

## Investigation of the Ga-rich GaAs(001) Surface Reconstructions Stability and Interaction with Halogens

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(Received 29 June 2013; revised manuscript received 06 July 2013; published online 03 September 2013)

Atomic and electronic structures for a number of GaAs(001) surface geometries were studied within the density functional theory in order to re-examine the energy stability of surface reconstructions in the Ga-rich limit. It was shown that among geometries with (4×2) symmetry so-called ζ-model is most stable but the energetically favored Ga-rich (2×4) reconstructions are stabilized by dimerized Ga and As atoms. Our calculations predict the coexistence of (2×4) and (4×4) reconstructions on GaAs(001) in the Ga-rich limit. Comparative study of the halogens (F, Cl, I) adsorption on the ζ-GaAs(001)-(4×2) surface were performed. The energetically preferable positions for all considered halogens are found on-top sites above dimerized and nondimerized Ga atoms. The electronic properties of the semiconductor surface and its change upon halogen adsorption are discussed. It was shown that the interaction of halogen with the Ga dimerized atoms leads to the weakening of the chemical bonds between surface atoms that determines the initial stage of surface etching.

**Keywords:** Semiconductor Surface, Electronic Structure, Adsorption, Halogens.

PACS numbers: 68.35.Bg, 68.43.Fg, 73.20.At

### 1. INTRODUCTION

GaAs(001) is a technologically important substrate for microelectronic and photonic devices. It is well-known that polar A<sup>III</sup>B<sup>V</sup>(001) surface displays a variety of surface reconstructions depending on the method of sample preparation, temperature and composition [1]. The Ga-rich surface geometry has attracted special attention, because it appears to be preferable for the deposition of ferromagnetic metals (iron or cobalt) that may be relevant to the nanotechnology of magnetic materials and spintronics [2].

The ζ(4×2) structure suggested in [3] was calculated to be energetically favorable under the Ga-rich conditions: its energy was found to be lower than that of all the previously proposed models [3, 4]. This theoretically predicted structure was confirmed by analyses of scanning tunneling microscopy (STM), low-energy electron diffraction and surface X-ray diffraction [5]. In the same time according to the calculations [4], the Ga-rich structure with (2×4) symmetry, called mixed-dimer, was found to be lower in energy with respect to ζ(4×2) structure. The cation-rich (2×4) structures on A<sup>III</sup>B<sup>V</sup> semiconductor (001) surface were observed only in case of InP and GaP [6-8]. The general trend in calculated phase diagrams [4] for A<sup>III</sup>B<sup>V</sup> semiconductors (GaAs, GaP, InP, InAs) is the fact that, for extreme cation-rich conditions, the mixed-dimer (2×4) structure is the most favorable reconstruction. The absence of Ga-rich (2×4) structure on GaAs(001) surface may indicate that the formation of the Ga-(2×4) structure is kinetically limited on GaAs(001) surface. Recently, a new Ga-rich structure with the symmetry of (2×4) has been obtained experimentally [9]. Thus, the GaAs phase diagram in the Ga-rich limit remains under question.

It is necessary to point out that during last two dec-

ade methods of layer-by-layer or “digital” etching of crystals which makes it possible to controllably remove crystal monolayers and to maintain surface atomic smoothness were intensively developed. In binary A<sup>III</sup>B<sup>V</sup> compounds “digital” etching can be implemented using adsorbates (halogens for instance) reacting with atoms of group III or V. Despite the efficient implementation of “digital” etching [10, 11], the microscopic mechanism of adsorbate induced weakening of the bonding of substrate surface atoms remains unclear. Depending on the surface orientation and its stoichiometry molecular halogens interacting with semiconductor surface, form the ordered structures on one type of (001) surface, whereas other surface is disordered. This indicates different a chemical activity and selectivity of the interaction of halogens with semiconductor surface atoms. There are contradictory experimental and theoretical data regarding the interaction of halogens with semiconductor surfaces [12–14].

Thus, in the present paper we present the first principles total energy studies of the energetic stability and atomic topology of GaAs(001) surface in the Ga-rich limit. The effect of halogen adsorption on the structure and electronic properties of the GaAs(001) surface are also studied.

