NAP-2013

Influence of Fluorine and Oxygen Adsorption on the Electronic Properties of the InAs(111)A-(2×2) Surface

A.V. Bakulin[1,*], S.E. Kulkova[1,2], N.A. Valisheva[3]

[1] *Institute of Strength Physics and Materials Science of Siberian Branch Russian Academy of Science, 2/4, Akademichesky pr., 634021 Tomsk, Russia*
[2] *National Research Tomsk State University, 36, Lenina pr., 634050 Tomsk, Russia*
[3] *Rzhanov Institute of Semiconductor Physics, SB RAS, 13, Lavrentyev pr., 630090 Novosibirsk, Russia*

Atomic and electronic structures of the reconstructed InAs(111)A-(2×2) surface are studied within density functional theory. The most stable adsorption positions of oxygen and fluorine on the surface are determined. Our calculations show that oxygen adsorption leads to appearance of electronic states in band gap and the structure of these surface states strongly depends on adsorption geometry. An increase of oxygen concentration and its coadsorption with fluorine leads to substantial structural changes in the surface and subsurface layers due to adsorbate penetration into semiconductor. Evolution of the electronic structure upon oxygen and fluorine adsorption on the reconstructed InAs(111)A-(2×2) surface in dependence on adsorbate geometry is analyzed. It is shown that surface states induced by oxygen adsorption can be partially removed by fluorine, when it forms bonds with the surface indium atoms. The formation of the indium–fluorine or indium–oxygen bonds proceeds due to charge transfer from arsenic atoms to indium ones in the surface layers. The microscopic mechanism of fluorine influence on the interface states at InAs–oxides interface is suggested.

Keywords: Semiconductor, Electronic Structure, Surface States, Adsorption, Oxygen, Fluorine.

PACS numbers: 68.35.bg, 68.43.Bc, 73.20.At

1. INTRODUCTION

The elucidation of the nature of the electronic states in the fundamental band gap at the interface between $A^{III}B^{V}$ semiconductors and an anodic oxide remains a difficult problem because the latter represent a mixture of the semiconductor element oxides with different composition. It was shown in [1] that growth of a thin (10–15 nm) fluorine containing anodic oxide layer on the InAs(111)A surface makes it possible to form an InAs/oxide interface with low surface state density $<5 \times 10^{10}$ cm^{-2} eV^{-1}. A substantial decrease of the density of surface states is also observed as a result of fluorination of the GaAs(001) surface by oxidation in a N_2O–CF_4 plasma [2]. *Ab initio* methods which allow performing calculations of semiconductor surface and its interface structure with oxides can be useful tools for understanding of the nature of these states in the band gap.

Theoretical studies of the halogen adsorption on $A^{III}B^{V}$ surfaces [3, 4] showed that there is a pronounced dependence of the binding energy on the adsorbate geometry. Electron charge density changes substantially not only at cation atoms but also at the nearest arsenic atoms. These results were mainly obtained by studying GaAs surface with the orientations (001). Experimental study of the interaction of oxygen with a polar InAs(001) surface, at a temperature of 140 K in a vacuum, by the method of the anisotropic reflection spectroscopy showed that the process of oxidation depends strongly on surface stoichiometry [5]. It was shown that oxygen predominantly interacts with the In-rich InAs(001)-(4×2) surface. Almost the same conclusion was obtained for the InAs(111) surface in [6].

It is well-known that the most stable reconstruction for the InAs(111)A surface (the letter A marks that the InAs (111) surface is In-terminated) is the (2×2) reconstruction [7]. In our earlier paper [8] we considered oxygen adsorption on InAs(111)A surface and demonstrated the appearance of the oxygen induced electronic states in the fundamental gap. It was also shown that these states can be partially removed by the fluorine coadsorption on the unreconstructed (1×1) surface. Less attention in this paper [8] was paid to the reconstructed InAs(111)A-(2×2) surface and some aspects of the bonding formation due to the increase of both oxygen and fluorine concentration.

In this paper, we present more detailed *ab-initio* study of the evolution of the electronic structure due to oxygen and fluorine coadsorption on the reconstructed InAs(111)A surface in order to get better insight on the mechanism of fluorine influence on the surface states.

