Changes in the electronic properties of the GaN/Si(111) surface under Li adsorption

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The electronic structure of the epitaxial GaN/Si(111) layers and the Li/GaN/Si(111) interface with a monolayer Li coverage has been studied *in situ* under ultrahigh vacuum conditions. The experiments were carried out using photoelectron spectroscopy with synchrotron radiation in the photon energy range 75−850 eV. The photoemission spectra in the valence band and the core levels of Ga 3*d*, N 1*s*, and Li 1*s* are studied for the monolayer Li coating. It is found that Li adsorption causes a significant decrease in the intensity of the photoemission line of the intrinsic surface state and the appearance of an induced surface state due to charge transfer between the adsorbed Li layer and surface Ga atoms. It has been found that the GaN/Si(111) surface has predominantly Ga polarity. The Li/GaN/Si(111) interface has a semiconductor character.

Keywords: III-nitrides, electronic structure, metal-GaN interface, photoelectron spectroscopy.

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1. Introduction

The study of the properties of group III nitrides is of great interest both for fundamental science and for technological applications in high-power high-frequency electronic and optoelectronic devices operating in a wide spectral range from infrared to ultraviolet [1–3]. Close attention to nitrides is due to unique physical properties, such as a direct and wide band gap, high mobility of charge carriers, high breakdown voltage, excellent mechanical, thermal and chemical resistance, relatively high melting point and good thermal conductivity. Modern electronic devices are formed on the basis of heterostructures. All of them contain a simple metal/semiconductor contact, so the state of the semiconductor surface plays a crucial role in the functioning of electronic devices. Changes in surface characteristics can also be caused by interaction with adsorbed atoms.

The electronic structure of the GaN surface has been extensively studied in numerous experimental and theoretical papers [4–10]. The electronic and photoemission properties of the Ru/GaN, Ni/GaN, Pd/GaN, Cs/GaN and Ba/GaN [11–18] interfaces have been investigated. Lithium adsorption was investigated only on the N-polar GaN/SiC/Si(111) substrate [19]. In this paper, lithium adsorption was investigated on a Ga-polar GaN/Si(111) substrate [20].

Sapphire, Si, SiC and GaN substrates are usually used to grow epitaxial GaN layers. Silicon can be considered as a promising substrate due to its low cost, large plate size. Also, the development of technology for the growth of heterostructures of group III nitrides on silicon attracts close attention due to the possibility of integration with a well-studied silicon technology. However, the strong mismatch of the parameters of the crystal lattices of these materials and the difference in the coefficients of thermal expansion cause difficulties in growing GaN films of good quality on a Si substrate. In order to successfully grow GaN on silicon substrates, it is necessary to use various transition layers to reduce the thermal and lattice mismatch at the heterointerface between the GaN layer and the silicon wafer. The electronic and photoemission properties of GaN epitaxial layers on Si have not been studied sufficiently. In our previous work, the electronic structure of GaN grown on a hybrid SiC/Si(111) substrate [19] was investigated.

In this paper, changes in the electronic and photoemission properties of the epitaxial GaN/Si(111) layers during adsorption of a lithium monolayer coating are investigated. It is shown that the spectra of the valence band and surface states and the spectra of the Ga 3*d* and N 1*s* core levels significantly modified due to the adsorption of Li. A comparison was made with the previously obtained results of studies of the GaN/SiC/Si(111) sample. It should be noted that the epitaxial GaN/Si(111) and GaN/SiC/Si(111) layers were grown on two different types of substrates in the same growth process under the same growth conditions.

2. Experiment

Epitaxial GaN layers were grown on the Veeco GEN200 unit by molecular beam epitaxy with plasma nitrogen activation. The Veeco GEN200 molecular beam epitaxy unit is multi-substrate and allows the synthesis of epitaxial layers on various types of substrates in a single growth process with a maximum load of up to 7 three-inch plates. A high-frequency (13.56 MHz) plasma source Riber RFN 50/63 was used to activate nitrogen. A semi-insulating silicon plate Si(111) was used as a substrate for the sample. The substrate was previously prepared using the Shiraki method. Immediately before growth, the substrate was subjected to thermal cleaning *in situ* at a temperature of $T_S = 850^\circ$C for 30 min. After that, the substrate was nitridized at a temperature of $T_S = 850^\circ$C for 60 min in order to form a nitride surface layer. The conditions of epitaxial growth are similar to the conditions described in [21]. The GaN sample was grown without additional doping during growth. Hall measurements of the GaN/Si(111) sample showed that it has a *n*-type conductivity with an electron concentration $7.6 \cdot 10^{18}\,\mathrm{cm}^{-3}$. The thickness of the obtained epitaxial GaN layers was ~ 800 nm.

