The Peculiarities of Halogens Adsorption on $A_3B^5(001)$ Surface

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Abstract. Theoretical study of the F, Cl, Br, I adsorption on GaAs(001) surface is presented. The most stable configurations of halogens on Ga-rich $\zeta$-(4×2) reconstruction are determined with increasing of adatoms concentration. The bonds weakening is found more significant for the F and Cl atoms which can induce stationary etching whereas I-induced changes in Ga-As binding energy is not sizable and its adsorption lead to the surface passivation.

1. Introduction

The investigation of halogen adsorption on semiconductor surfaces is very important from both scientific and technological point of view [1]. Since halogens and halogen compounds are widely used in the etching technologies it is necessary to understand the mechanism of their interaction with semiconductor surfaces on the microscopic level [2]. On other hand, the halogens are good model adsorbates to study their chemisorption on the covalently bonded materials caused by relative simple nature of their bonds. Semiconductors $A_3B^5$ are widely used in microelectronics, optoelectronics, spintronics, etc. The (001) surface is of practical interest in this regards. Halogen (F, Cl, I) adsorption on the (001) surface with $\zeta$-(4×2) reconstruction for GaAs and InAs were studied in our papers [3, 4] at low halogen coverage of 0.125 monolayer (ML). The influence of the halogen concentration on the atomic and electronic structure of the (001) surface has not been studied for $A_3B^5$ semiconductors theoretically. The adsorption of 0.75 and 1.0 ML of F, Cl, Br and I was considered on Ge(001) surface in [5, 6]. It was found that the stable atomic structures are almost the same for considered halogens. The only difference was found in the position of adatoms above the substrate [5]. However, the F-covered surface exhibits slightly different features because fluorine local density of states near the Fermi level was significantly smaller than those of Ge, Cl and I atoms.

In the present paper the influence of halogen adsorption on the atomic structure of GaAs(001) surface and surface atoms bonding as a function of halogen coverage have been studied.

2. Computational details

Atomic and electronic structures of $A_3B^5(001)$ surface were calculated using projector augmented wave (PAW-DFT) method [7, 8]. Generalized gradient approximation (GGA-PBE) for the exchange-correlation functional was employed. The surface was simulated by periodic slabs with a supercell containing eight atomic layers of semiconductor and vacuum gap of ~10 Å. The bottom anion layer was passivated by pseudo-hydrogen atoms with fractional charge $Z$ equal to 0.75e that allows us to...
make this layer bulk-like. Two bottom semiconductor layers and pseudo-hydrogen layer were fixed during the structure optimization, whereas the atomic positions in other layers were relaxed using damping Newton method up to the forces at atoms ~0.01 eV/Å. The binding energy ($E_b$) of halogen adatom with the semiconductor surface was calculated using equation:

$$E_b = -(E_{halogen/A3B5} - E_{A3B5} - E_{halogen}),$$

where $E_{halogen/A3B5}$ and $E_{A3B5}$ are the total energies of both halogen-adsorbed system and adsorbate-free semiconductor surface, respectively, and $E_{halogen}$ is the total energy of halogen atom.

3. Results and discussion

The $\zeta$(4×2) reconstruction of GaAs(001) surface is known the most stable in the Ga-rich limit [9]. Our calculations also confirm its stability among considered structures with (4×2) geometry [10, 11]. The calculations of F, Cl and I binding energies at low coverage [3, 4] reveal that halogen adatom prefers to be bonded in the $M_1$-site above Ga dimerized atoms (figure 1). Table 1 summarizes binding energies for several positions above Ga and As surface atoms in which halogens behave differently. The mentioned above trend is valid for Br as well. Note that it was not studied in our papers [3, 4]. Binding energy of Br in the $M_1$-site is lower than that of Cl but it is higher than that of I, in agreement with assumption of electronegativity concept. It should be noted that halogen adsorption influences on the bond lengths between Ga surface atoms and neighboring As atoms. The change of bond lengths depends considerably on the adsorbate sites [4]. For instance, the bond length in Ga dimer increases by 0.08-0.10 Å when I, Br, Cl and F are adsorbed in the $M_1$-site. One can expect that the increase in the dimer bond lengths contributes to the halogen-induced decrease in the binding energies of surface atoms and as a consequence, leads to monohalide desorption. To confirm this assumption we estimated the influence of halogen on the binding energy of Ga or As surface atoms with the substrate.