### 2. COMPUTATION DETAILS

The atomic and electronic structures of the GaAs(001) surface were calculated by the projector augmented wave method [15] implemented in the VASP software package [16]) with the exchange-correlation functional in the generalized gradient approximation. The surface was simulated by the repeated slab method with a slab containing eight and nine atomic layers for cation- and anion-terminated (001)

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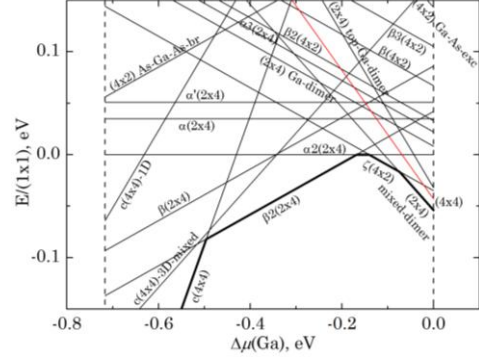
surface, and vacuum region of  $\sim 10 \text{ \AA}$ . The bottom As layer was passivated by a layer of fractionally charged hydrogen atoms that allows the layer to mimic tetrahedral bonds of bulk semiconductor. A  $3 \times 6 \times 1$  grid of  $k$ -points was used for Brillouin zone (BZ) integration in case of  $(4 \times 2)$  structures while a  $6 \times 3 \times 1$   $k$ -points grid was used for  $(2 \times 4)$  structures, a  $3 \times 3 \times 1$  grid for  $c(4 \times 4)$  structures. The plane wave cutoff was 500 eV. Two bottom layers of As and Ga were fixed during the structure relaxation, whereas the positions of atoms in other layers were relaxed till the forces at the atoms were smaller than  $0.002 \text{ eV/\AA}$ . In order to find out the most stable structures depending on the cation concentration, from the energetic point of view, we compared the formation energies ( $H_f$ ) of different surface reconstructions of GaAs(001). The formation energy of semiconductor surfaces can be estimated as [4]:  $H_f = E_{tot} - n_{\text{Ga}}\mu_{\text{Ga}} - n_{\text{As}}\mu_{\text{As}}$ , where  $n_i$  is a number of atoms (Ga or As) and  $\mu_i$  represents their chemical potential which is restricted by upper limits  $\mu_i \leq \mu_i(\text{bulk})$ . The orthorhombic and rhombohedral structures were used for bulk Ga and As, respectively. An additional equilibrium condition is  $\mu_{\text{GaAs}}(\text{bulk}) = \mu_{\text{Ga}} + \mu_{\text{As}}$ , where  $\mu_{\text{GaAs}}(\text{bulk})$  is the energy of bulk semiconductor. The lower limits for chemical potentials are obtained by the addition of the heat of GaAs formation ( $\Delta H_{\text{GaAs}}$ ):  $\mu + \Delta H_{\text{GaAs}}$ . The calculated  $\Delta H_{\text{GaAs}}$  was 0.72 eV, which is close to the values of 0.74–0.77 eV obtained in [3, 17]. Actually the above mentioned equation for formation energy might be rewritten as a function of a single variable. This variable can be related to the Ga chemical potential with respect to its bulk phase  $\Delta\mu_{\text{Ga}} = \mu_{\text{Ga}} - \mu_{\text{Ga}}(\text{bulk})$ . In other words it is possible to calculate the dependence of the formation energy on the Ga concentration. For the Ga-rich region,  $\Delta\mu_{\text{Ga}}$  is equal to 0 and  $\Delta\mu_{\text{As}} = -\Delta H$ , whereas for the As-rich surface,  $\Delta\mu_{\text{Ga}} = -\Delta H$  and  $\Delta\mu_{\text{As}} = 0$ .

The halogen–substrate binding energy was calculated by the formula  $E_b = -[E(\text{halogen/GaAs}) - E(\text{GaAs}) - E(\text{halogen})]$ , where  $E(\text{halogen/GaAs})$  and  $E(\text{GaAs})$  are the total energies of the system with adsorbed halogen and clean surface,  $E(\text{halogen})$  is the halogen atom energy estimated by calculating the atom in an empty cell.