2. COMPUTATIONAL DETAILS

The atomic and electronic structure of the InAs(111)A surface was calculated by the method of projected augmented waves [9, 10] implemented in the VASP code [11, 12] using generalized gradient approximation (GGA) [13] for exchange-correlation functional. For simulation of the In-terminated InAs (111) surface a slab model with eight-layers of In and As separated by vacuum region of ~10 Å was used. The bottom surface terminated by arsenic was saturated with pseudo hydrogen atoms with the fractional charge of 0.75 electron, thus, one of the surfaces of the film was a bulk-like. The positions of hydrogen atoms were determined by the energy minimization as in [4]. The theoretical value of the InAs lattice parameter (6.202 Å) obtained

with GGA approximation is somewhat larger than the experimental value (6.050 Å). Note that InAs structure in the [111] direction is represented by the alternation of atomic layers of indium and arsenic, however, indium vacancy occurs in case of the In-terminated reconstructed (2×2) surface. In our calculations, four upper atomic layers from the side of the In-terminated surface were optimized, whereas two layers of indium and arsenic on the opposite side were fixed at bulk values. Atomic positions were relaxed till the forces at the atoms were smaller than 0.025 eV/Å. Integration over the Brillouin zone (BZ) was carried out using Monkhorst–Pack [14] (6×6×1) grid of k-points.
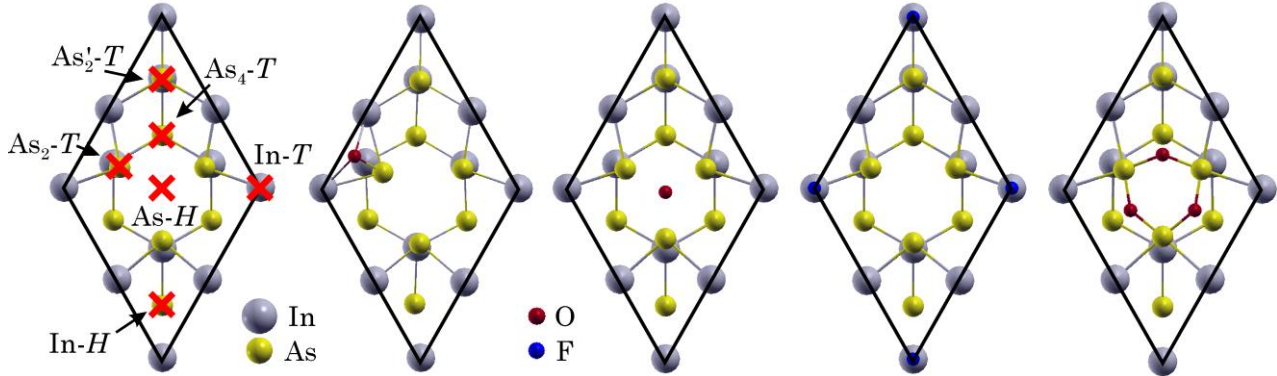
Fig. 1 – Atomic structure of the clean InAs(111)A-(2×2) reconstructed surface and with adsorbate (top view): considered adsorption positions are given by crosses (a); equilibrium structures with oxygen atom initially positioned in As_2-T (b), As-H (c) sites and with fluorine atom in In-T position (d) as well as structure with three oxygen atoms in As-H (e).

The binding energies of oxygen and fluorine with the semiconductor substrate were calculated using the formula

$$E_b = -[E(O/InAs) - E(InAs) - E(O)],$$

where $E(O/InAs)$ and $E(InAs)$ are the total energies of a system with adsorbed oxygen (or fluorine) and a clean surface, respectively, $E(O)$ is the energy of an atom of oxygen (or fluorine), estimated from the calculation of an atom in a cubic cell with the size 10×10×10 Å.

3. RESULTS AND DISCUSSION

The equilibrium atomic structure of reconstructed InAs(111)A-(2×2) surface has trimers of both indium and arsenic atoms and also separate arsenic atom in the surface layer [7]. A main interesting feature of this reconstruction is the location of the In and As atoms within one surface layer since the inward relaxation -91.1 % of the interlayer distance between In and As layers was calculated. This leads to the presence of In vacancy in the surface layer and to a significant lateral shift (~0.4 Å) of neighboring As atoms towards In vacancy.

