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Ab-initio Study of Cation-rich InP(001) and GaP(001) Surface Reconstructions and Iodine Adsorption

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Abstract. Atomic and electronic structures for a number of InP and GaP (001) surface geometries were studied within the density functional theory (DFT) in order to reexamine the energy stability of surface reconstructions in the cation-rich limit. It is shown that in both cases the mixed dimer (2×4) reconstruction is the energetically favored in the cation rich limit. The ζ(4×2) reconstruction has the lowest surface energy among considered (4×2) surface structures. Comparative theoretical study of iodine adsorption on the semiconductor surface with ζ(4×2) and mixed dimer (2×4) structures was performed. It was shown that iodine prefers to be bonded with dimerized cation atoms irrespective on the surface reconstruction.

1. Introduction

It is well-known that A^3B^5 semiconductors are widely used in the production of devices such as light-emitting diodes, light detectors, integrated circuits, solar cells, etc. The cation-rich surface geometries attract a special attention because they are preferable for the deposition of ferromagnetic metals and alloys [1] that may be relevant to the nanotechnology of magnetic materials and spintronics [2]. For many technological applications atomically smoothed surface morphology are needed. In order to obtain such surface it is necessary to develop the “digital etching” technique. Usually halogens and halogen-containing molecules are used for this goal. As was shown in [3] the formation of strong ionic bonding between halogen and cation with the charge transfer via depletion of filled orbitals of the surface anion atoms leads to a weakening of bonds in the surface layer of semiconductor. Namely this condition is important in the initial stage of dry etching process on the semiconductor surface. The comparative study of halogen adsorption on the ζ-(4×2) reconstruction was performed for GaAs and InAs in [3, 4] and Ge [5, 6]. In the latter case the halogen coverage of 0.75 and 1.0 monolayer was studied. Less attention was paid to halogen adsorption on other semiconductors. As was shown in [4, 7] iodine having a lower electronegativity and a larger covalent radius provides a delicate selective action depending on the composition and reconstruction of the semiconductor surface. In this work we present the calculations of the surface reconstructions stability for GaP and InP as well as the comparative study of iodine adsorption on the (001) surface in the cation-rich limit.

2. Method of calculation

Atomic and electronic properties of the InP and GaP (001) surfaces were calculated using the projector augmented-wave (PAW) method [8, 9] and corresponding PAW potentials supplied with the VASP package [10]. The generalized gradient approximation (GGA-PBE) [11] for the exchange-correlation

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functional was used. The surface was simulated using the periodic slab geometry with a supercell containing eight-nine atomic layers of semiconductor and vacuum gap of ~10 Å. Earlier works [12, 13] performed on oxide and semiconductor systems showed that the thickness of the metal slab becomes important in determining the electronic structure. A surface energy is converged quickly with increasing number of atomic layers. In general, a slab consisting of six-eight layers describes well cation-rich $A^3B^5(001)$ surface. The saturation of dangling bonds of semiconductor compounds was performed using pseudo-hydrogen atoms approach suggested by K. Shiraishi [14]. The bottom P layer was passivated by pseudo-hydrogen atoms (two atoms per P atom) with fractional charge Z equal to $0.75e$ that allows us to make this layer bulk-like. The arrangement of pseudo-hydrogen atoms was determined by the energy minimization. The resulting bond length between P and pseudo-hydrogen atom was 1.469 Å. 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 until the forces at atoms ~0.01 eV/Å. A 3×6×1 grid of k points, obtained by the Monkhorst-Pack method [15] was used for Brillouin zone integration for surface reconstruction (4×2), a 6×3×1 grid for (2×4) structures, as well as a 3×3×1 grid for c(4×4) structures. The plane wave cutoff was 500 eV. The calculation for the clean $A^3B^5(001)$ surfaces were carried out using theoretical bulk lattice constants of 5.53 Å for GaP and 6.00 Å for InP. Following linear dimensions of supercells for (2×4) and (4×2) surface geometries $a\sqrt{2}\times 2a\sqrt{2}\times 4$a and $2a\sqrt{2}\times a\sqrt{2}\times 4$a were used while for the c(4×4) geometry the size of supercell was ($2a\times 2a\times 4a$). Since slab thickness is $2a$ the vacuum gap of ~$2a$ is enough avoid self-interaction between neighbor slabs. Other computational details can be found in our paper [16].

The binding energy (E_b) of iodine adatom with semiconductor substrate was calculated using equation:

$$E_b = -(E_{I/A^3B^5} - E_{A^3B^5} - E_I)\,, \tag{1}$$

where E_{I/A^3B^5} and $E_{A^3B^5}$ are the total energies of both iodine-adsorbed system and adsorbate-free semiconductor surface, respectively, and E_I is the total energy of isolated halogen atom. The halogen coverage of 0.125 monolayer (ML) is considered only in this work.