### 3. RESULTS AND DISCUSSION

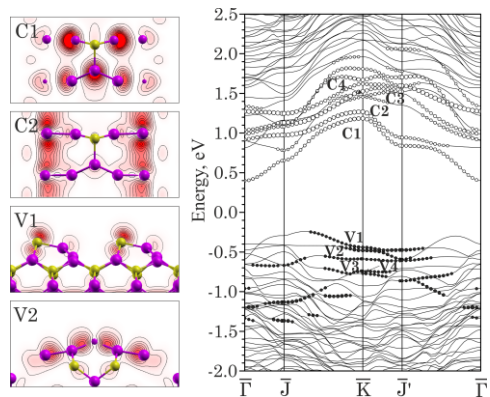
Figure 1 shows the calculated phase diagram in case of GaAs(001). In general, our results are in agreement with the previously obtained theoretical data. In case of As-rich limit, our calculations confirm that the  $c(4 \times 4)$  structure with three As dimers in the surface layer is stable [3, 4, 18]. The same can be said about the  $\beta 2(2 \times 4)$  phase which is the most favorable structure for the As-rich surface [3, 4, 18, 19]. The  $\Delta\mu$  region of this phase (0.33 eV) is found to be in good agreement with an earlier result [4]. In the earlier paper [19] the  $\alpha 2(2 \times 4)$  geometry was found to be the most stable for the Ga-rich surface because the  $\zeta(4 \times 2)$  structure was not studied in this paper. It is seen in Fig. 1 that  $\alpha 2(2 \times 4)$  phase can be also energetically stable, but in a very narrow region of Ga concentration that agrees well with the results of Ref. [3]. The  $\zeta(4 \times 2)$  structure is energetically stable at the range of  $-0.14 \text{ eV} < \Delta\mu_{\text{Ga}} < -0.07 \text{ eV}$ . It was believed for a long time that this structure is energetically preferable

up to the Ga-rich limit with the exception of the calculation result [4], where InP-type  $(2 \times 4)$  mixed-dimer reconstruction was calculated to be stable. Our calculations confirm this finding and show a 19 meV/( $1 \times 1$ ) gain for the  $(2 \times 4)$  mixed-dimer structure with respect to  $\zeta(4 \times 2)$  structure in the Ga-rich limit that is in agreement with the value of  $\sim 20 \text{ meV/(1} \times 1)$  obtained in an earlier work [4].



**Fig. 1** – Relative formation energy per  $(1 \times 1)$  unit cell for GaAs surface reconstructions depending on the Ga chemical potential. Dashed lines denote anion- and cation-rich limits of the thermodynamically allowed range of  $\Delta\mu(\text{Ga})$ .

It is necessary to emphasize that, in the Ga-rich limit, two of three low-energy structures in Fig. 1 have the periodicity  $(2 \times 4)$ : the structure with mixed As-Ga dimer as well as with top Ga dimer. The electronic energy spectrum of the GaAs(001)- $(2 \times 4)$  mixed dimer structure presented in Fig. 2 (right) is typical of GaAs(001)- $(2 \times 4)$  structures. It has a bunch of occupied (Vi) and unoccupied (Ci) surface states (SS) primarily at the Brillouin zone edge. The orbital character of several the highest occupied and lowest unoccupied surface states is shown in Fig. 2 (left) also. The highest occupied SS (V1) is localized mainly at the As mixed-dimer atom and it is related to the As dangling bond, while lower lying SS (V2–V4) are mostly derived from the orbitals of Ga-dimer atoms. It is necessary to point out that the lowest unoccupied SS (C1), as well as the higher lying SS (C2–C4), is mainly localized at the Ga-dimers atoms.

