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Electronic structure of the valence band of gallium nitride during sodium adsorption

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The electronic structure of the Na/GaN interface was studied using synchrotron radiation photoelectron spectroscopy in the photon energy range of 75−770 eV. To determine the physical properties of the GaN surface upon Na adsorption, the density of states was calculated using the density functional theory. The 2D GaN layer was modeled by a GaN(0001) $2 \times 2 \times 2$ supercell containing 10 GaN bilayers. It was shown that the adsorption of Na atoms in the hollow position and over the surface N atoms is preferable, and the adsorption energies of sodium atoms are -1.96 and -1.93 eV, respectively. It was found that Na adsorption leads to the formation of surface states whose electron density is localized near the Fermi level.

Keywords: GaN, sodium, adsorption, photoelectron spectroscopy, density functional theory.

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1. Introduction

Intensive studies of gallium nitride are associated with improved quality of epitaxial layers and increased availability of substrates. The unique physicochemical properties, such as wide and direct band gap, high electron mobility, excellent thermal conductivity and high breakdown voltage, make GaN a promising candidate for various electronic and optoelectronic devices, including high-power and high-frequency applications [1,2]. Also, this semiconductor has high chemical and thermal resistance, which allows electronic equipment based on it to operate in extreme environments. Proper device operation depends on the structure, properties and quality of the surface. The contact between the metal and the semiconductor, which can exhibit different electrical properties, also plays a key role.

The electronic structure of GaN surface has been widely studied in many aspects. Studies of the electronic and photoemission properties of GaN(0001) surface in case of alkali metal adsorption have received much attention [3–6]. There are a large number of calculations of the GaN surface and adsorption of various chemical elements, including alkali metals, which are referenced in the detailed review [7]. The existence of a zone of surface states at the Fermi level is shown in Refs. [8–11]. The adsorption of sodium atoms at coatings less than 1/8 monolayer (ML) on the surface of a hexagonal g-GaN monolayer has been calculated in Ref. [12]. It was shown that the bond energy (E_b) decreases with the increase of sodium coverage, and at 1/8 ML coverage E_b equals -1.04 eV, and a zone of Na states is located at the Fermi level. The adsorption of sodium atoms on the end surface of a nanowire composed of two GaN bilayers was studied in Ref. [13]. The adsorption of Na atom is preferred at the hollow position in the center of the nanowire, and the bond energy is -1.19 eV. A zone of Na states at the Fermi level is also observed, which is attributable to the hybridization of Ga $4p$, N $2p$, and Na $2p$ orbitals. The calculation performed in Ref. [14] showed that adsorption of alkali metals, including Na, on the surface of g-GaN leads to an improvement in the adsorption properties of g-GaN, and it can be applied to the development of simple gas sensors.

In this paper we set a task to study for the first time the effect of Na atoms adsorption on the valence band of GaN(0001) by photoelectron spectroscopy using synchrotron radiation, and to calculate the adsorption of Na atoms on the GaN(0001) surface using the density functional method.

2. Experimental setup and receiving of samples

GaN samples were epitaxially grown using Veeco GEN200 industrial unit by the molecular beam epitaxy method with plasma-assisted activation of nitrogen (PA MBE). A GaN/c-Al_2O_3 template (thickness $\sim 2\,\mu$m) grown using the metal-organic chemical vapor deposition method was used as the substrate. The virtual substrate was pre-degreased to continue growth using the PA MBE method. The template was nitridized immediately before growth at substrate temperature of $T_S = 870$ K for 60 min.

A well-established purification procedure consisting of a special Ga deposition procedure was then applied [15]. Growth was carried out at constant substrate temperature $T_S = 960\,K$ and fluxes of gallium $F_{Ga} \approx 0.25\,\mu m/h$ and nitrogen $F_N \approx 0.05\,\mu m/h$. The carrier concentration was $n \approx 2 \cdot 10^{17}\,sm^{-3}$ based on the results of the Hall effect measurement at room temperature. The thickness of the obtained GaN epitaxial layers was $\sim 200\,nm$.

