Comment on "Anomalous Mobility of Strongly Bound Surface Species: Cl on GaAs(001)-c(8 × 2)"

In a recent Letter, McLean *et al.* [1] reported anomalously fast diffusion of Cl adatoms on the Ga-rich GaAs(001) surface. They presented a systematic scanning tunneling microscopy (STM) study as well as Hartree-Fock cluster calculations. Their analysis was based on a surface model (the $\beta2$ structure) that recently has been shown to be less stable than the new ζ structure [2]. The ζ structure was found by density-functional theory (DFT) calculations [2] and confirmed by experimental analyses [2,3]. The geometry of the ζ model is so very different from the originally assumed one [compare Fig. 1(a) with Fig. 1(c) in Ref. [1]] that we decided to reanalyze the experimental results of McLean *et al.* and to perform calculations for the Cl adsorption and diffusion. We used DFT, the generalized gradient approximation, and norm-conserving pseudopotentials. The electronic wave functions were expanded in plane waves (cutoff 12 Ry). The surface was modeled by a (4×4) supercell, and in terms of the Brillouin zone of a (1×1) cell we used 64 **k** points. Figure 1(a) [cf. also Fig. 1(b)-(left)] shows that the ζ structure has at the center of the F channels one Ga dimer per unit cell *in the surface*, and in addition, there are two *subsurface* Ga dimers (significantly below the top layer). The calculated adsorption geometry for a single Cl adatom is displayed in Fig. 1(b)-(middle) ($E_1^{ad} = 1.06$ eV
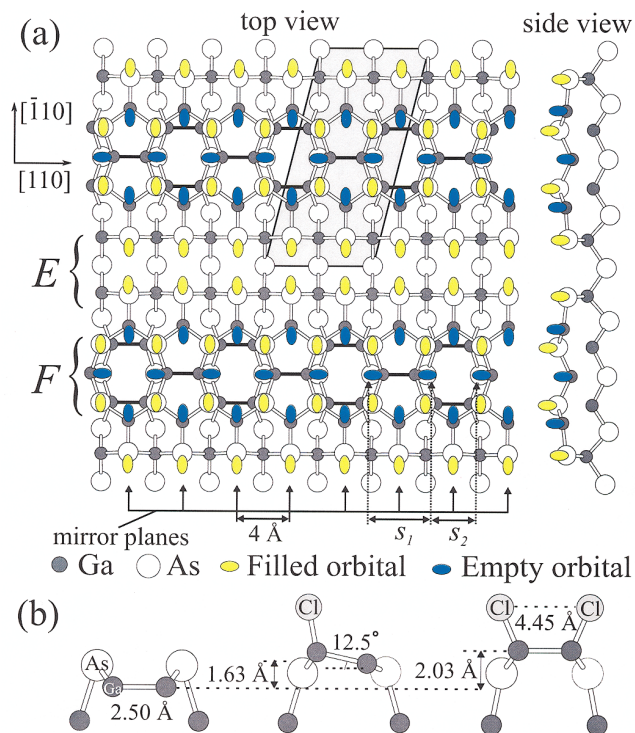
with respect to the energy of $1/2Cl_2$). We therefore identify the S features in the STM data of Ref. [1] with this situation. Note that the Cl adatom lifts the *in-surface* Ga dimer from its initial position to above surface without an activation energy barrier. With an energy barrier of $E_1^b = 0.47$ eV, the Cl adatom can hop from one side of the dimer to the other one ($s_1 = 4.45$ Å). For a hop along [110] from one dimer to the next one, the calculated distance and energy barrier is $s_2 = 3.72$ Å, and $E_2^b = 0.87$ eV. Assuming the prefactor ν_0 as 10^{12} Hz [1], the experimentally deduced values are $E_1^{b\text{-}exp} = 0.74$ eV ($s_1^{exp} = 4.5 \pm 0.3$ Å) and $E_2^{b\text{-}exp} = 0.80$ eV ($s_2^{exp} = 3.5$ Å) along [110]. We cannot rule out that the part of the difference between E_1^b and $E_1^{b\text{-}exp}$ is due to approximations in our theory, but we also note that it would vanish if the attempt frequency for the experimental analysis of the s_1 hop would be 10^8 Hz instead of 10^{12} Hz. Additional experimental work on this question would be valuable.

In the ζ structure, there is only one row of *in-surface* Ga dimers [along the F channel cf. Figure 1(a)]. The older model (the $\beta2$ structure), that was considered by McLean *et al.*, has two surface Ga dimers parallel to each other (distance 4 Å). Therefore they hypothesized a very rapid hopping (> 1 kHz) along $[\bar{1}10]$ between two neighboring dimers of the $\beta2$ structure. However, alternatively, this experimental result could be interpreted as evidence for no (or very slow) hopping, which corresponds to $E^{b\text{-}exp} > 0.95$ eV (assuming $\nu^{STM} < 10^{-4}$ Hz and $\nu_0 = 10^{12}$ Hz). Our DFT study gives $E^b = 0.98$ eV along $[\bar{1}10]$, which is consistent with the slow (experimentally not observed) diffusion along this direction. This is another strong hint that the reconstruction present in the experimental work [1] was indeed ζ and not $\beta2$. We also find that a second Cl adatom can bind to a Ga dimer, that binds one Cl already. The adsorption energy of the second Cl adatom is higher than that of the first one ($E_2^{ad} = 1.52$ eV with respect to $1/2Cl_2$), and the Cl-Cl distance is 4.45 Å [cf. Figure 1(b)-(right)]. We identify this geometry with the D features in the STM image [1]. Our DFT calculations show that two-Cl-adsorbed geometry is energetically favorable. However, a clustering of such Cl-pair structures is energetically unfavorable by 0.14 eV/Cl_2.

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FIG. 1 (color). (a) Top and side views of the GaAs(001)-$c(8 \times 2)$ ζ surface. The unit cell is noted by the dashed parallelogram. (b) Side views of different Ga dimers: clean (left), with one Cl adatom (middle), and with two Cl adatoms (right).