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Adsorption of potassium on the surface of $Al_{0.5}Ga_{0.5}N(0001)$

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The calculation for the adsorption of potassium atoms on the $Al_{0.5}Ga_{0.5}N(0001)$ surface was performed using the density functional method. The 2D layer of $Al_{0.5}Ga_{0.5}N$ was modeled by the $Al_{0.5}Ga_{0.5}N(0001)$ $2\times2\times2$ supercell containing 10 bilayers of $Al_{0.5}Ga_{0.5}N$. On the relaxed $Al_{0.5}Ga_{0.5}N(0001)$ surface, the Ga atoms are located above the Al atoms. It is shown that the adsorption of K atoms at a coverage of 0.25 monolayers is preferable in the bridge position either between the surface Ga atoms or between the surface N atoms. The adsorption of potassium atoms forms a surface states band, the electron density of which is localized near the Fermi level.

Keywords: AlGaN, potassium, adsorption, electron structure.

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1. Introduction

Semiconductor devices based on group III nitrides are currently being used widely. Materials based on AlGaN compounds of various stoichiometries deserve a special mention here. The produced semiconductor devices offer fine thermal performance, which provides an opportunity to use them in the design of high-power transistors, microwave electronics, solar-blind photodiodes, biosensors, etc. [1–4]. One may adjust the electronic properties of AlGaN and expand the scope of its application by altering its stoichiometry. Deposition of alkali metal atoms onto the AlGaN surface changes its state and electronic properties. This should make it possible to produce various sensors and use the $Al_{0.5}Ga_{0.5}N(0001)$ surface with a sputtered adsorbate as a catalyst.

The adsorption of alkali metal atoms on the $Al_{0.5}Ga_{0.5}N(0001)$ surface has been poorly studied. The effect of adsorbed cesium atoms on the electronic structure of the $Al_{0.5}Ga_{0.5}N(0001)$ surface has been calculated earlier in [5–8], and the optimal positions of adsorbed atoms have been determined. Four types of Cs coverage have been analyzed: 0.25, 0.50, 0.75, and 1.0 monolayers (ML) of cesium. The authors of [5] have calculated the adsorption of Cs atoms on the surface of a 2D $Al_{0.5}Ga_{0.5}N(0001)$ layer doped with Mg and consisting of 6 bilayers of $Al_{0.5}Ga_{0.5}N$. Cesium adsorption at the T4 site (above an N atom) is favored: with a coverage of 0.25 ML of cesium, the adsorption energy is $E_{ads} = -1.251$ eV; with a coverage of 1.0 ML, E_{ads} decreases to -0.979 eV. The authors of [6] have calculated the adsorption of Cs atoms on the surface of a 2D $Al_{0.5}Ga_{0.5}N(0001)$ layer consisting of 6 bilayers of $Al_{0.5}Ga_{0.5}N$. Cesium adsorption at a coverage of 0.25 ML is virtually independent of the adsorption site, and E_{ads} is -1.59 eV. With a coverage of 1.0 ML, Cs adsorption is favored at site T4 with $E_{ads} = -2.92$ eV. The adsorption of Cs atoms on the surface of a 2D *p*-type $Al_{0.5}Ga_{0.5}N(0001)$ layer consisting of 6 bilayers of $Al_{0.5}Ga_{0.5}N$ has been calculated in [7]. The adsorption sites of Cs atoms and the E_{ads} values were the same as in [5]; the joint adsorption of Cs and O atoms has also been examined. Cesium adsorption at a coverage of 1 ML is favored at the bridge site between N atoms (with $E_{ads} = -2.636$ eV). The authors of [8] have calculated the adsorption of Cs atoms on the surface of $Al_{0.5}Ga_{0.5}N$ nanowires consisting of 6 $Al_{0.5}Ga_{0.5}N$ hexagons. It has been demonstrated that the adsorption of Cs is favored around the bridge site between N atoms or at the bridge site between N and Al atoms. The adsorption energy has been estimated at -1.55 and -1.20 eV for a coverage of 0.25 and 1.0 ML of cesium, respectively. The total and partial densities of states for the surface layer and the inner hexgonal $Al_{0.5}Ga_{0.5}N$ have also been calculated. It has been demonstrated that Cs adsorption leads to surface metallization. The possibility of fabrication of ultraviolet photocathodes based on $Al_{0.5}Ga_{0.5}N$ activated by the joint adsorption of cesium and oxygen has been revealed in [7].

