: At high arsenic partial pressure the surface assumes a $c(4\times4)$ super structure; with decreasing As partial pressure one finds a (2×4), (1×6), (4×6), and finally, at As-poor (or Ga-rich rich) conditions, the surface periodicity is (4×2).[10] Through a comprehensive reflection-high-energy electron diffraction study, Farrell *et al.* identified three different (2×4) phases labeled α (two-As-dimers model), β (three-As-dimers model), and γ (extra As dimer on β phase).[11] The α and β phases had been also proposed by earlier tight-binding calculations by Chadi.[12] Furthermore, based on density-functional theory (DFT) total-energy calculations, modified structures of $\alpha2$ (single-As-dimer model)[13] and $\beta2$ (bilayer two-As-dimers model)[14] were proposed. The γ phase is known as the mixture of β and $c(4\times4)$ phase.[15] Similarly, (4×2) reconstructions has interpreted as β (three-Ga-dimers model),[16] $\beta2$ (bilayer two-Ga-dimers model),[17] $\beta3$ (single-Ga-dimer model),[18] and As-dimer model[19] based on high-resolution electron-energy-loss spectroscopy[16] and scanning tunneling microscopy (STM) data.[17–19] By theoretical calculations, Northrup and Froyen showed that the β phase was energetically unstable under any Ga chemical potential values and the $\beta2$ phase is the most plausible among several candidates.[14,20] The $c(2\times8)$ $[c(8\times2)]$ periodicity is reported as the out-of-phase arrangement of (2×4) $[(4\times2)]$ structures by half of the surface cell in $[\overline{1}10]$ ([110]) direction. A comprehensive review of GaAs(001) surface can be found in Ref. 10. The Ga-rich surface geometry has recently attracted special attention, because it appears to be preferable for the deposition of metals that may be relevant to spintronics. Also from a basic scientific point of view this surface is interesting, because by DFT studies[21] a qualitatively new type of surface reconstruction was recently found, termed the ζ model. This structure was calculated to be energetically favorable under Ga-rich conditions. In fact, its energy was found to be lower than that of all previously proposed models. Subsequently, this predicted structure was confirmed by analyses of STM, low-energy electron diffraction, and surface x-ray diffraction.[21–23] In this novel structure, the excess Ga atoms are located below the surface layer. Thus, from the vacuum side the surface looks as if it is As rich. The chemical properties are, however, very distinct to those of truly As-rich surface terminations. Recently such ζ reconstruction, though with a noticeable amount of disordered group-III surface vacancies, was also suggested to exist for other III-V surfaces such as InAs and InSb.[22,23]

The adsorption and etching processes of the GaAs surface with Cl, the most common etchant, has been extensively investigated in the literature, and Cl_2 is known to adsorb dissociatively.[3,4,7,24,25] Recently McLean *et al.* reported a systematic STM study on chlorine adsorption and diffusion on GaAs(001) $c(8\times2)$.[24] Their analysis was corrected by us[26,27] and below we give a detailed description and extension of our theoretical findings. The STM images obtained by McLean *et al.* show the following interesting Cl-related features. After deposition of Cl on the GaAs(001)-$c(8\times2)$ surface (they studied coverages up to ∼2.5% of a monolayer) two kinds of bright features occur in the center of dark channels of their STM images. One of them was round, occasionally it looked as if the lower half of the round feature was displaced along the scanning direction ([110]), giving rise to two touching crescents. The displacements were mostly 4.5 ± 0.3 Å and 3.5 Å. The round feature and the two crescents feature were both tagged *S*. The other feature, tagged *D* looked like a simple pair of two round features separated by 4.5 Å. The discontinuity of the *S* features was interpreted as hopping of a single Cl adatom along [110]. The longer (4.5 ± 0.3 Å) displacement was more frequently observed than the shorter one, and for it the hopping rate was measured as 0.45 Hz. The shorter hops occurred as an order of magnitude less frequent. Hopping along $[\overline{1}10]$, on the other hand, was not observed in the experiments.