Photoemission studies were conducted in Russian-German BESSY II synchrotron line (Berlin, Germany) using photoelectron spectroscopy (PES). The photon energies ranged from 75 to 770 eV. Studies were conducted *in situ* in ultrahigh vacuum of $5 \cdot 10^{-10}$ Torr at room temperature. The samples were pre-annealed at $\sim 870\,K$. Minor amounts of oxygen O 1*s* and carbon C 1*s* were recorded. Atomically pure sodium was sputtered stepwise onto a clean sample surface from a standard source. The spectra are normalized to energy relative to the Fermi level E_F. For all the photoelectron spectra shown, the background was subtracted using the Shirley method [16].

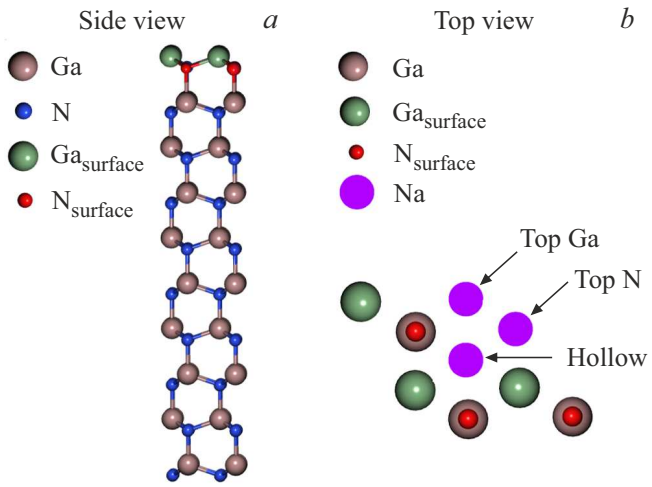

Figure 1. Scheme of the 2D layer of GaN(0001): *a* — side view; *b* — top view. Locations of adsorption of Na atoms on a 2D layer of GaN. Blue ball is N atom, brown ball is Ga atom, green ball is Ga surface atom, red ball is N surface atom, purple ball is Na atom.

3. Calculation details

Theoretical calculations have been carried out within the framework of density functional theory (DFT) implemented in the QUANTUM ESPRESSO [17] package using the exchange-correlation functional described in the local density approximation (LDA — local density approximation) in the form of Perdew-Zunger (PZ) interpolation [18]. Gallium nitride (GaN) has a wurtzite structure with the following lattice parameters: $a = b = 3.219\,Å$ and $c = 5.240\,Å$. A supercell (0001) $2 \times 2 \times 2$ consisting of 10 bilayers of GaN was used in calculations (see Figure 1). One Na atom is accounted for by 4 surface Ga atoms. The nitrogen atom bonds of the GaN lower bilayer were saturated with pseudo hydrogen atoms. The vacuum gap between the 2D layers was 18 Å to avoid the influence of parasitic electric fields. The kinetic energy constraint and charge density constraint were chosen to be 39 and 350 Ry, respectively. Only the top GaN bilayer was subjected to relaxation. Relaxation of the supercell parameters was performed until the moduli of the forces were smaller than 10^{-7} Ry/Bohr.