The binding energies of oxygen atom on InAs(111)A-(2×2) surface were calculated in positions shown in Fig. 1a. It is seen from Table 2 that the most preferential site for oxygen adsorption is on top site above the atoms of an arsenic trimer (As_2-T). Figure 1b shows that the oxygen atom moves towards the nearest indium atoms due to relaxation. Thus, in this site the oxygen atom is bonded both to an arsenic atom and to two indium atoms. The bond lengths of O-As_2 and O-In are 1.93 Å and 2.28 Å, respectively. The binding energy of oxygen on the reconstructed surface is only minor lower (~0.33 eV) than that in the most preferential In-bridge site (between two In atoms) on the unreconstructed (1×1) surface. It is seen also from Table 1 that the binding energies in the In hollow site

(In-H) between three indium atoms and on top site above As atom of the fourth layer from surface (As_4-T) are insignificantly lower in comparison with As_2-T site. The bond length of O-As changes in the range 1.76-1.93 Å for all considered top sites above As atoms. The bond length of O-In is almost the same (1.93 Å) for In top site.

It is known that surface states are absent in the electron energy spectrum of the pure reconstructed InAs(111)A-(2×2) surface but they are occurred in case of (1×1) surface [7, 8]. Our calculations show that oxygen adsorption leads to appearance of the surface states in case of InAs(111)-(2×2) structure (Fig. 2). One can see in this figure that the structure of induced electronic states depends strongly on the oxygen adsorption sites. In spite of small difference in oxygen binding energies in As_2-T and In-H sites in the latter case the density of the surface states is larger (Fig. 2b). One can see in Fig. 2c, that the surface states are mainly located at the BZ edges in case of As-H site but this position is less preferable for oxygen adsorption. It is necessary to point out that the appearance of the surface states in the band gap is not connected with crystal lattice distortion because oxygen is located above surface layer but it is due to charge transfer from surface to electronegative oxygen atom.

It is seen from Fig. 3a that the accumulation of negative charge near oxygen atom takes place whereas there is the depletion region near As atoms. Since In states are almost empty, the formation of O-In bonds is possible due to charge redistribution between As and In surface atoms only. Figure 3b demonstrates the charge depletion region between In surface atoms due to charge transfer to O atom. In case of the oxygen interaction with semiconductor surface the splitting of the electronic states from the top of the bulk valence band (VB) and their partial depletion takes place. This is due to decrease of a number of electrons

in VB with respect to the number of the electronic states in this band because strong charge transfer to oxygen atom as was mentioned above. The analysis of the orbital composition of the states in the fundamental band gap shows their localization on the arsenic atoms in the surface layer and also at oxygen atoms.

The different configurations in case of three adsorbed oxygen atoms on the surface were also considered. It was found that with increasing number of oxygen atoms their adsorption on top site As$_2$-*T* is less preferable (by 1.1 eV) than in the hollow site As-*H*. It is seen from Fig. 2e that the density of the oxygen induced states is significantly less for As-*H* configuration in comparison with As$_2$-*T* one (Fig. 2d). In the former case three oxygen atoms located between arsenic surface atoms, lie almost in the one surface layer together with As and In atoms. The surface states are presented only at the BZ edges and moreover they are shifted to the bottom of the conduction band (CB) and to the VB top. In general, the increase of oxygen concentration leads to increase of surface states. The charge density difference (Fig. 3d) demonstrates the same features which were mentioned above: the accumulation of charge near oxygen atoms and its depletion near As atoms.

Table 1 – Binding energies (in eV) of oxygen and fluorine on InAs(111)A-(2×2)

InAs(001)A-(2×2)	As$_2$-*T*	As-*H*	As'$_2$-*T*	As$_4$-*T*	In-*H*	In-*T*
E_b(O)	5.80	5.10	4.82	5.45	5.59	4.46
E_b(F)	3.50	2.90	3.45	4.01	4.42	4.43
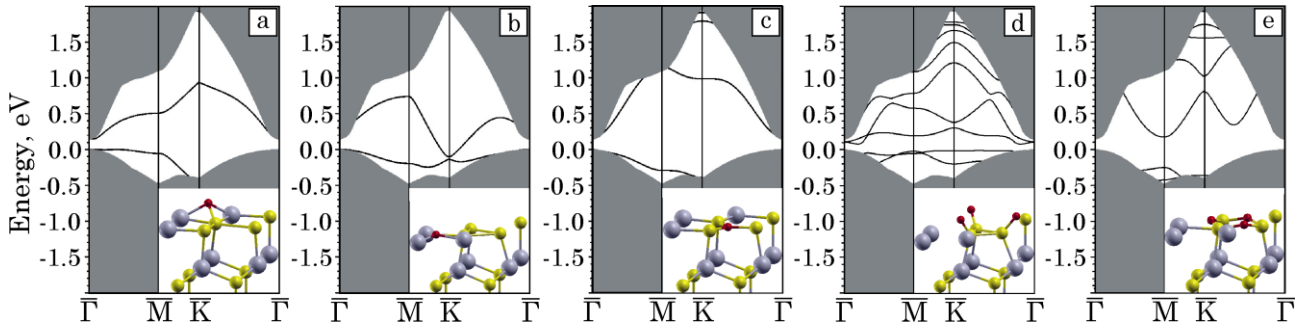
Fig. 2 – The electron energy spectrum of the reconstructed InAs(111)A-(2×2) surface with one O atom adsorbed in As$_2$-*T* (a), In-*H* (b), As-*H* (c) and three O atoms adsorbed in As$_2$-*T* (d) and As-*H* (e). The corresponding atomic structures are shown in inserts to figures. Bulk-projected states are shown by grey color.