In this paper, we investigate the adsorption and diffusion of a Cl adatom on the GaAs(001)-$c(8\times2)$ ζ surface using DFT calculations. The technicalities are given in Sec. II. Our

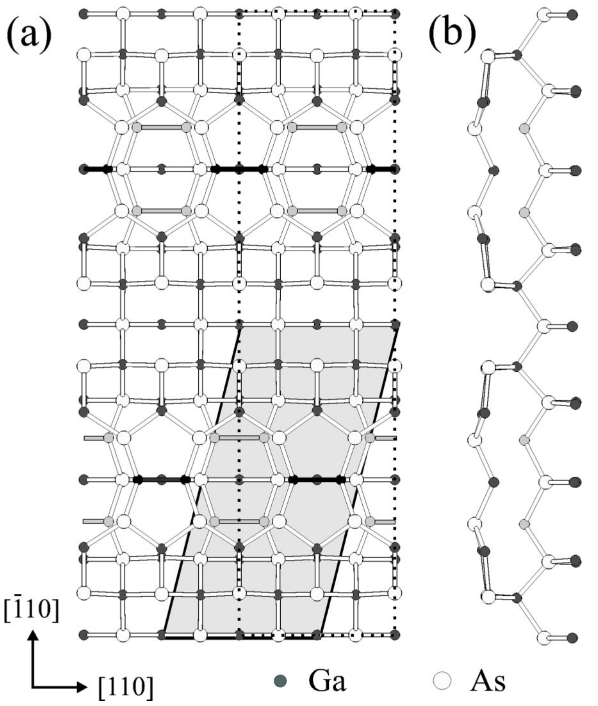

FIG. 1. (a) Top and (b) side views of GaAs(001)-$c(8\times2)$ ζ-surface geometry up to four layers down from the surface. The monoclinic (4×2) surface unit cell is marked by a gray parallelogram, while $c(8\times2)$ cell is drawn with the dotted line. The in-surface Ga dimer bonds are colored black and subsurface Ga dimers and bonds are colored gray.

results (see Sec. III) show that a Cl adatom preferentially binds at the edge of an *in-surface* Ga dimer [the structure of the GaAs(001)-$c(8\times2)$ ζ surface is discussed below, cf. Fig. 1]. Upon adsorption, this Ga-dimer lifts above the surface. The diffusion energy barriers of Cl adatom along the various pathways are obtained from the calculated potential-energy surface (PES). We also find that a second Cl adatom can adsorb on the same in-surface Ga dimer, but clustering of such Cl-pair structure is found to be energetically unfavorable. Our results are compared to available experimental data. Section IV summarizes our results and conclusions.

II. COMPUTATIONAL DETAILS

Over the last years, DFT calculations[28] have been used successfully to analyze and explain clean semiconductor surfaces as well as adsorption and diffusion thereon (see, e.g., Refs. 29,30). For the present work we employed the generalized gradient approximation (GGA) by Perdew, Burke, and Ernzerhof for the exchange-correlation functional[31] and norm-conserving pseudopotentials.[32,33] The substrate was modeled by a slab with seven layers and a (4×2) surface cell. The bottom Ga layer was passivated by pseudohydrogen atoms (two H* atoms per Ga atom and $Z_{H*}=1.25$) to mimic tetrahedral bonds of bulk GaAs. The position of pseudohydrogens was determined by the energy minimization, i.e., relaxing the H* positions but keeping the As and Ga layer fixed at their positions. The resulting Ga—H* bond length is 1.57 Å. The bottom Ga and pseudohydrogen layers were fixed during other calculation for the further studies. For numerical reasons the slab was repeated periodically with a (sufficiently large) vacuum region of about 9 Å, between adjacent slabs. The electronic wave functions were expanded in a plane-wave basis set with energy cutoff of 12 Ry. The bulk modulus of GaAs, obtained via the Murnaghan equation of state is calculated as 55 GPa and the equilibrium lattice constant is 5.78 Å. The experimental values are 76 GPa and 5.65 Å.[36] Our theoretical values are practically identical to those obtained with a larger cutoff energy of 30 Ry. The **k**-point integration was performed on a mesh corresponding to 64 **k** points in the (1×1) surface Brillouin zone. To find the lowest-energy structures, all atoms were allowed to relax till the maximum force in the system smaller than 0.025 eV/Å.