4. Results and discussion

4.1. Electronic structure

The adsorption energy (E_{ads}) of sodium adatoms at three positions: on top of the Ga atom (top Ga), on top of the N atom (top N), and in the hollow position (hollow) was calculated (see Figure 1, *b*) using the following formula:

$$E_{ads} = (E_{GaN\_Na} - E_{GaN} - E_{Na}), \qquad (1)$$

where E_{GaN_Na} and E_{GaN} are the total energies with and without adsorbed sodium, E_{Na} is the total energy of the sodium atom. The bridge positions between Ga (N) atoms are unstable. The highest adsorption energy, which corresponds to the preferred adsorption site of Na, is obtained for the hollow position: $E_{ads} = -1.96\,eV$, a slightly smaller $E_{ads} = -1.93\,eV$ is obtained for the position above the N atom, and an even smaller value $E_{ads} = -1.68\,eV$ is obtained for the position above the Ga atom. The difference from the values of E_{ads} obtained in Refs. [12,13] is attributable to the different 2D models of the GaN layers. The distance between the Na atom and the plane of surface Ga atoms is 2.38 Å in the case of adsorption at the hollow position. A slight reconstruction of the GaN surface induced by the adsorption of Na atoms due to the interaction of the valence electrons of the adsorption system is observed: the surface S atoms of the GaN bilayer are shifted upward by 0.15 Å relative to the S-1 of the GaN bilayer. When sodium atoms adsorb over a nitrogen atom, the distance between the Na atom and the plane of surface Ga atoms is 2.38 Å. The S surface atoms of the GaN bilayer shift upward by 0.14 Å relative to S-1 bilayer GaN.

Figure 2 shows the results of electron density calculation of relaxed pure GaN(0001) surface for the surface S (Figure 2, *a*–*c*), second S-1 (Figure 2, *d*) and sixth S-5 bilayers from GaN surface (Figure 3, *e*). The valence band S-5 of the GaN bilayer corresponds to the valence band of the GaN crystal. The band gap width is $\sim 2.3\,eV$. The valence band is formed with a predominant contribution of N 2*p* states and Ga 4*s* and Ga 4*p* states with two maxima at energies $-3.4\,eV$ and $-8.0\,eV$. The partial densities of localized states of the surface nitrogen and gallium atoms, respectively, are presented in Figure 2, *a* and 2, *b*. Surface metallization is indicated by the presence of a narrow peak at the Fermi (E_F) level of the surface states zone, which is formed mainly by Ga 4*p* states. There is also a peak of