The formation energy of semiconductor surfaces was estimated using equation

$$E_f = E_{tot} - \sum_i^2 n_i \mu_i\,, \tag{2}$$

where n_i is a number of atoms of species i, with i = Ga (In) or P and μ_i represents the chemical potential of cation or anion which is restricted by upper limits $\mu_i \leq \mu_i$(bulk). Other computational details can be found in [16].

3. Results and discussion

To determine the atomic structure of the lowest cation-rich reconstruction, we have reexamined the stability of both InP and GaP (001) surface reconstructions. The calculations of the relative formation energies of about 20 different surface structures in dependence on the chemical potential of cation were performed. It should be noted that the thermodynamic equilibrium condition between surface and substrate atoms supposes that μ_{AB}(bulk) = $\mu_A + \mu_B$. The lower limit for cation chemical potential can be obtained by the addition of the heat of formation of semiconductor (ΔH): $\mu_i + \Delta H$. The reconstructions with the lowest surface energies, which are energetically preferable among the considered ones, are given in figure 1 by solid lines. The chemical potential of cation is changed within the range $-\Delta H < \Delta\mu < 0$. The calculated value of ΔH for InP is 0.45 eV, which is close to the value of 0.43 eV obtained in [17]. It is necessary to emphasize that in [17] for the determination of upper and lower limits of chemical potentials on the surface were used the following bulk values of μ for In, P and InP: -3.270 eV, -6.028 eV, 9.728 eV, respectively, that allowed us to estimate above mentioned value of ΔH for InP. In case of GaP, ΔH is 0.85 eV that agrees satisfactory with the value of 0.91 eV [18]. For

determination of ΔH the chemical potential of black phosphorus was used. The calculated ΔH are significant less than experimental ones: 0.73±0.05 eV for InP and 1.07±0.02 eV for GaP [19]. It can be due to ΔH in [19] was determined relative to amorphous phase of red phosphorus which is less stable than the black one. In general, our diagrams are in good agreement with the previously obtained ones [18].

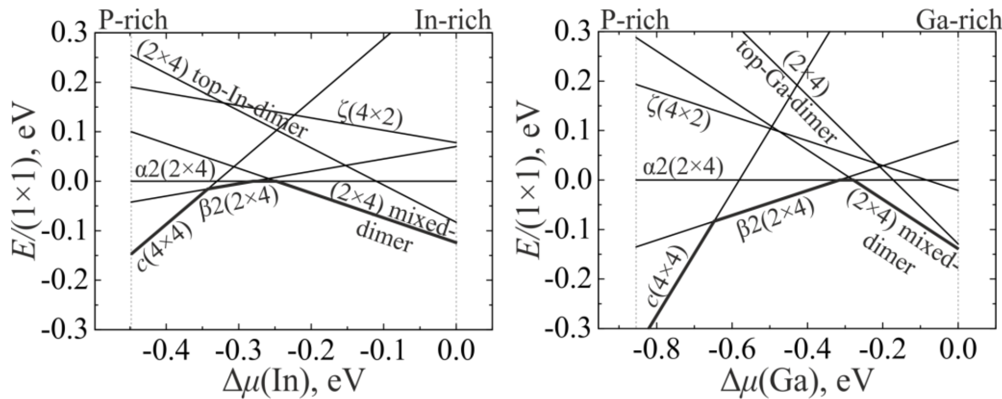

Figure 1. Relative formation energy per (1×1) unit cell for InP (left) and GaP (right) surface reconstructions depending on the In (Ga) chemical potential. Dashed lines denote P anion- and In(Ga) cation-rich limits of the thermodynamically allowed range of $\Delta\mu$.

In the P-rich limit, our calculations confirm that the c(4×4) structure with three P dimers in the surface layer is stable for both semiconductor surfaces. The same can be said about the β2(2×4) structure with two P dimers in the surface layer and one P dimer in the third layer. Mixed-dimer (2×4) reconstruction is the most stable structure in the cation rich limit for both semiconductors whereas the structure with the top Ga dimer was found to be stable in case of GaP in [18]. The surface energy of the mixed dimer (2×4) structure is only of 0.01 eV/(1×1) and 0.04 eV/(1×1) lower than that with the top-In(Ga)-dimer structure for GaP and InP, respectively. Phase α2(2×4) can be also stable but in a very narrow region of the cation concentration that agrees well with earlier results [18]. It should be stressed that the ζ(4×2) reconstruction is the most stable among structures with (4×2) geometry in the cation-rich limit. The same trend was obtained for GaAs and InAs in [3, 4]. The calculations show a 118 meV/(1×1) gain for the mixed-dimer (2×4) structure with respect to ζ(4×2) in the Ga-rich limit GaP(001) that is in good agreement with the value of ~115 meV/(1×1) [18]. This gain is of 202 meV/(1×1) in case of InP(001) but it was only 130 meV/(1×1) in [18]. In the latter case ΔH was found to be twice more (-0.91 eV) than the value calculated in the present paper. In general, our diagrams (figure 1) support the preference of the mixed dimer (2×4) structure for the (001) surface of GaP and InP semiconductors in the cation-rich limit.