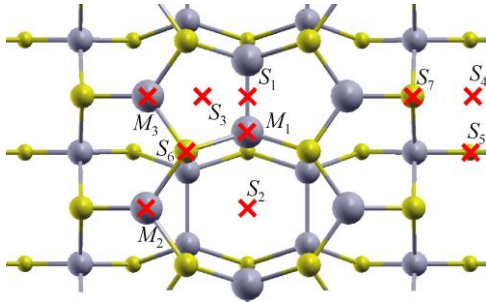


**Fig. 2** – Electron energy spectrum of the GaAs(001)- $(2 \times 4)$  mixed dimer structure with surface states depicted in filled and empty circles (right) and the orbital composition of the highest occupied and lowest unoccupied (left) surface states at the K point of the two dimensional BZ.

If we turn back to the diagram of stability (Fig. 1)

one can see that in the Ga-rich limit, the energy of the top-Ga-dimer ( $2 \times 4$ ) structure is only 3 meV/( $1 \times 1$ ) higher in comparison with  $\zeta(4 \times 2)$ , and the mixed-dimer ( $2 \times 4$ ) structure is 19 meV lower with respect to  $\zeta(4 \times 2)$ . This allows us to suggest that the combination of both structures of ( $2 \times 4$ ) symmetry, which gives the ( $4 \times 4$ ) geometry can be lower in energy than  $\zeta(4 \times 2)$ . Our calculation of the formation energy for this ( $4 \times 4$ ) structure confirms our suggestion (Fig. 1) and its energy is 8 meV lower than that of  $\zeta(4 \times 2)$ , but only 11 meV higher as compared to the ( $2 \times 4$ ) mixed dimer structure. Thus, both ( $2 \times 4$ ) and ( $4 \times 4$ ) structures can coexist at moderate temperatures on GaAs(001) surface.

Due to disagreement between theoretical and experimental results regarding to chlorine adsorption on  $\zeta$ -GaAs(001)-( $4 \times 2$ ) surface, we performed comparative study of halogen adsorption on this surface. The atomic structure of  $\zeta$ -( $4 \times 2$ ) and halogens (F, Cl, I) positions are shown in Fig. 3. In case of chlorine adsorption the preferential adsorption site was found to be on top ( $M_1$ ) position above the surface Ga dimer atoms. The binding energy (2.87 eV) in this adsorption site is found to be in quite good agreement with the value of 2.86 eV obtained in [14]. The binding energy of Cl at  $M_2$ -site is only by 0.04 eV weaker as compared to that at  $M_1$ -site. It should be noted, that the binding energy of chlorine in the Ga dimer bridge ( $S_1$ ) position is only slightly higher (by 0.06 eV) than that at  $M_3$ -site. The opposite trend was found in [14] but the difference in the binding energies of Cl in the  $M_3$  and  $S_1$  positions is too small ( $\sim 0.07$  eV).



**Fig. 3** – Atomic structure of the  $\zeta$ -GaAs(001)-( $4 \times 2$ ) surface. Crosses are the considered adsorption positions.

It is seen from Table 1 Cl adsorption is found to be less preferable in the hollow ( $S_2$ ,  $S_3$ ) positions as well as in the Ga-missing row ( $S_4$  or  $S_5$ ) sites in contrast to conclusion made in [12]. The binding energy is high enough on top As trench edge site ( $S_7$ ) near the Ga missing row, however, it remains smaller than those in on-top Ga dimerized and undimerized atoms. The calculated values of binding energies are by  $\sim 2$  eV higher in case of F adsorption, whereas for I, they are by  $\sim 1$  eV smaller as compared to those for Cl. The difference in the binding energies for  $M_3$  and  $S_7$  sites (Fig. 3) is significantly less in the case of iodine adsorption as compared to fluorine or chlorine that can be attributed to larger covalent ra-