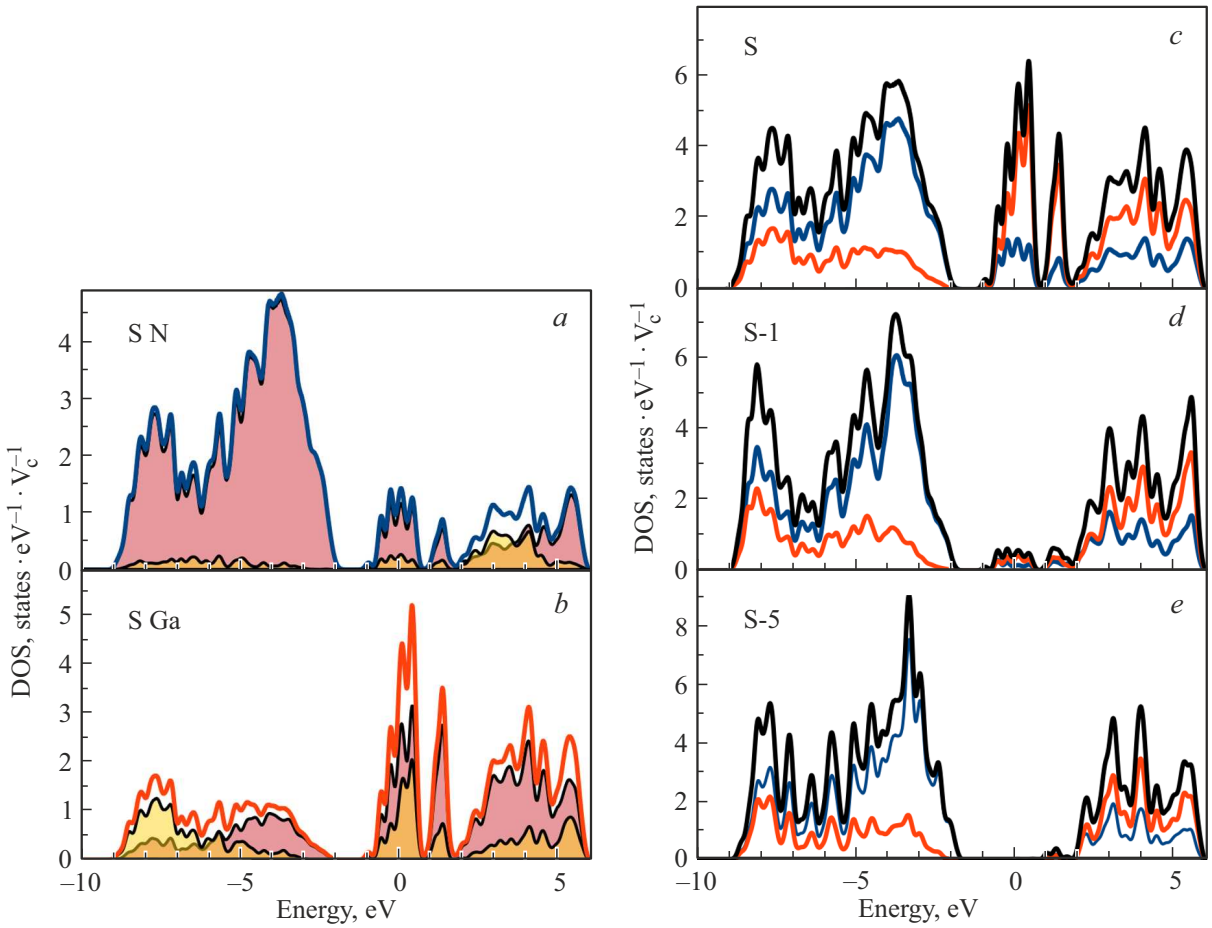

Figure 2. Calculated total and partial densities of states of the 2D layer of GaN(0001). Partial densities of states of N (a) and Ga (b) for the surface (S) bilayer GaN. Total and partial densities of states for S (c), S-1 (d) and S-5 (e) GaN bilayers. V_c — lattice cell volume. Total density of states — black color, N — blue color, N 2s — yellow color with filling, N 2p — brick color with fill, Ga — red color, Ga 4p — brown fill, and Ga 4s — yellow fill.

N 2p states at E_F, which reflects the fact that in the GaN bilayer, the nitrogen atoms are located 0.75 Å below the Ga atoms, and there is a pseudo-gap with a width of 0.62 eV. The density of surface electronic states decreases sharply with distance from the surface, so that for the S-1 bilayer it is smaller by a factor of almost 10 times than for the surface S bilayer. The electronic structure of the S-5 bilayer corresponds to the electronic structure of the GaN crystal (Figure 2, e). Similar changes in the density of electronic states for layers as they move away from the surface are shown, for example, in Ref. [19]. The net surface results agree well with theoretical calculations [7,12,13,20] and experimental data [7].

The results of electron density calculation after sodium adsorption on GaN(0001) surface at the hollow position and above the surface nitrogen atom are shown in Figure 3 and Figure 4, respectively. The adsorption of Na atoms on GaN at different adsorption sites has no effect on the valence band in the depth of GaN layer (Figure 3, f and Figure 4, f).

Figures 3, a and 4, a show the zone of surface states of sodium which is formed after adsorption on GaN. The occupied states zone is located below E_F and it consists of two peaks with bond energies -0.78 and -0.26 eV for sodium adsorption at the hollow position and with bond energies -0.72 and -0.23 eV for sodium adsorption over nitrogen atom. This slight discrepancy is attributable to the fact that the zone of occupied surface states is formed from Na 3s states. The zone of unoccupied states is formed by Na 3s and Na 3p states.