The adsorption of other alkali metal atoms (Li, Na, K, Rb) on the surface of a 2D $Al_{0.5}Ga_{0.5}N(0001)$ layer has not been calculated yet. In the present study, we examine the submonolayer adsorption of potassium atoms on the surface of a two-dimensional $Al_{0.5}Ga_{0.5}N(0001)$ layer via quantum mechanical modeling with the aim of identifying the most energetically favorable adsorption sites and changes in the electronic properties of the surface.

2. Calculation details

Calculations were performed for a 2D $Al_{0.5}Ga_{0.5}N(0001)$ layer with adsorbed potassium. This $Al_{0.5}Ga_{0.5}N(0001)$ layer was modeled as a 10-layer film consisting of $Al_{0.5}Ga_{0.5}N$ bilayers. The surface cell consisted of two Ga

and Al atoms positioned opposite each other and N atoms located above them. Only the top four $Al_{0.5}Ga_{0.5}N$ bilayers were subjected to relaxation. The position of the remaining $Al_{0.5}Ga_{0.5}N$ bilayers was fixed to simulate the bulk of $Al_{0.5}Ga_{0.5}N$. One K atom corresponds to four surface atoms. The adsorption of K atoms was calculated for the following highly symmetric adsorption sites: above the surface atoms of Al, Ga, and N (T_{Al}, T_{Ga}, and T_N, respectively); the hollow site; and the bridge site between Ga atoms (B_{Ga}), N atoms (B_N), and Al and Ga atoms (B_{AlGa}). K atoms could migrate to the calculated local minimum. Ab initio density functional theory calculations were performed in the Quantum Espresso [9] using the exchange-correlation functional in the local density approximation [10]. The supercell parameters were relaxed up to a point where the moduli of forces became $< 10^{-4}$ *Ry*/Bohr.

3. Calculation results

Reconstruction of the clean surface of the relaxed 2D $Al_{0.5}Ga_{0.5}N(0001)$ layer was observed: surface Ga atoms are located 0.78 Å above the surface Al atoms, which matches qualitatively the data for $Al_{0.125}Ga_{0.875}N(0001)$ [11]. The distance between Al atoms relative to the plane of N atoms in the surface layer is 0.28 Å. In the surface $Al_{0.5}Ga_{0.5}N$ bilayer, Ga atoms are raised by 0.11 Å above the Al atoms (Figure 1, *a*).

A band of surface states is formed (primarily by N 2*p* and Ga 4*sp* electrons with a significantly smaller contribution from Al 3*sp* electrons) at the Fermi level (E_F), which is indicative of surface metallization. The peaks of surface states are located at the following energies: −0.87, −0.66, and 0.02 eV (Figure 1, *b*). The valence band is formed primarily by N 2*p* electrons. The gap between the valence band maximum and the bottom of the band of surface states (E_1) is 0.40 eV (Figure 1, *b*). The density of surface states for the subsurface layer (S-1) decreases sharply (Figure 1, *c*), while E_1 increases slightly to 0.53 eV. A wide band gap (2.84 eV) is seen for the fourth layer from the surface (S-4; Figure 1, *d*). The valence band assumes a shape characteristic of $Al_{0.5}Ga_{0.5}N$ with two maxima located at the energies of 1.5 and 5.6 eV relative to the maximum of the valence band [12].