TABLE I. Binding energies (E_{bind}) and bond length (l_{bond}) of a GaCl and Cl_2 molecules. The unit of E_{bind} and l_{bond} are (eV/molecule) and (Å), respectively.

	GaCl		Cl_2	
	E_{bind}	l_{bond}	E_{bind}	l_{bond}
This work	5.39	2.27	3.40	2.05
LDA[a]	5.43	2.22	3.41	2.00
Expt. (Ref. 36)	5.01±0.13	2.20	2.53	1.99

[a] Local-density approximations (Refs. 34 and 35).

We also performed DFT-GGA calculations for the GaCl and Cl_2 molecules (see Table I). A simple cubic supercell of sufficiently large size ($20\times20\times20$ bohr^3) and a 12 Ry energy cutoff is used. Compared to experimental values,[36] our theoretical results exhibit a overbinding in energy and very good interatomic distances.

The PES of a Cl adatom on the ζ-reconstructed GaAs surface, $E(X,Y)$, was mapped on an equidistant (X,Y) grid with spacings of 1 Å along [110] and [$\bar{1}\bar{1}0$]. For each (X,Y) position of the Cl adatom we started at 4 Å above the surface As height, and then relaxed the height of the adatom. All Ga and As, except the bottom layer bound H* atoms, were fully relaxed during calculations. At minima of the PES we also allow the optimization of the (X,Y) coordinates of Cl adatom.

III. RESULT AND DISCUSSION

A. ζ-GaAs(001) surface

The ζ reconstruction is qualitatively different from the usual on-surface dimer based reconstructions of III-V semiconductor (001) surfaces: Per $c(8\times2)$ cell, the ζ structure has eight *subsurface* Ga dimers, which are covered by a nearly planar surface layer, as shown in Fig. 1.

The surface layer consists of 12 Ga atoms, including two in-surface dimers, and 16 As atoms per $c(8\times2)$ cell. Thus, there are more As atoms than Ga atoms. In contrast to the well-known GaAs surface reconstructions that are assumed under As-rich conditions, in the ζ structure the As atoms do not dimerize. The surface As atoms moved towards the vacuum and the surface Ga dimers move slightly below the surface forming nearly planar sp^2 bonded geometry.[37]