The valence band of GaN in the surface layer changes after sodium adsorption (Figure 3, b–d and 4, b–d). Thus the pseudo-band decreases from 0.62 to 0.12 eV in the case of Na adsorption at the hollow position and 0.14 eV in the case of adsorption over the nitrogen atom. The surface state zone of GaN near the Fermi level changes from a broad peak to three well-separated peaks with maxima -0.81, 0.08 and 1.25 eV in the case of Na adsorption at the hollow position and -0.76, 0.09 and 1.19 eV in the case of Na adsorption over the nitrogen atom. The peak with energy -0.81 (-0.76) eV is formed mainly by Ga 4p and N 2p electrons, the contribution of s-electrons is noticeably smaller. The peak with energy 0.08 (0.09) eV is formed

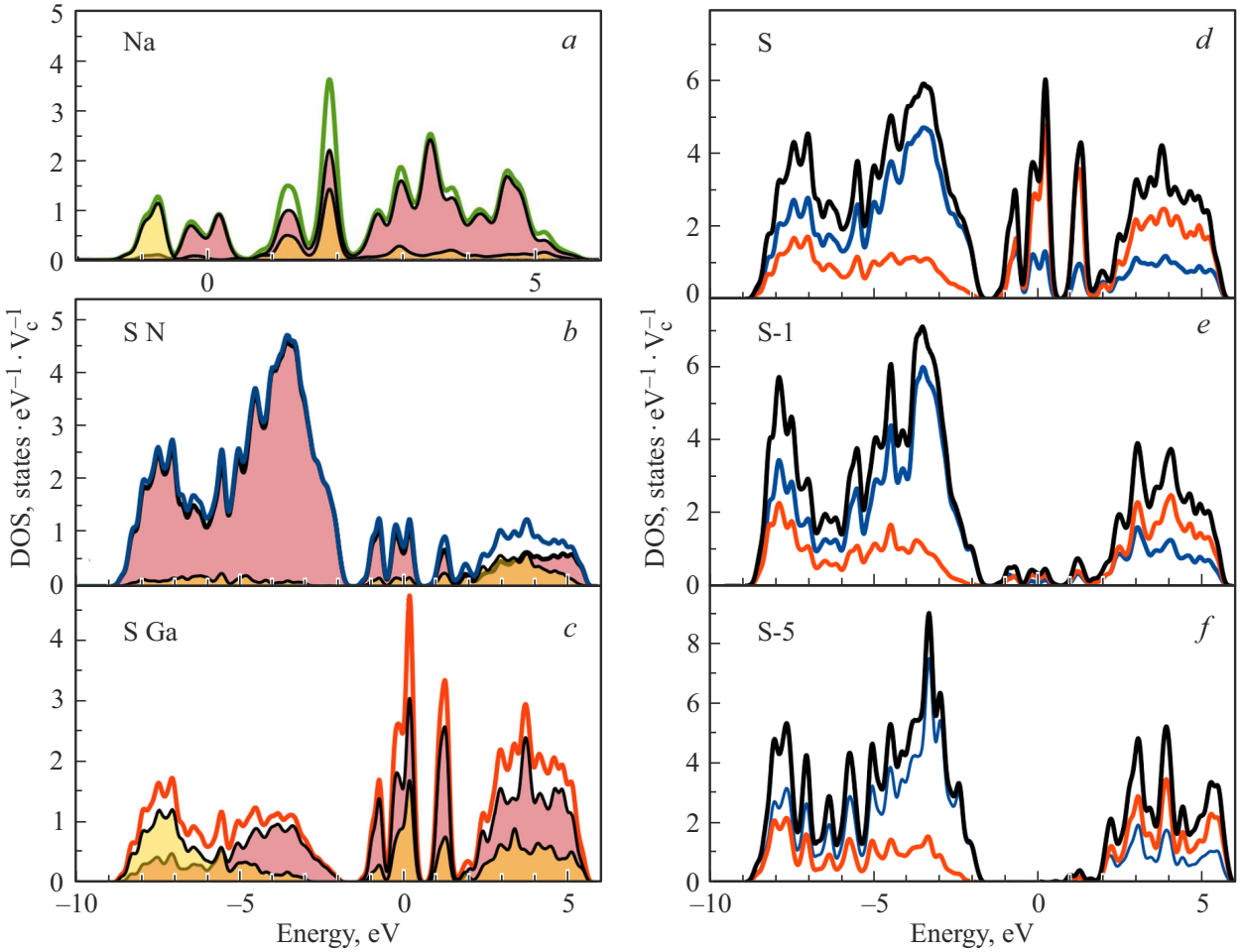

Figure 3. Calculated total and partial densities of 2D-layer of GaN(0001) states in the case of Na adsorption at the hollow position. Total and partial density of Na states (a): total density of states — green color, Na 3s — yellow fill, Na 3p — brown fill. Partial densities of states of N (b) and Ga (c) for the surface S of GaN bilayer. Total and partial densities of states for S (d), S-1 (e), and S-5 (f) of GaN bilayers. V_c is the lattice cell volume. Total density of states — black color, N — blue color, N 2s — yellow color with filling, N 2p — brick color with fill, Ga — red color, Ga 4p — brown fill, and Ga 4s — yellow fill.

mainly by Ga 4p, Ga 4s, and N 2p electrons. Ga 4p and N 2p states are the main contributors to the peak with energy 1.25 (1.19) eV. All changes in the electronic structure of the GaN surface state zone are due to the interaction of the valence electrons of the GaN surface