Adsorption energy E_{ads} of K atoms on the relaxed $Al_{0.5}Ga_{0.5}N$ surface for energetically stable adsorption sites of K atoms was calculated using the following formula:

$$E_{ads} = (E_{K/AlGaN} - E_{AlGaN} - E_K), \qquad (1)$$

where $E_{K/AGalN}$ and E_{AlGaN} are the total surface energies with and without adsorbed K and E_K is the total energy of a K atom. If E_{ads} is negative, adsorption is an exothermic chemical process and the adsorption system is stable. The distance between an adsorbed K atom and the plane of N atoms in the surface layer was also determined. Following relaxation of the 2D $Al_{0.5}Ga_{0.5}N(0001)$ layer, not all symmetric points of the adsorption sites match the local

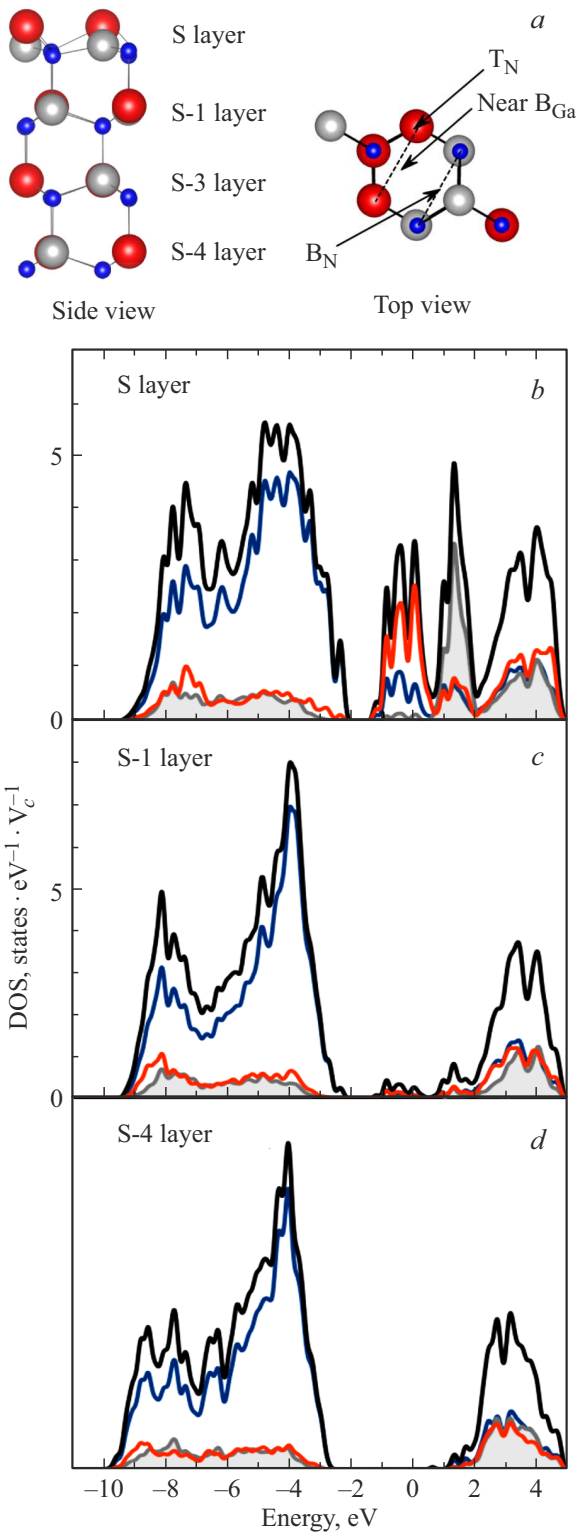

Figure 1. Structure of a 2D $Al_{0.5}Ga_{0.5}N(0001)$ layer (*a*): side view and top view. Red sphere — Ga atom, gray sphere — Al atom, and blue sphere — N atom. Arrows indicate energetically stable sites of adsorption of K atoms. Calculated total density of states of the 2D $Al_{0.5}Ga_{0.5}N(0001)$ layer for layers S (*b*), S-1 (*c*), and S-4 (*d*). $E_F = 0$ eV. V_c is the lattice cell volume. Total density of states — black, N — blue, Al — gray (fill), and Ga — red.