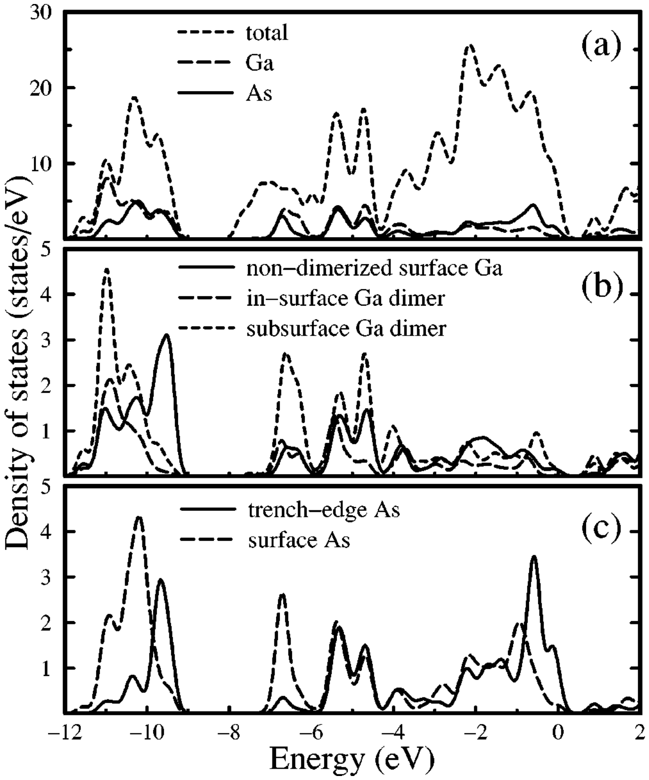

FIG. 2. The total and projected density of states (PDOS) of the clean ζ-GaAs(001) surface: (a) the total DOS (dashed), PDOS of Ga (long dashed), and As atoms (solid) of the surface layer, (b) PDOS of Ga atoms: nondimerized surface Ga atoms (solid), in-surface Ga dimers (long dashed), and subsurface Ga dimers (dashed), (c) PDOS of As atoms: at the trench-edge (solid), neighbor of the in-surface Ga dimer (long dashed). The maximum value of the valence band is taken as reference.

The electron density of states (DOS) of the clean ζ surface (cf. Fig. 2) shows that the surface Ga atoms contribute to the conduction-bands edge, while the As atoms there does to the valence-band edge. In detail the tail of conduction bands mostly originated from in-surface Ga dimers, as shown in Fig. 2(b). The subsurface Ga dimers also have empty p_z orbitals which would not react directly with adatom due to their deep position from the surface. For the surface As atoms [cf. Fig. 2(c)], we find that those at the trench edge contribute to the top of the valence band more than those near the surface Ga dimer. Note that all the dangling orbitals of As atoms in the surface layer are filled and those of Ga atoms were empty, which makes a definite difference from As-rich surface.[21]

B. Adsorption of a Cl atom on ζ GaAs(001)

We positioned a Cl adatom on ζ surface at the equidistance grid points (X,Y) with a 1 Å spacing. The adatom height and the position of the substrate atoms are fully relaxed. At minima of the PES also the (X,Y) coordinates were optimized. The PES for a Cl adatom on GaAs(001)-$c(8\times2)$ ζ surface and the corresponding surface geometry are shown in Fig. 3. Three adsorption sites are found and labeled as $\mathbf{M}_1$, $\mathbf{M}_2$, and $\mathbf{M}_3$. For each of them there are four equivalent positions per $c(8\times2)$ cell. We found four saddle points labeled as $\mathbf{S}_x$. At adsorption sites, the Cl adatom binds to the Ga atoms rather than As atoms, in agreement with experiments.[24] It is worth noting that at minima Cl adatom pulls up the bound Ga atoms to the surface enhancing sp^3 hybridized orbitals. At $\mathbf{M}_1$ position, the Cl adatom pulls up the in-surface Ga dimer atom from its initial in-surface to above-surface position.

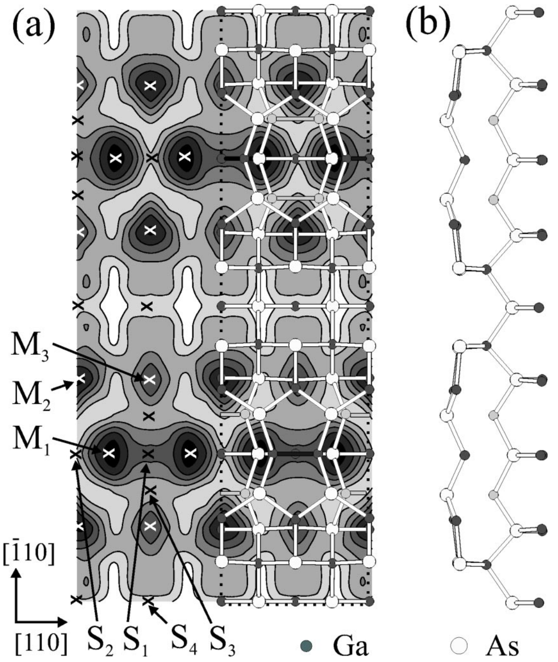

FIG. 3. (a) Potential-energy surfaces for a Cl adatom on the GaAs(001)-$c(8\times2)$ ζ surface. The adsorption sites ($\mathbf{M}_1$,$\mathbf{M}_2$, and $\mathbf{M}_3$) are marked by white, while the saddle points ($\mathbf{S}_1$, $\mathbf{S}_2$, $\mathbf{S}_3$, and $\mathbf{S}_4$) are marked by black. The contour-line spacing is 0.2 eV, and the data between equidistance mesh points are obtained by interpolation. The $c(8\times2)$ clean surface geometry of four surface layers is also shown (in dashed line). (b) Side view of $c(8\times2)$ ζ surface.