bilayer with the valence electrons of the adsorbed Na atoms, which agrees with the experimental data. The density of surface electronic states decreases sharply with distance from the surface, so for the S-1 bilayer (Figures 3, e and 4, e) it is smaller by almost 10 fold than for the surface S bilayer.

5. PES studies

Figure 5 shows the photoemission spectra in the valence band region for the GaN sample and for the Na/GaN interface at Na 0.05 and 0.10 ML coating at different excitation energies. The photoemission spectrum has a width of ~ 10 eV. The peaks at bond energies -5.2 and -9.7 eV are associated with hybridized Ga 4p — N 2p and Ga 4s — N 2p states. The increase in the intensity of peaks at bond energies -5.2 and -9.7 eV is observed at an excitation energy of 150 eV, which is attributed to the increase of the probing depth of the sample with the increase of the excitation energy. Photoelectron escape depth (λ) calculated using the Tanuma-Powell-Penn equation (TTP-2M) is 5.38 Å for electrons with kinetic energy $E_{\text{kin}} = 100$ eV, and $\lambda = 5.95$ Å for electrons with $E_{\text{kin}} = 150$ eV [21]. It should be emphasized that for GaN, the value λ calculated using the TTP-2M equation is 30% larger than that determined from the experimental data [22]. It should be noted that the distance between GaN bilayers is 2.62 Å. We hypothesize that there is an increase in photoemission due to another layer of gallium atoms deep within the GaN sample. The position of the valence band edge on the E_{VBM} surface relative to the Fermi level (~ 3.0 eV) has also been determined. The GaN sample has n-type of conductivity, so the Fermi level is located near