In case of fluorine adsorption on the InAs(111)A-(2×2) surface, our calculations reveal that fluorine prefers to interact with indium atoms as on the InAs(001) surface [3]. The binding energies of fluorine in In-*T* and In-*H* sites are almost the same (Table 1). It should be noted that the binding energy of fluorine with surface is lower by ~1.4 eV than that of oxygen in the most preferential site. Furthermore it is larger by ~0.9 eV than the value of fluorine binding energy on unreconstructed (1×1) surface.

The changes in the energy spectrum of InAs(111)A-(2×2) surface as a result of fluorine coadsorption above oxygen atom in the center of indium trimer (In-*H*) is shown in Fig. 4a,b. It is seen that increase of F atoms leads to large splitting of surface states at the $\overline{K}$-point in comparison with only oxygen adsorbed system (Fig. 2b). In case of fluorine molecule adsorption above the oxygen atom it dissociates as shown in insert to Fig. 4b. In general, both configurations are less preferable than those with oxygen atom in In-*H* site and the same number of F atoms adsorbed in In-top sites. It is seen that in case of the adsorption of a single fluorine atom above each indium atom, the surface states are shifted significantly to the CB bottom and VB top and they are disappeared in the band gap (Fig. 4c). Unfortunately, the following increase of F concentration up to three atoms above every In trimer atom leads to the depletion of valence band states and their shift in the band

gap. It should be noted that both adsorbates appreciably affect the positions of surface atoms closest to the adsorption sites. In particular, adsorption of fluorine leads to a shift of indium atoms towards vacuum by 0.55 Å. At the same time oxygen atom located previously 0.32 Å above indium atoms is penetrated into the subsurface layer and is located now 0.47 Å below indium atoms.