The binding energy (E_{bind}) is obtained by comparing the total energy of the Cl-adsorbed surface with that of ideal ζ surface and that of a Cl atom; $E_{bind}=E(\text{Cl/GaAs})-E(\text{GaAs})-E(\text{Cl})$, where $E(\text{Cl/GaAs})$ and $E(\text{GaAs})$ represents the total energy of the Cl-adsorbed GaAs(001) and that of clean ζ-GaAs(001), respectively. The binding energies of a Cl adatom at adsorption sites and saddle points are listed in Table II.

The $\mathbf{M}_1$ is the most stable adsorption site, whereas the $\mathbf{M}_2$ and $\mathbf{M}_3$ sites give weaker binding energies by 0.13 eV and 0.39 eV than $\mathbf{M}_1$ site. Comparing the clean [Fig. 4(a)—(left)]

TABLE II. Binding energies (E_{bind}) of a Cl adatom on GaAs(001)-$c(8\times2)$ ζ surface. The corresponding positions of each sites can be found in Fig. 3. All values are in units of eV/Cl atom.

Site	$\mathbf{M}_1$	$\mathbf{M}_2$	$\mathbf{M}_3$	$\mathbf{S}_1$	$\mathbf{S}_2$	$\mathbf{S}_3$	$\mathbf{S}_4$
E_{bind}	−2.87	−2.74	−2.48	−2.41	−2.01	−2.02	−1.89

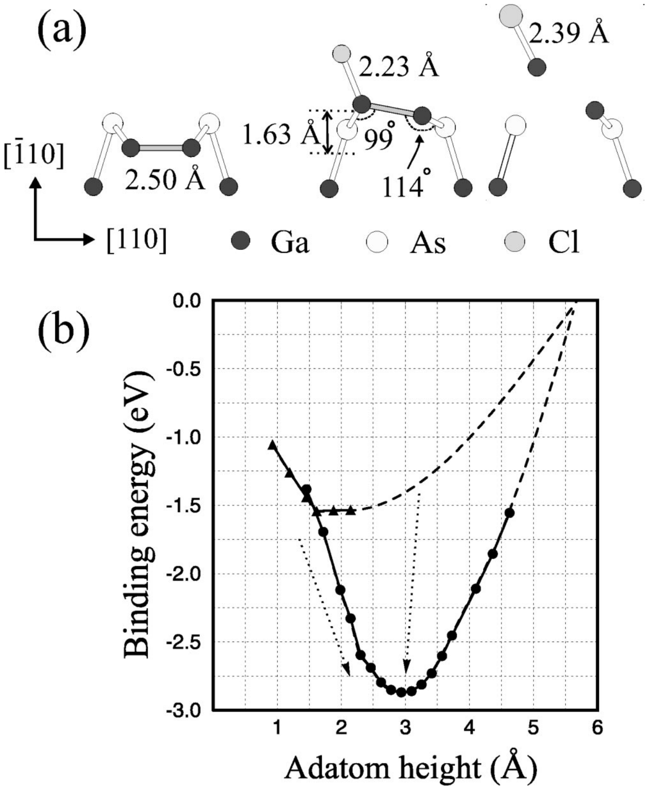

FIG. 4. (a) Side views of different Ga dimers: clean (left), with one Cl adatom at $\mathbf{M}_1$ site (middle), and with two-Cl adatoms (right). (b) Binding energy of a Cl adatom as a function of the adatom height at $\mathbf{M}_1$ site, during the adsorption (filled triangle) and the desorption (filled circle). The height of surface As atom was taken as the reference of the adatom height.

