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Abstract. The projector augmented-wave method was applied for investigation of oxygen and fluorine atom adsorption on the InSb(111) surface depending on its termination. It was shown that oxygen adsorption leads to appearance of additional surface states in the fundamental gap in case of the In-terminated surface while the density of surface states decreases for the Sb-terminated surface. Fluorine co-adsorption results in partial or complete removal of the surface state and an unpinning of the Fermi level. The increase of fluorine concentration leads to considerable changes of the near-surface-layer structure due to the penetration of both electronegative adsorbates (O and F) into the substrate.

1. Introduction

Semiconductors based on elements of III and V groups are promising materials for various device applications due to their superior electron mobility, as compared to silicon. The progress in manufacturing of devices based on $A^{III}B^{V}$ semiconductors is connected with the development of a special technique, which provides the low density of states (DOS) at insulator−semiconductor interfaces caused by the formation of native oxide on a semiconductor surface [1]. Controlled growth of fluorine-containing anodic oxide layers (FAOL) in different media is one of the ways to modify a semiconductor surface. For example, this method provides low DOS ($<5×10^{10}$ eV^{-1} cm^{-2}) at the interfaces Au/FAOL/InAs(111)A and In_2O_3/SiO_2/FAOL/InAs(111)A [2]. The letter A in $A^{III}B^{V}$(111)A means that the surface terminates by atomic layer of A atoms. In case of GaAs the formation of FAOL/GaAs interface leads to decrease of DOS by 50 times in comparison with the interface formed without fluorine [3]. The complex composition of the FAOL/$A^{III}B^{V}$ interface transition region considerably complicates finding out the microscopic nature of the interface states.

The investigations of the FAOL/InAs(111)A interface morphology carried out earlier by the high-resolution electron microscopy, which showed the formation of a well-ordered crystalline interface and a transition region of four to six atomic layers thickness [2]. Thus, the structure of the semiconductor at the interface is rather ideal than reconstructed one. In this connection *ab-initio* methods, which allow to understand the origin of the interface states and the chemical bonding of an adsorbate on a semiconductor surface, are actively used. Earlier the initial stage of formation of interface between FAOL and InAs(111)A, GaAs(111)A substrates was investigated in [4,5]. It was shown that the fluorination of indium and arsenic oxides, forming the native oxide layers on the (111) surface leads to radical changes of the atomic structures of the subsurface region. The oxygen-induced surface states are complete or partial removed from the band gap if fluorine forms bonds with the

indium atoms involved in an interaction with oxygen. At the same time, the question of generality of this surface passivation mechanism for $A^{III}B^{V}$ semiconductors remains under debate. In the present work, in order to understand the FAOL/InSb interface formation mechanism, we study the influence of oxygen and fluorine atom adsorption and their co-adsorption, and also fluorine concentration (up to three atoms) on the electron properties of the InSb(111) unreconstructed surface.

2. Method of calculation

The atomic and electronic structures of the InSb(111) unreconstructed surface were calculated using the projector augmented-wave [6,7] method (PAW) implemented in the VASP code. The generalized gradient approximation within PBE form [8] for the exchange-correlation functional, as well as the hybrid functional HSE06 [9] was employed. The surface was simulated by repeated slabs separated by a vacuum region of ~10 Å in thickness between them. The slab consists of eight atomic layers of a semiconductor and a layer of pseudo-hydrogen atoms with fractional number of valence electrons. One surface was saturated with pseudo-hydrogen atoms to passivate dangling bonds; therefore, one film side was a bulk-like. On the opposite film side fluorine and oxygen atom adsorption was considered. Two indium and antimony layers from the side of the hydrogen-saturated film were fixed at bulk positions, whereas atoms of other layers can relax during the structure optimization. The relaxation of atomic positions was carried out until the forces at atoms ~0.01 eV/Å. A plane-wave cutoff of 500 eV was used throughout. Integration over the Brillouin zone was carried out using a grid of k-points (7×7×1) obtained according to the Monkhorst-Pack scheme. Since the (111) surface is a polar one, dipole corrections were taken into account. Electronic states were considered to be surface states if virtually all of their charge was contained within the top few surface layers, whereas bulk states have most of their charge confined to deeper layers. The theoretical lattice parameters of bulk InSb (6.652 Å), obtained within the PAW-PBE approximation, are slightly larger than the experimental ones, 6.479 Å [10]. The binding energies of oxygen and fluorine atoms with the InSb substrate were calculated using the equation (2) from [4].