Iodine adsorption was considered on both ζ(4×2) and mixed dimer(2×4) reconstructions in the positions given in figure 2. Let's to discuss firstly I adsorption on ζ(4×2). Iodine binding energies on this reconstruction are listed in table 1. The values obtained in [3] for GaAs and InAs are given also for comparison. It is seen that I prefers to be adsorbed in the M_1-site above dimerized In(Ga) surface atoms on both InP(001) and GaP(001) like in case of GaAs and InAs. It is interesting that the I adsorption is only minor preferable in the M_1-site over that in the S_2-site between adjacent surface dimers on the InP(001), however this difference is higher (0.26 eV) in case of GaP(001). The difference of 0.21-0.23 eV in I adsorption energies in the bridge dimer S_1-site and M_2-site were calculated whereas the adsorption of I in the M_2-site was found to be preferable of 0.10 eV than that in the S_1-site in case of GaAs [4]. Note that almost the same values were obtained for both sites on ζ-InAs(001)-(4×2) surface [3]. It is seen from table 1 that the smallest I binding energy in the M_3-site among considered on top sites above cation atoms (M_1-M_3) is consistent with results obtained for other semiconductors in [3]. Iodine adsorption on top sites above P is found to be less preferable.

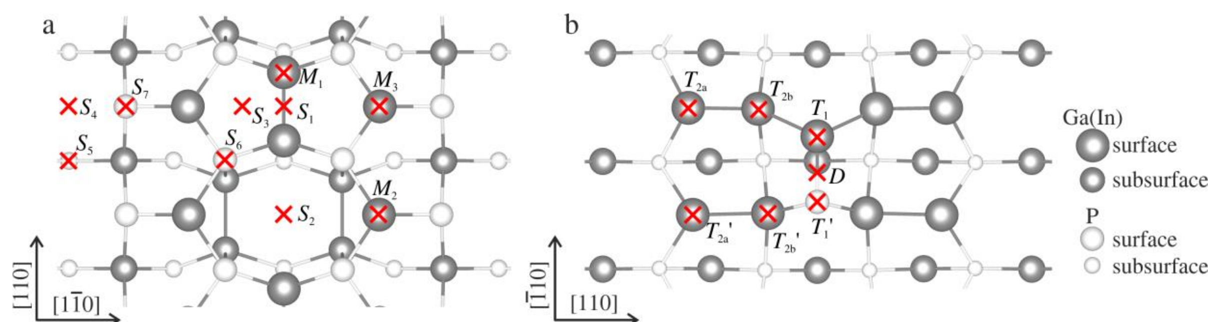

Figure 2. Iodine adsorption sites on ζ(4×2) (a) and mixed-dimer (2×4) (b) reconstructions.

Table 1. Iodine binding energies (eV) on ζ-(001)-(4×2) structure (figure 2a) for A^3B^5 semiconductors.

I sites	M_1	M_2	M_3	S_1	S_2	S_3	S_4	S_5	S_6	S_7
I-InP	2.43	1.99	1.76	2.20	2.41	1.79	1.31	0.81	1.33	1.66
I-GaP	2.19	1.79	1.53	2.02	1.93	1.53	0.74	0.83	1.01	1.52
I-InAs [3]	2.07	1.99	1.68	2.00	1.49	1.42	1.48	1.25	1.42	1.90
I-GaAs [3]	1.86	1.78	1.59	1.68	0.89	0.95	1.13	0.89	1.07	1.54

The interaction of iodine with semiconductor surface results in a large displacement of surface atoms. At all sites, except S_7, halogens pull the atoms involved into interaction from their initial position toward vacuum. A large displacement of the In dimer atom (~1.76 Å) toward vacuum in the M_1-site and opposite displacement (−0.39 Å) toward bulk in case of S_7-site is occurred. The displacements of In nondimerised atoms in the M_2 and M_3 sites are smaller (0.70-0.75 Å) as in case of I adsorption on InAs(001) surface [3]. Indium dimer lies by 0.43 Å higher than the three-fold coordinated P atoms when iodine is adsorbed in the bridge S_1-site. The interaction of iodine with InP(001) in the S_2-site results in a large displacement of surface In dimer as well. It locates by 1.07 Å higher that the corresponding P surface atoms whereas it lies by 0.70 Å lower than P surface atoms on pure InP(001) surface. In general, the atomic displacements of surface atoms in considered sites driven by halogens are slightly larger on ζ-InP(001)-(4×2) with respect to ζ-GaP(001)-(4×2). The same trend was found for InAs and GaAs on this reconstruction.