![Figure 1](image-url)  
**Figure 1.** Adsorption sites (crosses) of halogens on the $\zeta$-GaAs(001)-(4×2) surface. Ga and As atoms are shown by dark and white balls.

| Halogen adsorption sites | $M_1$ | $M_2$ | $M_3$ | $S_6$ | $S_7$ |
|--------------------------|-------|-------|-------|-------|-------|
| F                        | $E_b$(halogen-surface) | 4.74  | 4.71  | 4.52  | 3.51  | 4.07  |
|                          | $E_b$(monohalide-surface) | 2.22  | 2.70  | 3.06  | 4.14  | 4.98  |
| Cl                       | $E_b$(halogen-surface) | 2.86  | 2.82  | 2.56  | 1.87  | 2.38  |
|                          | $E_b$(monohalide-surface) | 2.25  | 2.75  | 3.15  | 4.16  | 4.85  |
| Br                       | $E_b$(halogen-surface) | 2.51  | 2.49  | 2.29  | 1.58  | 2.09  |
|                          | $E_b$(monohalide-surface) | 2.25  | 2.75  | 3.14  | 4.25  | 4.82  |
| I                        | $E_b$(halogen-surface) | 1.86  | 1.78  | 1.59  | 1.07  | 1.54  |
|                          | $E_b$(monohalide-surface) | 2.30  | 2.82  | 3.23  | 4.44  | 4.87  |

* Cases when $E_b$ of halogen with surface is greater than that of Ga monohalide with surface are shown by bold numbers.

In order to demonstrate the “back bonds” weakening, we removed the Ga or As atoms from the clean $\zeta$-GaAs(001)-(4×2) surface and the Ga- or As-monohalides from the halogen adsorbed system as well. Table 1 shows that in the $M_1$-site the binding of GaF, GaCl and GaBr molecules with the substrate is considerably weaker than the bonding energy of halogen atom (F, Cl, Br) with surface. On the contrary, the binding energy of GaI with substrate is of 0.44 eV higher than that of I with Ga dimerized atom. In the latter case, one can expect that I adsorption should lead to the surface passivation with subsequent desorption of GaI induced by temperature activation. This conclusion is in agreement with the experimental results [1, 12]. The same behavior occurs in the $M_2$-site where only minor difference in the binding energies of halogen atoms compared to $M_1$-site was calculated. At the same time when halogen atoms are adsorbed in $S_6$ or $S_7$ sites their binding energies decrease whereas the binding energies of As monohalides increase considerably. It means that the removing of the corresponding As monohalides from the semiconductor substrate is not energetically favorable with respect to halogen desorption. The calculated decrease in the binding energy ($\Delta E_b$) of Ga atom with
the nearest surface atoms averaged over the three bonds is 0.86-0.88 eV for M₁-site. Almost the same change of ΔEₚ is found if halogens are adsorbed above Ga nondimerized atoms. It should be noted that initially the binding of Ga dimerized atom with substrate is weaker than that of Ga nondimerized atoms by 0.19 eV and 0.31 eV in M₂ and M₃ sites, respectively. For all halogens adsorbed in the S₁-site ΔEₚ is in the range of 0.59-0.62 eV. The binding of As atom with substrate in the S₁-site is stronger than that of Ga one in the M₁-site by 0.62 eV therefore the decrease of ΔEₚ is smaller in case of halogen adsorption above As-sites. Thus, the formation of bond between halogen and Ga surface atoms on GaAs(001) surface results in decrease of Ga binding energy with substrate. Almost the same values of ΔEₚ (0.78-0.81 eV) were calculated for I, Cl and F adsorption on ζ-InAs(001)-(4×2) in the M₁-site [4]. In general, our results reveal that in case of the Ga-terminated GaAs(001) surface Ga atoms should be removed from the surface layer by halogens at the first step of etching. This result was confirmed by the experimental observation for the I/GaAs(001) interface: desorption of Ga-halides observed at I concentration below 0.5 ML, while above this value, only iodine molecules were desorbed [12]. It is seen from Table 1 that in case of F the transition from the chemisorption state to etching is possible whereas an additional energy is needed in case of less electronegative halogens.