3. Results and discussion

The calculation of the atomic structure of InSb(111)-(1×1) unreconstructed surface demonstrates the inward relaxation of upper atomic layer irrespective of surface termination. The relaxation of the first interlayer distance Δ_{12} is equal to -5.5% in case of the In-terminated InSb(111)A surface, whereas it is -2.1% for InSb(111)B surface. It should be noted that smaller values in magnitude (-3.8% and -5.4%) were obtained for InAs(111)A and GaAs(111)A surfaces [4]. This indicates a shorter distance between cation and arsenic layers on the surface, which is due to the decrease of surface cation coordination. Our calculations show that the relaxation of interlayer distances has oscillation character and decreases into the film depth. Electronic structure calculations demonstrate that in case of clean surfaces there are surface states in the fundamental band gap, which are pinning the Fermi level (Figure 1). These
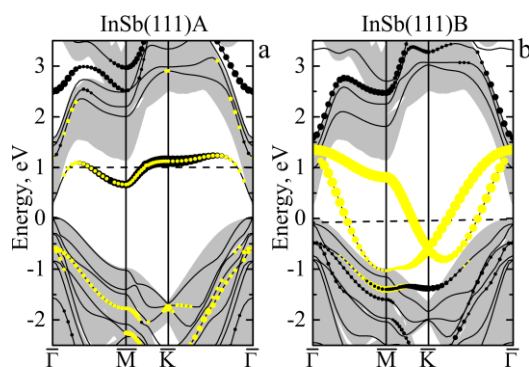
Figure 1. Electronic band structure along high-symmetry directions of Brillouin zone for InSb(111) with the In (a) and Sb (b) terminations.
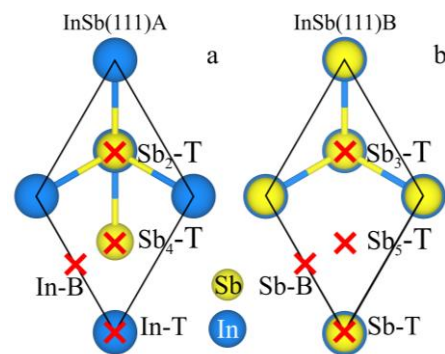
Figure 2. Atomic structure of the InSb(111) surface with the In (a) and Sb (b) terminations and the adsorbate positions (crosses).

states spread over the whole two-dimensional Brillouin zone. On the In-termination the surface states are conditioned by surface In and subsurface Sb atoms while in case of the Sb-termination they are connected with Sb surface atoms. In both cases these surface states are formed by the dangling *p*-orbitals. It should be noted that the black and yellow circles in Figure 1 are indium and antimony surface states, and their size is proportional to the localization degree of electronic states on the surface atoms. We remind that the electronic structure of the surface was calculated within HSE06 method and the band gap was found to be 0.254 eV, which agrees with the experimental value of 0.235 eV [11]. However, a band gap value of zero was obtained within the PAW-PBE calculation.

The adsorption of oxygen and fluorine atoms was considered at high-symmetry sites shown in Figure 2. The binding energies on both surfaces are presented in Table 1. It is seen that fluorine has the largest binding energy in the top T-site above the indium surface atom, whereas oxygen prefers to be adsorbed in the bridge B-site on both surface terminations. The preference of the latter site is connected with the fact that oxygen has bonds with two In surface atoms (the bond length is ~2.40 Å) and additionally with Sb atom of the subsurface layer (the bond length is ~2.06 Å). Note that the similar trend was observed earlier on InAs(111)A and GaAs(111)A surfaces [4]. It is interesting that the oxygen binding energies with the substrate change slightly when it is adsorbed at the sites above antimony atoms of the second (third) and fourth (fifth) layers on the In(Sb)-terminated InSb(111) surface. In all cases the Bader charge of oxygen atom is larger than that of fluorine. It is seen that the interaction of both adsorbates with the surface has ionic character irrespective of its termination.

Table 1. Binding energies (in eV) and the Bader charges (in *e*, in brackets) of F and O adatoms on the both InSb(111)-(1×1) surface terminations.

| Surface	Adatom	In(Sb)-B	In(Sb)-T	$Sb_2(Sb_3)$-T	$Sb_4(Sb_5)$-T
InSb(111)A	F	4.54 (0.76)	5.14 (0.59)	4.22 (0.75)	4.42 (0.79)
	O	5.93 (1.04)	4.35 (0.65)	4.98 (1.02)	4.84 (1.00)
InSb(111)B	O	6.05 (1.01)	5.30 (0.70)	5.78 (0.97)	5.81 (0.97)