and Cl at $\mathbf{M}_1$ [Fig. 4(a)—-(middle)], one can clearly see that the position of the in-surface Ga dimer is drastically changed: The average Ga dimer height is shifted up by 1.63 Å and the symmetric in-surface Ga dimer becomes asymmetric by 0.48 Å with bond angles of 114° and 99°. The positions of other atoms were not changed by the adsorption of Cl adatom. We note that for the clean surface the total energy of the system less favorable by 0.2 eV when the in-surface Ga dimer is forced to the above-surface geometry. Only the Cl adatom stabilize the above-surface geometry by the newly formed Cl—Ga bond. It is worth noting that our calculated projected density of states (PDOS) of the Cl adatom has dominant peak at deeper than Fermi level by 2.5 eV.

The Cl adatom at other adsorption sites ($\mathbf{M}_2$ and $\mathbf{M}_3$) also lifts the Ga atom to the surface by 0.7 and 0.4 Å, respectively, keeping all the other atoms close to their original positions. Similar to the $\mathbf{M}_1$ case, the energy loss due to the bond-angle distortion at surface is compensated with the Cl—Ga bond, finally result in stable geometry.

It has reported that the total energy was significantly lowered by the dissociation of the surface As dimer as the Ga adatom approached on the center of As dimer on the As-rich $\beta 2$-GaAs(001) surface.[29,30] However, Cl adatom at bridge site was energetically unfavorable by our calculations: in-surface Ga dimer breaking was not obtained by sequential calculation of lowering the initial height of the Cl adatom. It can be understood by the bond character of the Cl (group-VII element) which prefer single bond in contrast to the Ga (group-III element) case.

We also studied the desorption of Cl adatom from ζ-GaAs(001) surface. As the Cl adatom moved from the surface toward the vacuum, the Ga—Cl bond was maintained, eventually a Ga—Cl molecule desorbed. Figure 4(a) (right) depicted the corresponding geometry and the energy curves during desorption was shown in Fig. 4(b). It may explain why the GaCl molecules are desorbed at high temperature in experiments.[7]

In the STM measurement, new bright features were observed at the center of the dark line after dosing of the Cl_2 molecule: a single round feature and a oblong feature.[24] We identify this single round feature with the single Cl adatom bound at $\mathbf{M}_1$ site. Based on the $\beta 2$ model, the single round features were interpreted as a Cl adatom at the edge of a Ga dimer. Indeed, its fast hopping back and forth along $[\bar{1}10]$ was also suggested although there was no clear evidence supporting this diffusion.[24] This indeed confirms that the surface reconstruction was ζ model, instead of $\beta 2$.

C. Diffusion of a Cl adatom on ζ GaAs(001)

The diffusion barrier of Cl adatom on ζ surface is estimated from the PES. We take the differences of the binding energies at adsorption sites and that at saddle points on the chosen pathways as the diffusion barrier (E_{barr}). The effective diffusion barrier can be determined more precisely by applying the formalizm of continuous time random walk[38] and the transition state theory.[39] However, this analytic analysis has given same value as obtained by simple counting of energy difference between the energy at minima and that at saddle point in previous studies.[29,30] From the minimum site at the edge of in-surface Ga dimer ($\mathbf{M}_1$), we consider two diffusion directions of along $[110]$ and $[\bar{1}10]$. Along $[110]$, a Cl adatom can hop between $\mathbf{M}_1$ sites on a in-surface Ga dimer with the energy barrier of 0.47 eV and the distance of 4.45 Å ($\mathbf{M}_1 \rightarrow \mathbf{S}_1 \rightarrow \mathbf{M}_1$). Moreover, the diffusion to the adjacent in-surface Ga dimer (distance: 3.5 Å) requires the diffusion barrier of 0.87 eV ($\mathbf{M}_1 \rightarrow \mathbf{S}_2 \rightarrow \mathbf{M}_1$). Thus, along $[110]$, the Cl intradiffusion (or hoping) on in-surface Ga dimer is more favorable than its interdiffusion between dimers. The full diffusion pathway of a Cl adatom along $[110]$ for the $c(8\times 2)$ unit cell follows [cf. dotted line in Fig. 5(a)], $\mathbf{M}_1 \rightarrow \mathbf{S}_1 \rightarrow \mathbf{M}_1 \rightarrow \mathbf{S}_2 \rightarrow \mathbf{M}_1$. The corresponding potential energy profile is shown in Fig. 5(b).