The photoemission studies were performed in the Russian-German Laboratory of the Helmholtz-Zentrum Berlin (Germany) using photoelectron spectroscopy with synchrotron radiation in the photon energy range of 75−850 eV. The experiments were carried out *in situ* in an ultrahigh vacuum $P \sim 5 \cdot 10^{-10}$ Torr at room temperature. Photoelectrons along the surface normal were recorded, an exciting beam was incident on a sample surface at the angle of 45°. Photoemission spectra were recorded in the valence band and core levels of Ga 3*d*, N 1*s* and Li 1*s*. For the spectra in this paper, the background was subtracted using the Shirley method.

Before the studies, the GaN sample was annealed *in situ* at a temperature of $\sim 680^\circ$C. Insignificant amounts of oxygen and carbon were detected when registering the core levels of O 1*s* and C 1*s*. Atomically pure Li was deposited step by step onto a clean sample surface at room temperature from a standard SAES Getters. The coating was determined using quartz microweights by changing the oscillation frequency of the quartz resonator. Note that one monolayer (ML) of Li is accepted to be a concentration of $1.0 \cdot 10^{15}\,\mathrm{at/cm}^2$, forming a complete layer of the Li atoms.

3. Results and discussion

Fig. 1 shows the photoemission spectra for the clean GaN/Si(111) surface (*1*) and the Li/GaN/Si(111) interface with Li 1.0 ML coating at an excitation energy of 110 eV. The curves illustrate the characteristic photoemission peaks of the core levels of Ga 3*d* and Li 1*s* and photoemission spectra in the valence band region. The position of the maximum of the valence band E_{VBM} on the surface was determined by linear approximation of the low-energy edge of the spectrum. E_{VBM} is located at the binding energy of ~ 2.9 eV below the Fermi level for the GaN/Si(111) sample. It was also found that the core level of Ga 3*d* is located at 17.2 eV lower in binding energy from E_{VBM}.

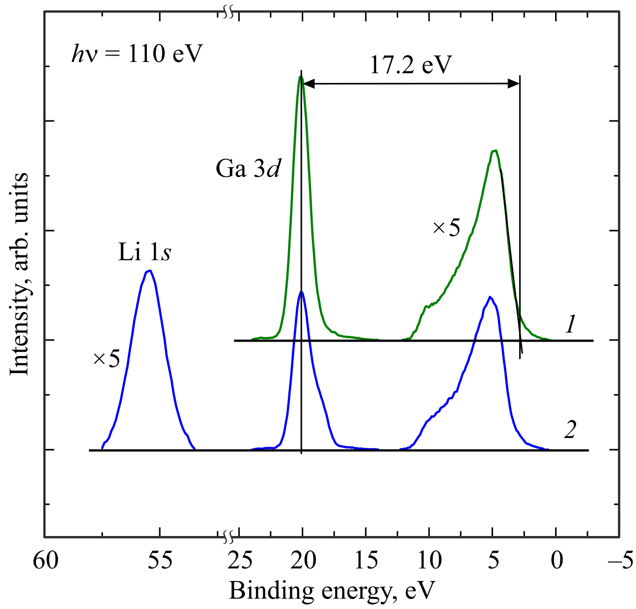

Figure 1. Photoemission spectra in the valence band region and the core levels of Ga 3*d* and Li 1*s* for the clean GaN/Si(111) surface (*1*) and the Li/GaN/Si(111) interface (*2*).

The obtained values of the location of the core level of Ga 3*d* practically coincide with the literature data [22,23]. Minor discrepancies may be related to the modification of the electronic structure on the surface for different samples. The peak of Li 1*s* is located at a binding energy of 55.5 eV.