Oxygen adsorption on both terminations of InSb(111) surface results in significant changes of surface states (Figure 3). In case of the In-terminated surface the oxygen adsorption leads to the appearance of additional states in the band gap and, as it can be seen from Figures 3a and 3b, the structure of these surface states depends strongly on an adsorbate site on the surface. The opposite trend is observed on the Sb-terminated surface (Figures 3c and 3d). In this case the surface states are unoccupied and they are significantly shifted towards the conduction band due to adsorption of oxygen. As the result the Fermi level crosses the states which are mainly conditioned by bulk-like atoms. Such changes of the surface electronic structure at the first step of oxidation are in line with experimental observations: density of states at the interface between InSb and native oxide is smaller in case of the Sb-terminated surface in comparison with the In-terminated one [12].
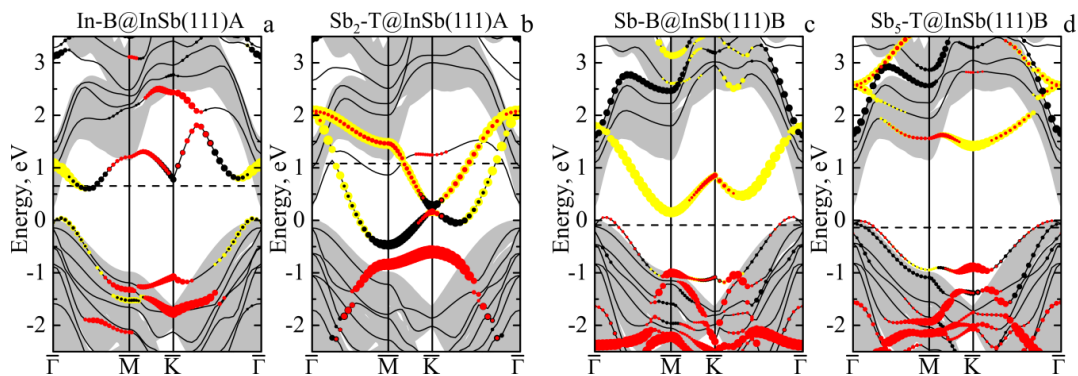
Figure 3. Electronic band structure of the InSb(111) surfaces with oxygen adsorbed in In-B (a) and Sb_2-T (b) sites on the In-termination as well as with oxygen adsorbed in Sb-B (c) and Sb_5-T (d) sites on the Sb-terminated surface.

Finally, let's discuss the changes in the surface electronic structure of InSb(111)A due to oxygen and fluorine co-adsorption. It is seen in Figure 4a that fluorine co-adsorption leads to decrease of the density of surface states in the band gap. The oxygen-induced surface states are practically complete removed by the co-adsorption of three F atoms (Figure 4b): only the states near the band gap edges remain. In this case oxygen and two fluorine atoms lie in the subsurface region (Figure 4c) that can be considered as initial stage of interface formation between InSb substrate and fluorine-containing anodic oxide. The increase of fluorine concentration at more than three atoms per (1×1) surface cell leads to the appearance of additional states near top of the valence band due to their partial depletion.
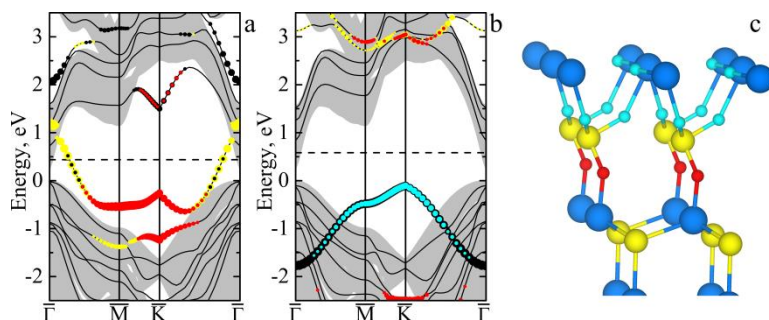
Figure 4. Electronic band structure of the InSb(111)A surfaces with oxygen adsorbed in the In-B site and with one (a) and three (b) fluorine atoms as well as corresponding atomic structure (c).

4. Conclusion

The influence of fluorine and oxygen adsorption and their co-adsorption on the surface states in the band gap was studied on both In- and Sb-terminated InSb(111) surface. It was shown that in former case oxygen results in appearance of additional surface states, while density of surface states in the gap decreases sharply in case of the Sb-termination. The oxygen-induced surface states on InSb(111)A are complete or partial removed from the band gap by fluorine co-adsorption if it forms bonds with the indium atoms involved in an interaction with oxygen. The fluorine co-adsorption and an increase of its concentration up to three atoms result in significant structural changes in the subsurface region due to the penetration of both oxygen and fluorine atoms into substrate that leads to breaking of semiconductor bonds in the near-surface region.

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