Along $[\bar{1}10]$, from the same starting point of $\mathbf{M}_1$, the diffusion barrier is 0.98 eV, as depicted in Fig. 5(c), following the pathways of $\mathbf{M}_1 \rightarrow \mathbf{S}_3 \rightarrow \mathbf{M}_3 \rightarrow \mathbf{S}_3 \rightarrow \mathbf{S}_4 \rightarrow \mathbf{S}_3 \rightarrow \mathbf{M}_2 \rightarrow \mathbf{S}_3 \rightarrow \mathbf{M}_1 \rightarrow \mathbf{S}_3 \rightarrow \mathbf{M}_2 \rightarrow \mathbf{S}_4 \rightarrow \mathbf{S}_3 \rightarrow \mathbf{M}_3 \rightarrow \mathbf{S}_3 \rightarrow \mathbf{M}_1$.

The diffusion barriers are compared to the experimental observations. Two kinds of discontinuities of a single round feature were observed in the STM measurement along $[110]$ direction:[24] one was relatively fast (0.45 Hz) and long (4.5 ± 0.3 Å), while the other was relatively slow by an order of magnitude and short (3.5 Å). Applying an assumed prefactor ν_0 as 10^{12} Hz in Arrhenius expression of $\nu = \nu_0 \exp(-E_{barr}/kT)$,[24] the experimentally deduced values were 0.74

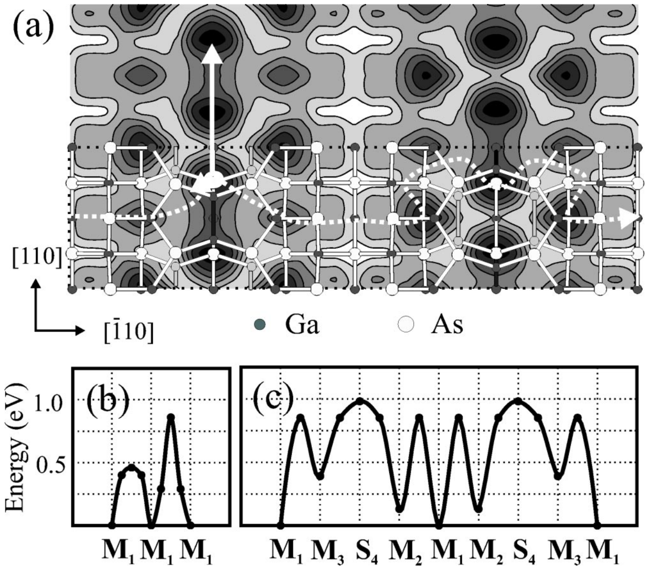

FIG. 5. The potential profiles for diffusion of a Cl adatom on GaAs(001)-$c(8\times2)$ ζ surface and diffusion pathways. (a) Two diffusion pathways are superimposed on PES. The white solid and dotted lines indicate the diffusion paths of Cl adatom along $[110]$ and that of $[\bar{1}10]$, respectively. The energy profile in diffusion direction as a function of diffusion pathway (b) along $[110]$, and (c) along $[\bar{1}10]$ are depicted. The total energy of Cl at $\mathbf{M}_1$ site is taken as reference.