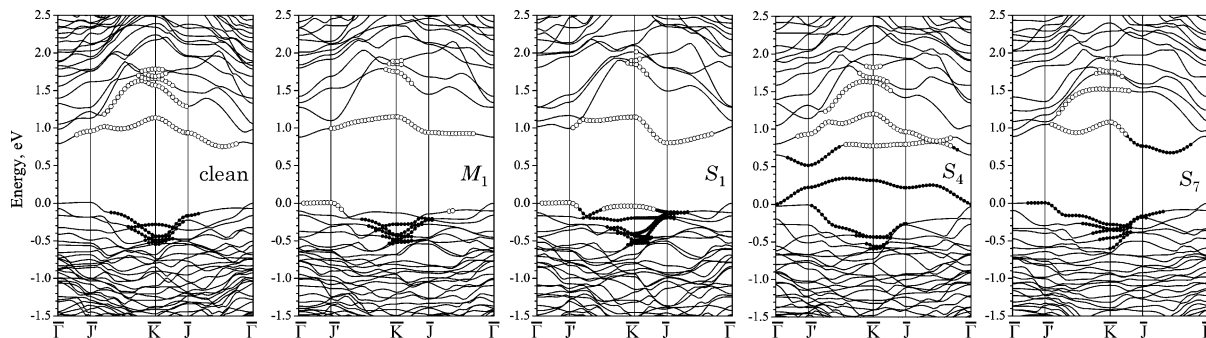
dius of iodine. This suggests also the low energy barrier for I migration between  $M_3$  and  $S_7$  sites. Considered halogen affect the atomic positions of surface layers to a greater extent than, e.g., alkali metals [20]. When a halogen atom is adsorbed, the large displacements of surface atoms occur. For example, in case of  $M_1$ -position, Cl pulls up the Ga dimer atom from its initial position towards vacuum. The Ga dimer atom attached by Cl is located by 0.53 Å higher than the nearest As atoms. It should be stressed that in our calculations, the Ga second dimer atom without Cl is located below the nearest As atom, in contrast to result of reference [14]. If Cl is adsorbed at  $M_2$  or  $M_3$  sites, it shifts the Ga atoms towards the vacuum by 0.76 Å ( $M_2$ ) and 0.68 Å ( $M_3$ ), respectively, relatively to the adsorbate-free surface (0.7 Å and 0.4 Å [14]). Chlorine adsorption even at Ga bridge dimer sites does not lead to dimer bond breaking. When the two chlorine adatoms are bonded at both  $M_1$  sites, the distance between the former is of 4.33 Å (4.45 Å [14]). In this case, the asymmetric Ga dimer becomes symmetric again as for clean surface but its position is shifted towards the vacuum by 2.00 Å (2.03 Å [14]) in comparison with the clean surface. The trend in the atomic displacement of As atoms in  $S_7$  site, when Cl adatom is attached to them at on-top sites, is opposite to that observed for Ga atoms since As atoms are shifted into the bulk by 0.43 Å, whereas in  $S_6$  site, As atoms are shifted to vacuum by 0.25 Å. Note, that the bond length between Cl adatom and Ga dimer atom is  $\sim 2.22$  Å that is in a good agreement with 2.23 Å obtained in reference [14]. F–Ga and I–Ga bond lengths are 1.82 Å and 2.58 Å, respectively. It should be stressed, that the trends in the atomic displacements and preferential adsorption sites remain the same at low coverage limit for F and I atoms adsorbed on the  $\zeta$ -GaAs(001)-( $4 \times 2$ ) surface.

Since iodine influences the electronic structure of GaAs(001) more delicate than fluorine and chlorine we discuss its adsorption in details. The calculated electron spectra (Fig. 4) for GaAs(001) with adsorbed iodine in above mentioned positions show partial depletion of surface states for positions above Ga since the number of states in the valence band becomes larger than the number of electrons occupying them. Note that iodine has five  $p$  electrons in its valence band, it tends to pick a necessary electron from gallium to completely fill this band. The bond between gallium and iodine implies a large charge transfer from the surface to the adsorbate.