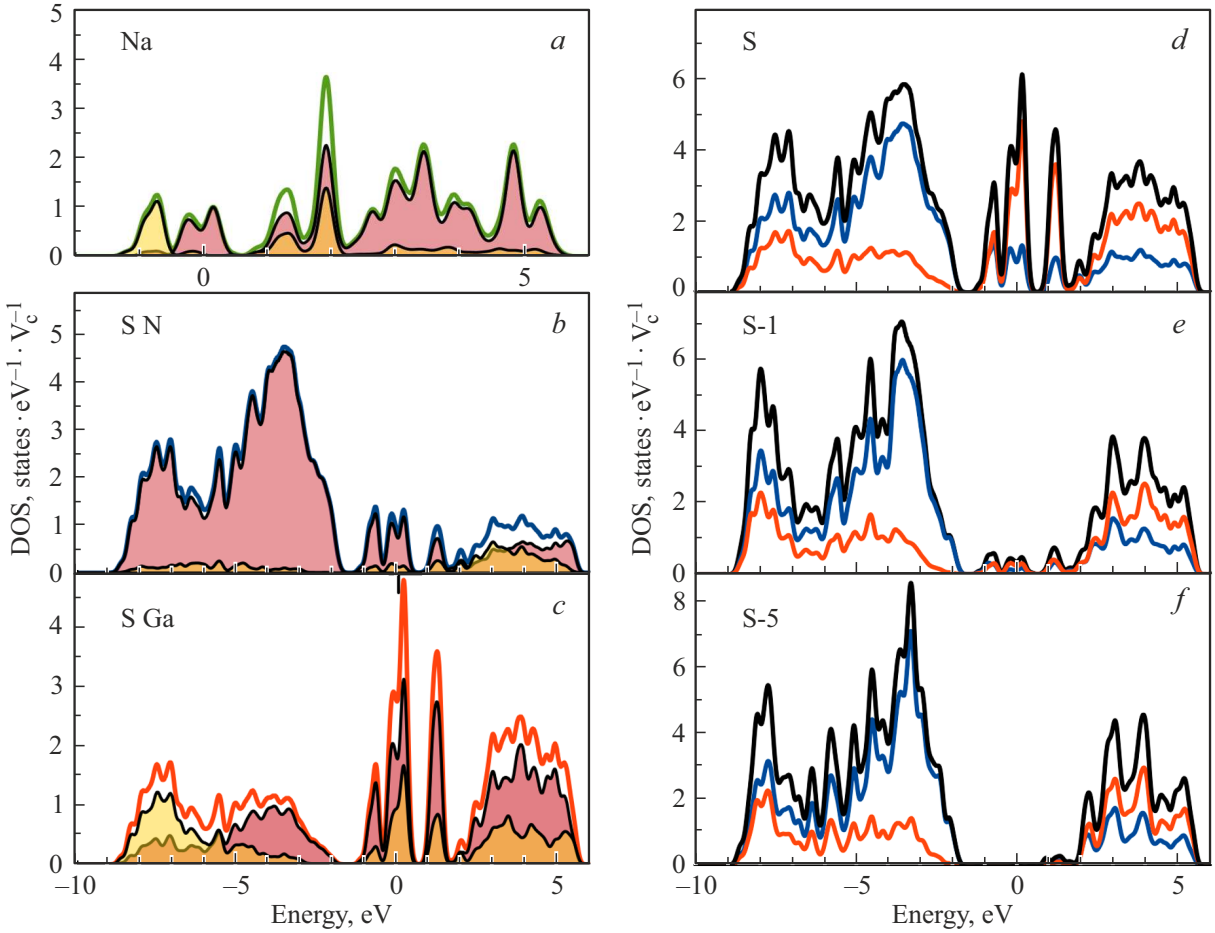

Figure 4. Calculated total and partial densities of states of the 2D-layer of GaN(0001) in the case of adsorption of Na on the surface atom N. Total and partial densities of states Na (a): total density of states — green color, Na 3s — yellow fill, Na 3p — brown fill. Partial densities of states of N (b) and Ga (c) for the surface S bilayer of GaN. Total and partial densities of states for S (d), S-1 (e), and S-5 (f) of GaN bilayers. V_c is the lattice cell volume. Total density of states — black color, N — blue color, N 2s — yellow color with filling, N 2p — brick color with fill, Ga — red color, Ga 4p — brown fill, and Ga 4s — yellow fill.

the conduction band in the volume. Thus, the zones bend upwards at the sample surface, which is consistent with the results [6,23]. When Na is adsorbed onto the GaN surface, the intensity of the peaks of hybridized states in the valence band region decreases. For an excitation energy of 150 eV, the intensity of the photoemission spectrum decreases by 3% when the Na coating is 0.05 ML; when the Na coating is increased to 0.10 ML, the intensity decreases by 13%. For an excitation energy of 100 eV, the changes are more significant due to the decrease in the photoelectron yield depth, the decrease in the intensity of the photoemission spectrum is 5 and 26% at Na 0.05 and 0.10 ML coatings, respectively.