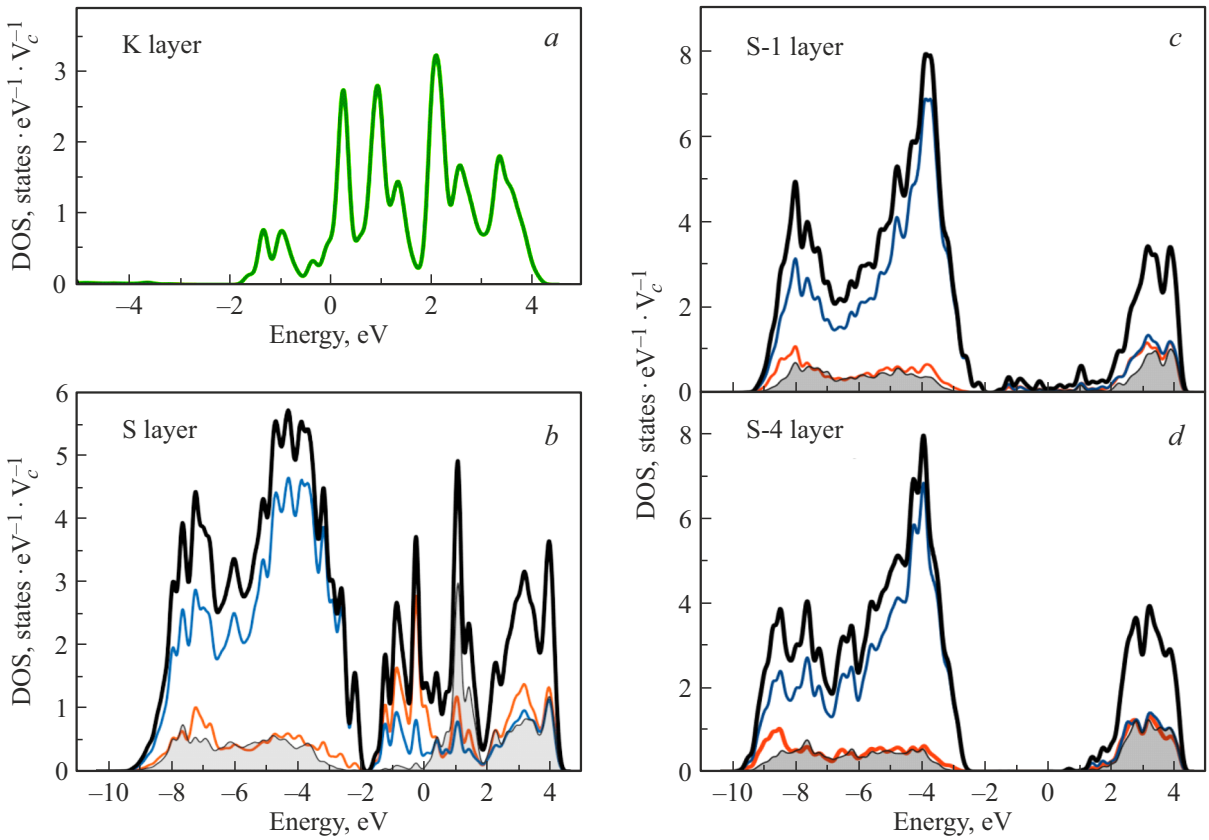

Figure 2. Calculated density of states of the 2D $Al_{0.5}Ga_{0.5}N(0001)$ layer with adsorbed K. Total density of states for the layer of K (*a*) and layers S (*b*), S-1 (*c*), and S-4 (*d*) of $Al_{0.5}Ga_{0.5}N(0001)$. $E_F = 0$ eV. V_c is the lattice cell volume. Total density of states — black, N — blue, Al — gray (fill), Ga — red, and K — green.