The integrated charge density difference ( $\Delta\rho = \rho_{\text{GaAs}} + \rho_{\text{halogen}} - \rho_{\text{halogen/GaAs}}$ ) in the sphere around  $M_1$ -site is presented in Fig. 4a. Since F has a higher electronegativity than Cl or I, a larger electronic charge is transferred from semiconductor surface to F adatom (Fig. 5). One can see that the charge transfer for all adsorbates is equal to  $\sim 0.7$ - $0.8e$  (for ionic radii). Our calculations show that the charge transfer when I is adsorbed above Ga-sites, is  $\sim 0.7$  electron (at integration radii of 2.0-2.1 Å). A significantly less charge transfer is

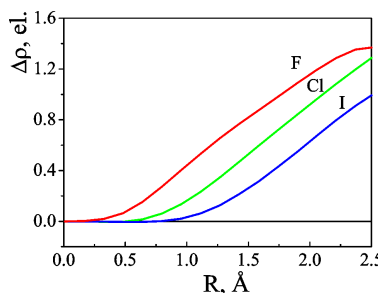
**Table 1** – Halogen adsorption energies (in eV) for the considered positions on Ga-terminated  $\zeta$ -GaAs(001)-( $4 \times 2$ ) surface

Positions	$M_1$	$M_2$	$M_3$	$S_1$	$S_2$	$S_3$	$S_4$	$S_5$	$S_6$	$S_7$
F	4.74	4.71	4.52	4.51	4.08	3.39	3.58	3.76	3.51	4.07
Cl	2.86	2.82	2.56	2.62	2.03	1.70	1.82	1.52	1.87	2.38
Cl [14]	2.87	2.74	2.48	2.41	2.01	2.02	1.89	-	-	-
I	1.86	1.78	1.59	1.68	0.89	0.95	1.13	0.89	1.07	1.54



**Fig. 4** – Electron energy spectrum of the  $\zeta$ -GaAs(001)-(4 $\times$ 2) surface and the surface with adsorbed iodine at  $M_1$ ,  $S_1$ ,  $S_4$  and  $S_7$  adsorption positions.  $E = 0$  corresponds to the valence band top.

observed at the  $S_2$ ,  $S_5$ ,  $S_6$  and  $M_3$  position, where the iodine has smaller binding energy. Since the Ga orbitals are almost empty the redistribution of charge between Ga and As surface atoms takes place. Our calculations also show the decrease in electron density between the Ga dimer atom and neighboring As surface atom, that is, the formation of “holes” in the Ga-As bond.



**Fig. 5** – Sphere-integrated charge density difference of valence electrons ( $\Delta\rho$ ) of halogens in  $M_1$ -site (left) and  $\Delta\rho$  of I for considered adsorbate site as a function of the integration radius.

Probably, both the increase in the dimer bond length by 0.08 Å and the decrease in electron density between Ga and As surface atoms contribute to the iodine-induced decrease in the surface Ga dimer atom binding energy and, as a consequence, to the desorption of iodine and gallium under annealing at relatively low temperatures. The calculated decrease in the binding energy averaged over the Ga-Ga and two Ga-As bonds is of 0.86 eV.

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## 4. CONCLUSION

Thus the present DFT total energy calculations confirmed the stability of the  $\zeta$ -GaAs(001)-(4 $\times$ 2) reconstruction among ones with (4 $\times$ 2) geometry but (2 $\times$ 4) mixed dimer structure is most stable in the Ga-rich limit. It was shown that the (2 $\times$ 4) mixed dimer and (4 $\times$ 4) structures can coexist at moderate temperatures. Adsorption of halogens (F, Cl, I) was considered on the  $\zeta$ -GaAs(001)-(4 $\times$ 2) surface. Our study reveals that the bonding mechanism of halogens with semiconductor substrate involves a strong ionic bonding of adatom with Ga-dimerized and undimerized atoms in the surface layer. The bonding of halogens in the Ga missing row is found to be less preferable. The binding energies of iodine with GaAs(001) surface are smallest one among considered halogens. Iodine, due to its smaller electronegativity and larger covalent radius, does not perturb the surface so substantially as compared to other halogens which lead to more rude effects such as the stationary etching of semiconductors. Finally, our calculations for other semiconductors (InAs, InP, etc.) showed that independently of surface reconstruction the mechanism of interaction of halogens with surface in the cation-rich limit remains the same.

## ACKNOWLEDGEMENTS

Calculations were performed in the SKIF-Cyberia supercomputer at National Research Tomsk State University. The reported study was supported by RFBR, research project N 13-02-98017\_r\_a. The work is done partially under the project 2.3684.2011 of TSU.