The difference in the appearance of the photoemission spectrum in the region between the valence band maximum and the Fermi level from the calculated one may be due to the fact that an apparently non-ideal GaN surface is experimentally investigated, and there are adsorption sites on the surface associated with defects on the surface, which may lead to a wider zone of surface states.

6. Conclusion

GaN epitaxial layers were grown by molecular beam epitaxy with nitrogen plasma activation on a GaN/c-Al_2O_3 template. The electronic structure of GaN surface and Na/GaN interface has been investigated for the first time by photoelectron spectroscopy using synchrotron radiation. An upward bending of the zones on the surface is observed for the pure GaN sample. Based on theoretical calculations within the framework of density functional theory, we have studied the structure and electrical properties of GaN surface, adsorbed Na and bilayer GaN. It is found that when Na is adsorbed onto the GaN surface, the hollow position and the position above the N atom are the most stable with adsorption energies of sodium atoms E_{ads} equal to -1.96 and -1.93 eV, respectively. The calculation results show that the surface state zone of sodium is formed during sodium adsorption, and the surface state zone of GaN near the Fermi level is modified from a broad zone to a zone with three peaks, which is due to the interaction between

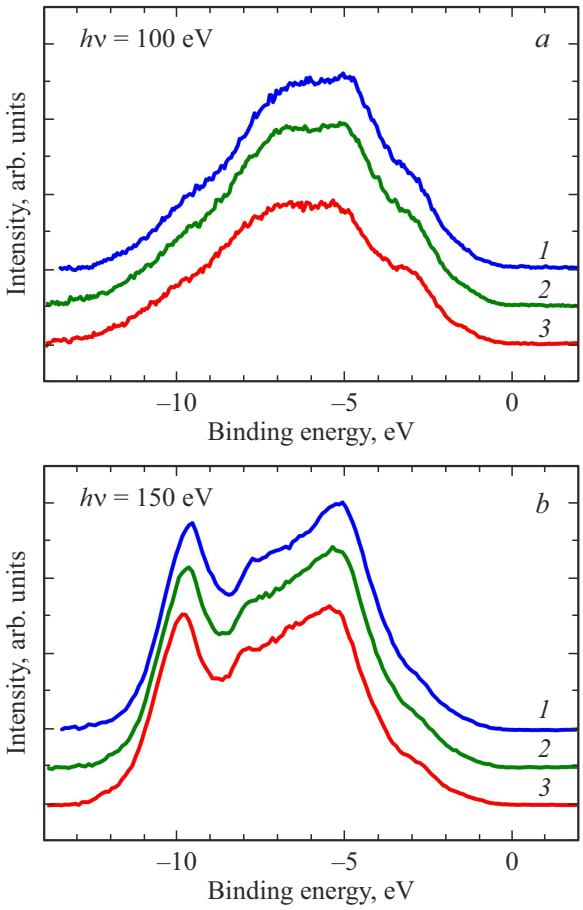

Figure 5. Photoemission spectra in the valence band region for the pure GaN (*1*) surface and for the Na/GaN interface at 0.05 ML (*2*) and 0.10 ML (*3*) Na coatings at excitation energies 100 eV (*a*) and 150 eV (*b*).

the valence electrons of the surface bilayer of GaN and the valence electrons of adsorbed atoms Na.

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Conflict of interest

The authors declare that they have no conflict of interest.

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