The adsorbate sites on the mixed dimer (2×4) reconstruction are basically cation ones (figure 2b). It is seen from table 2 that iodine binding energies on top sites above cation atoms are larger than that above P dimer atom. It is necessary to point out that iodine shifts differently during relaxation from T_{2b} and T_{2b}' sites which are nearest to mixed dimer: it relaxes to the bridge site between cation atoms from T_{2b}'-site nearest to P atom whereas I shifts slightly towards cation of the mixed dimer from T_{2b}-site. The bridge D-site (figure 2b) is found to be unstable because iodine relaxes towards T_1-site.

Table 2. Iodine binding energies (eV) on the mixed-dimer (2×4) structure (figure 2b) for InP and GaP semiconductors.

I sites	T_1	T_1'	T_{2a}	T_{2a}'	T_{2b}	T_{2b}'
I-InP	2.01	1.40	2.28	2.12	2.19	2.25
I-GaP	1.89	1.33	2.18	2.15	2.20	2.23

Finally, we considered I adsorption on the P-rich β2-InP(001)-(2×4) reconstruction. It was found also that the most preferential site for I adsorption is above In atom in the subsurface layer. The binding energy of 1.96 eV was calculated in this case. The analysis of the electron energy spectra and local densities of states shows similar behavior of the electron characteristics upon I adsorption as was found earlier [3, 4]. In particular, the charge transfer of 0.40-0.42e was calculated inside Bader

volumes for the M_1-site on the ζ(4×2) reconstruction and almost the same values was obtained in case of the T_1-site on the mixed dimer (2×4) reconstruction as well.

4. Conclusion

The present total energy calculations using PAW method within DFT confirm the stability of the mixed dimer (2×4) structure on both InP and GaP semiconductors (001) surface in the cation-rich limit. The existence of (2×4) surface structure in the cation-rich limit demonstrates a general tendency in minimization of the surface energy for A^3B^5(001) surfaces. The ζ(4×2) reconstruction has the smallest surface energy among considered surface structures with (4×2) geometry. Comparative study of I adsorption on InP(001) and GaP(001) surfaces with ζ(4×2) and mixed dimer (2×4) reconstructions was performed at the first time. The on-top cation dimer M_1-site was found energetically most favorable for iodine adsorption on ζ(4×2) reconstruction. Our study reveals an ionic mechanism of iodine bonding with the semiconductor substrate irrespective on the surface reconstruction.

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References

[1] Xu Y B, Kernohan E T M, Freeland D J and Ercole A J A C 1998 *Phys. Rev.* B **58** 890
[2] Tereshchenko O E, Lamine D, Lampel G, Lassailly Y, Li X, Paget D and Peretti J 2011 *J. Appl. Phys.* **109** 113708
[3] Bakulin A V, Kulkova S E, Eremeev S V and Tereshchenko O E 2014 *J. Phys. Chem.* C **118** 20097
[4] Bakulin A, Eremeev S, Tereshchenko O, Chulkov E and Kulkova S 2011 *IOP Conf. Ser.: Mater. Sci. Eng.* **23** 012015
[5] Mikolajczyk P and Stankiewicz B 2009 *Cent. Eur. J. Phys.* **7** 279
[6] Mikolajczyk P and Stankiewicz B 2010 *Appl. Surf. Sci.* **256** 4822
[7] Tereshchenko O E, Eremeev S V, Bakulin A V and Kulkova S E 2010 *JETP Letters* **91** 466
[8] Blöchl P E 1994 *Phys. Rev.* B **50** 17953
[9] Kresse G and Joubert J 1999 *Phys. Rev.* B **59** 1758
[10] Kresse G and Furthmüller J 1996 *Phys. Rev.* B **54** 11169
[11] Perdew J P, Burke K and Ernzerhof M 1996 *Phys. Rev. Lett.* **77** 3865
[12] Eglitis R I 2014 *Int. J. Mod. Phys.* B **28** 1430009
[13] Shah G A, Radny M W, Smith P V and Schofield S R 2012 *J. Phys. Chem.* C **116** 6615
[14] Shiraishi K 199 *J. Phys. Soc. Jpn.* **59** 3455
[15] Monkhorst H J, Pak J D 1976 *Phys Rev B* **13** 5188
[16] Bakulin A V, Kulkova S E, Eremeev S V and Tereshchenko O E 2013 *Surf. Sci.* **615** 97
[17] Castleton C W M and Mirbt S 2003 *Phys. Rev.* B **68** 085203
[18] Schmidt W G 2002 *Appl. Phys.* A **75** 89
[19] Yamaguchi K, Takeda Y, Kameda K and Itagaki K 1994 *Mater. Trans.* **35** 596