It is well known that indium and fluorine form a strong ionic bond. However, indium states in case of InAs(111)A surface are actually unoccupied. A charge of one electron is needed for fluorine in order to fill its *p*-shell and to form a bond with In. This electron can be obtained as a result of the redistribution of charge density between indium and neighboring arsenic, which, on the one hand, leads to weakening the In-As bond and, on the other hand, leads to pulling of indium atoms (bonded to fluorine) towards vacuum. At the same time, oxygen is found to be in the subsurface layer where it tries to form the bonds with arsenic. In turn an increase of fluorine concentration above each In atoms up to three atoms leads to penetration of fluorine into the subsurface layer. In this case only it can form the bond with As atom. This is initial stage of formation of fluorine-containing anodic oxide layer. It is necessary to emphasis that covalent contribution to bonding is increased during adsorbate diffusion into semiconductor whereas chemical bonding has primarily ionic character on surface.
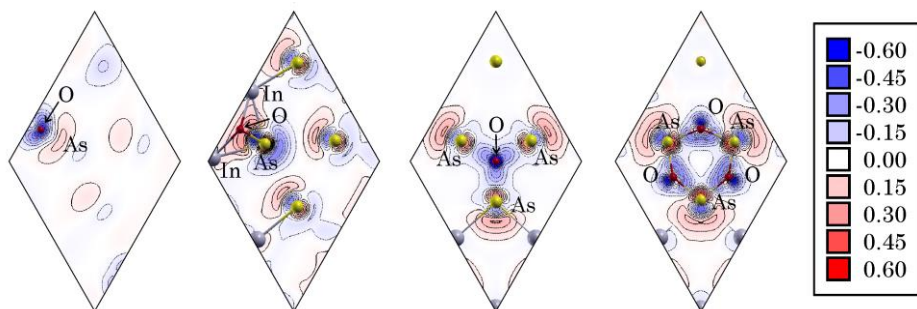
Fig. 3 – Charge density difference ($\Delta\rho = \rho_O + \rho_{InAs} - \rho_{O/InAs}$) for O/InAs(111)-(2×2) system (top view) in case of single oxygen atom adsorption in the As$_2$-*T* site in the plane going through oxygen atom (a) and through As and In surface atoms (b) as well as with one and three oxygen atoms in As$_2$-*H* site (c,d). In the latter cases $\Delta\rho$ is shown in the plane going through O-As bonds.
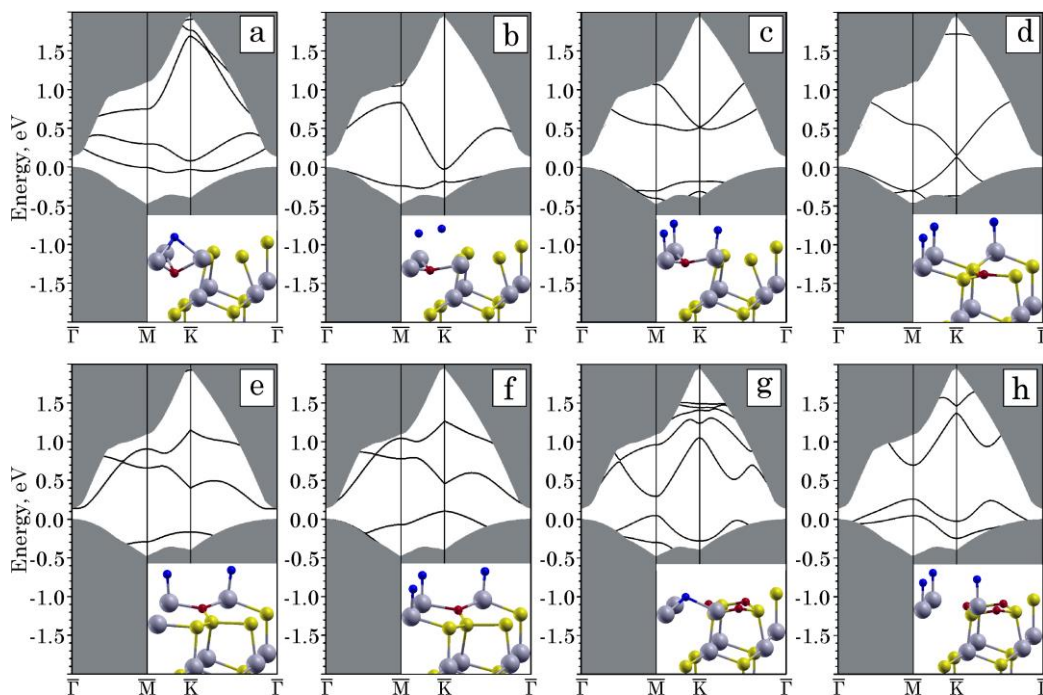
Fig. 4 – The evolution of electron energy spectrum of InAs (111)A-(2×2) due to coadsorption of oxygen and fluorine: a) one F atom above oxygen adsorbed in In-H; b) two F atoms above oxygen adsorbed in In-H; c) three F atoms on top In trimer atoms (In-T) and with oxygen adsorbed in In-H; d) three F atoms on top In trimer atoms (In-T) and with oxygen adsorbed in As-H; e) two F atoms adsorbed on top In atoms near oxygen atom adsorbed in As2-T site; f) the same but with three F atoms in In-T; g) three O atoms in As-H and one F atom in In-H; h) three O atoms in As-H and three F atom in In-T. Bulk-projected states are shown by grey color.

4. CONCLUSION

The investigation of oxygen and fluorine adsorption on the reconstructed InAs (111)A-(2×2) surface was performed by *ab-initio* method within density functional theory. It was shown that oxygen adsorption on semiconductor surface can lead to appearance of the surface states within band gap. The density of surface states strongly depends on oxygen adsorption geometry and its concentration as well. Observed oxygen-induced states are mainly localized on oxygen and arsenic surface atoms. It was shown that on the reconstructed InAs (111)A surface the oxygen induced states can be only partially removed by coadsorption of fluorine. This effect is most pronounced in case of fluorine adsorption above In atoms. An increase of fluorine concentration and its coadsorption with oxy-

gen leads to appreciable structural changes in the surface layers and formation of F–As bonds in additional to In-O and As-O ones. At the same time the formation of In–F bonds on the surface leads to weakening of In-As surface bonds due to charge redistribution between In and As atoms and electron charge transfer to fluorine that allows penetrating oxygen and excess fluorine atoms into semiconductor.

AKNOWLEDGEMENTS

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