minima of the system, as in the case of Cs adsorption on GaN(0001) [13]. Site B_{Al} is close to B_{Ga} in the calculated cell: the difference is just 0.03 Å. The actual position of potassium adsorption ($NearB_{Ga}$) is shifted relative to the B_{Ga} site by 0.098 Å toward the hollow site (Figure 1, *a*). The K adsorption energy is −1.48 eV. A slightly lower value of the K adsorption energy (−1.42 eV) was determined for site B_N. Site T_N with $E_{ads} = -1.30$ eV is also energetically stable. The obtained adsorption energies of K atoms on $Al_{0.5}Ga_{0.5}N$ are close to the values determined for the adsorption of Cs atoms [5–8]. It was demonstrated in [5,6] that the adsorption of Cs at site T_N on the surface of a 2D $Al_{0.5}Ga_{0.5}N(0001)$ layer is preferable. In the present study, the adsorption of K atoms at site T_N was found to be less probable than at site $NearB_{Ga}$. This difference may be attributed to the fact that a K atom is smaller than a Cs atom, which allows K atoms to occupy other sites on the surface of the 2D $Al_{0.5}Ga_{0.5}N(0001)$ layer.

The adsorption of K atoms at site $NearB_{Ga}$ leads to the formation of a band of surface states with two clearly defined maxima below E_F: −1.30 and −0.92 eV (Figure 2, *a*). A surface band with a maximum at 0.28 eV is also found at E_F. The band of surface states of K is formed from hybridized 4*sp* states. The peaks of surface states in the S layer shift toward lower energies: −1.32, −0.99, and −0.33 eV. The gap between the valence band maximum and the bottom of the surface state band vanishes for theS and S-1 layers (Figs. 2, *b* and *c*). The density of surface states for the subsurface layer (S-1) decreases sharply (Figure 2, *c*). The influence of the adsorbed layer of K atoms on the electronic structure of the 2D $Al_{0.5}Ga_{0.5}N(0001)$ layer is virtually nonexistent already at the S-3 layer. A wide band gap (2.75 eV) is seen for the fourth layer from the surface (S-4; Figure 2, *d*). The adsorption of K does not affect the shape of the valence band of $Al_{0.5}Ga_{0.5}N(0001)$. The authors of [5–7] have reported the results of calculations of just the total density of states, which is only slightly influenced by the adsorbate in a way that depends on the thickness of the 2D $Al_{0.5}Ga_{0.5}N$ layer. Study [8] is the only one where the influence of adsorbed Cs on the surface layer of a $Al_{0.5}Ga_{0.5}N$ nanowire was discussed. The reported results are qualitatively consistent with the data obtained in the present study: the adsorption of Cs or K leads to a shift of the surface states of $Al_{0.5}Ga_{0.5}N$ toward lower energies, and a band of surface states of Cs or K forms near E_F.

Adsorbed K interacts with the $Al_{0.5}Ga_{0.5}N(0001)$ surface via a chemical bond formed between the valence electrons of Ga and K. The electron density in the region of the bond

between Ga atoms in the bridge position increases, while the electron density near a K atom decreases accordingly.

4. Conclusion

It was demonstrated that surface Ga atoms on a clean relaxed $Al_{0.5}Ga_{0.5}N(0001)$ surface are shifted upward relative to the surface Al atoms by 0.78 Å. A band of surface states is formed (primarily by N 2*p* and Ga 4*sp* electrons with a significantly smaller contribution from Al 3*sp* electrons) at the Fermi level, which is indicative of surface metallization. It was found that a submonolayer coverage of K atoms on the surface of a 2D $Al_{0.5}Ga_{0.5}N(0001)$ layer alters the electronic structure of the surface and near-surface $Al_{0.5}Ga_{0.5}N$ bilayers. The adsorption of K atoms leads to the formation of a potassium band of surface states localized near E_F. Potassium atoms are adsorbed near the bridge site between Ga atoms or at the bridge site between N atoms. The corresponding adsorption energies differ by several hundredths of an electronvolt.

Conflict of interest

The author declares that he has no conflict of interest.

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