eV and 0.80 eV, respectively. As described above, the DFT calculations result in the diffusion barrier of 0.47 eV with the diffusion length of 4.45 Å for the intradimer diffusion, while those values are 0.87 eV and 3.72 Å for the interdimer diffusion. No discontinuities were observed along $[\bar{1}10]$,[24] which could be interpreted as evidence for no (or very slow) hopping along that direction. Assuming $\nu^{\mathrm{STM}}<10^{-4}$ Hz and $\nu_0=10^{12}$ Hz, the diffusion barrier corresponded to $E_{barr}>0.95$ eV. Our DFT study gives the diffusion energy barrier of 0.98 eV along $[\bar{1}10]$, which is consistent with the slow (experimentally not observed) diffusion along this direction. Therefore, the experimental data is only completely consistent with the ζ rather than the $\beta2$ model of the reconstruction.[24,26,27]

D. Clustering of Cl atoms on surface Ga dimer

We also find out that two Cl adatoms can bind at either edges of a in-surface Ga dimer, i.e., two Cl atoms at $\mathbf{M}_1$ sites of a in-surface Ga dimer. The asymmetric Ga dimer become symmetric and its position is shifted more toward vacuum by 0.4 Å as shown in Fig. 6. The second Cl adatom has higher adsorption energy by 0.46 eV than the first one with respect to 1/2 of Cl_2. The distance between two Cl adatoms on a in-surface Ga dimer is 4.5 Å. We identify this geometry with the *D* features in the STM image.[24] Note that the less stability of it agrees to the minor number of features in STM observations.[24] The STM measurements under high coverage of chlorine also showed that the number of clustered features separated one another by 8 Å instead of 4.5 Å.[40] Our DFT calculations show the clustering of the Cl-paired Ga dimers is energetically less favorable by 0.14 eV/Cl_2, in agreement with experimental observations.[40] This is due to the electrostatic repulsion between Cl adatoms at adjacent Ga dimers: the distance between two Cl adatoms at adjacent dimer is 3.72 Å, and large amount of charges are localized on Cl adatom as shown in Fig. 6.

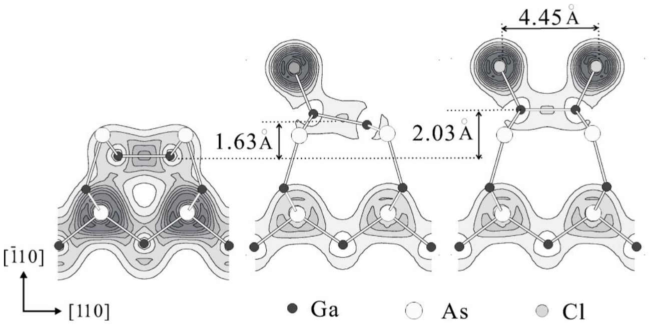

FIG. 6. The charge-density plot with the bonding configuration of in-surface Ga dimer of clean ζ surface (left), one Cl adatom (middle), and two Cl adatoms at both edge of an in-surface Ga dimer (right). Grid spacing is 0.01*e* for clean ζ surface and 0.025*e* for Cl-attached surfaces.

IV. SUMMARY

We investigated the adsorption and diffusion of a Cl adatom on the GaAs(001)-$c(8\times2)$ ζ surface using DFT-GGA calculations. The results show that a Cl adatom preferentially binds to Ga. At the most stable adsorption sites, labeled $\mathbf{M}_1$ (i.e., at the edge of a in-surface Ga dimer), the Ga dimer atom is lifted above the surface. The calculated diffusion energy barrier for a Cl adatom along $[110]$ on the in-surface Ga dimer ($\mathbf{M}_1\rightarrow\mathbf{S}_1\rightarrow\mathbf{M}_1$) is calculated as 0.47 eV, while that to adjacent dimer ($\mathbf{M}_1\rightarrow\mathbf{S}_2\rightarrow\mathbf{M}_1$) is calculated as 0.87 eV. Along $[\bar{1}10]$, the diffusion energy barrier is calculated as 0.98 eV. We also find that two Cl adatoms could bind to the same in-surface Ga dimer, binding to its two edges. However, clustering of more Cl adatoms is not energetically favorable.

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