Figure 2 presents the atomic structures of several Cl covered systems. Two Cl adatoms can be bonded with both Ga dimer atoms [13]. In this case the position of Ga surface dimer shifts toward vacuum by 2.00 Å (2.03 Å [13]). The average binding energy of Cl adatoms (3.06 eV/atom) is higher than that in case of single adsorbed chlorine in the M₁-site. It is necessary to point out that halogen-induced decrease of Ga dimer binding energy with the nearest surface atoms averaged over the four bonds, is 0.89 eV. The adsorption of two Cl atoms above Ga dimerized atoms reveals the decrease of the Ga–As bond energy by 0.07 eV, however this decrease is more pronounced (0.16 eV) in case of F adsorption on GaAs(001) and it is 0.19 eV on InAs(001). The adsorption of two Cl atoms in S₁ and S₂ sites (figure 1) is found to be more preferable than in M₁-M₁ sites (figure 2a). In this case the breaking of Ga dimer is occurred with shift of Ga atoms toward vacuum by 1.76 Å. The increase of the binding energy of Cl adatoms in S₁-S₂ with respect to adsorption in M₁-M₁ is 0.39 eV.

Figure 2. Atomic structures of Cl covered ζ-GaAs(001)-(4×2) surface up to 1 ML (top and side view).

Further we considered the configuration with two additional Cl adatoms adsorbed in M₂-sites (figure 2b). It is seen that chlorine bonding in both M₂-sites alongside with M₁-sites does not lead to breaking of Ga surface dimer bond as in case of Cl adsorption in M₁-M₁ sites. All positions above Ga surface atoms are occupied at the Cl coverage of 0.75 ML and as a consequence the transition to the (4×1) structure is observed (figure 2c). Finally, several structures with eight Cl adatoms which form the bond with dimerized, nondimerized Ga atoms as well as As atoms were considered also. One of these structures is shown in figure 2d. In case of simultaneous adsorption of two Cl atoms on one Ga atom in the M₂ or M₃ sites one of Cl adatom relaxes toward position in the missing dimer row (S₁ in figure 1). The formation of Ga dichloride can be obtained when two Cl adatoms are bonded with Ga in the M₁-site, however this structure is less stable than that shown in figure 2d. The average binding energies between substrate and Cl atoms with increase of their concentration are listed in table 2. In general, the binding energy of Cl adatom weakly depends on halogen coverage in agreement with Ref.
Table 2 presents the change in the binding energy of Ga atoms with substrate relative to its value on the clean surface (4.87 eV). In order to estimate $\Delta E_b$ we removed only one GaCl molecule from $M_1$-site with increase of Cl coverage. It is seen that maximal $\Delta E_b$ is observed for Cl coverage of 0.75 ML that corresponds to the adsorption in the most preferential sites, while decrease of $\Delta E_b$ above 0.75 ML reflects the saturation of unfavorable sites (As-sites) and possibly influence of adsorbates lateral interaction.

| Coverage | 0.125 ML | 0.25 ML | 0.50 ML | 0.75 ML | 1.00 ML |
|----------|----------|---------|---------|---------|---------|
| $E_b$ (eV/atom) | 2.86, 2.87 [13] | 3.06 | 3.12 | 3.05 | 3.05 |
| $d_{Cl-Ga}$ (Å) | 2.22, 2.23 [13] | 2.20 | 2.20 | 2.18 | 2.17 |
| $\Delta E_b$ (eV) | 2.62 | 2.69 | 2.80 | 2.89 | 2.63 |

4. Conclusion
The comparative analysis of halogen atom adsorption on $\zeta$-GaAs(001)-(4×2) surface were performed by ab-initio PAW-DFT method. Our results reveal that halogen adsorption leads to the weakening of Ga-As surface bonds and this effect is most pronounced with increase of electronegativity of halogens. It is shown that the transition from the chemisorption to etching state is occurred in case of F whereas adsorption of I leads to passivation of Ga-rich GaAs(001) surface. The consideration of Cl adsorption on GaAs(001) surface shows that the increase of halogen coverage above 0.75 ML weakly changes the binding energy of surface Ga atoms.

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