Fig. 2, *a* shows the photoemission spectra in the valence band region for the GaN/Si(111) sample at an excitation energy of 110 eV. The spectrum of the GaN sample is a structured photoemission band with a width of ~ 10 eV. The obtained spectrum is in good agreement with the theoretical and experimental data of [4,10]. In spectra, three features can be distinguished at binding energies of ~ 1.9 (A), ~ 4.2 (C), ~ 6.5 eV (B) relative to E_{VBM}. The spectra were decomposed by dividing into separate peaks using Gaussian functions. Peaks A and B are associated with hybridized states of Ga 4*p*−N 2*p* and Ga 4*s*−N 2*p*, respectively, with the dominant character of N 2*p*, whereas peak C is attributed to mixed orbitals or surface adsorbates [4]. Additionally, the position of the intrinsic surface state of SS was determined at a binding energy of 7.5 eV (Fig. 2, *a*). In contrast to [24,25], no surface states were detected in the region of the edge of the valence band.

It was found that the adsorption of Li onto the GaN surface causes a change in the photoemission spectrum of the valence band. Fig. 2, *b* shows the spectrum for the Li/GaN/Si(111) interface with a 1 ML lithium coating. It can be seen that the intensity of peaks A, B and C decreases. A new peak of the induced surface state of ISS was detected at a binding energy of 3.3 eV. These data are in good agreement with the previously published results for the Li/GaN/SiC/Si(111) interface [19]. It is also found that with lithium coating 1 ML, the intrinsic surface state of SS completely disappears. The Li/GaN/Si(111) interface has a semiconductor character.

Fig. 3 shows the photoemission spectra of the Ga 3*d* core level for the clean GaN/Si(111) surface (*1*) and the Li/GaN/Si(111) interface (*2*) at excitation energies of 110 eV. The spectra were decomposed using Gaussian functions. The photoemission spectrum of the core level of Ga 3*d* at an excitation energy of 110 eV corresponds to the surface photoemission. The main peak of the core level of Ga 3*d* (Fig. 3, curve *1*) at a binding energy of 20.1 eV is attributed to the Ga-N bond, and an additional peak at a binding energy of 18.3 eV is attributed to the Ga-Ga bond.

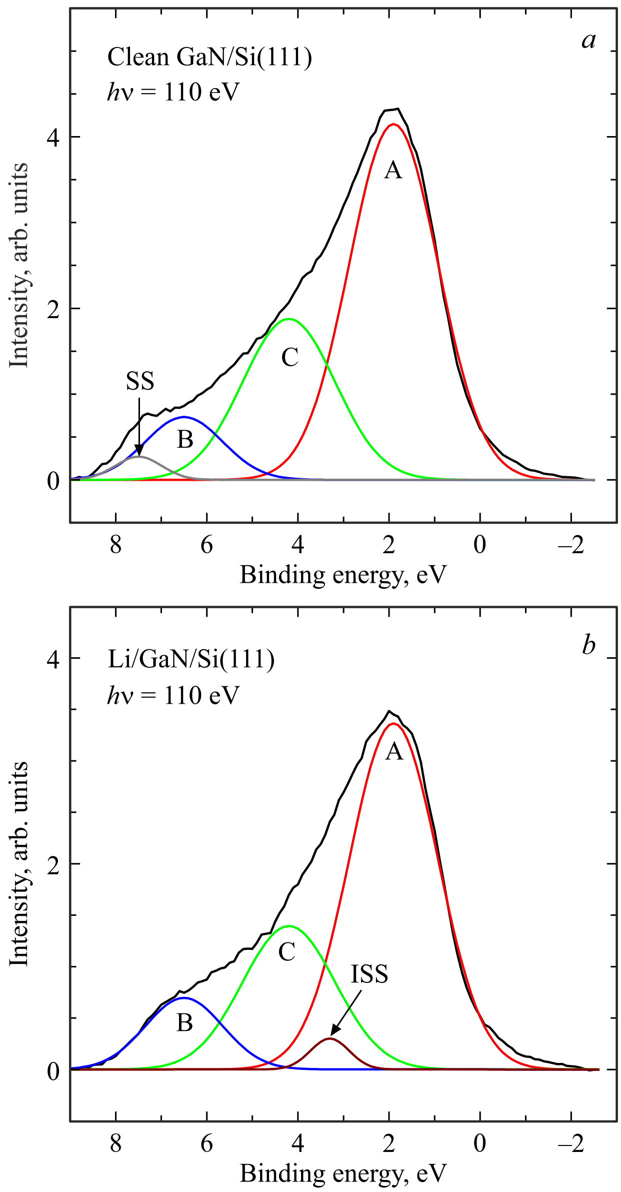

Figure 2. Photoemission spectra in the valence band region for the clean GaN/Si(111) surface and the Li/GaN/Si(111) interface.

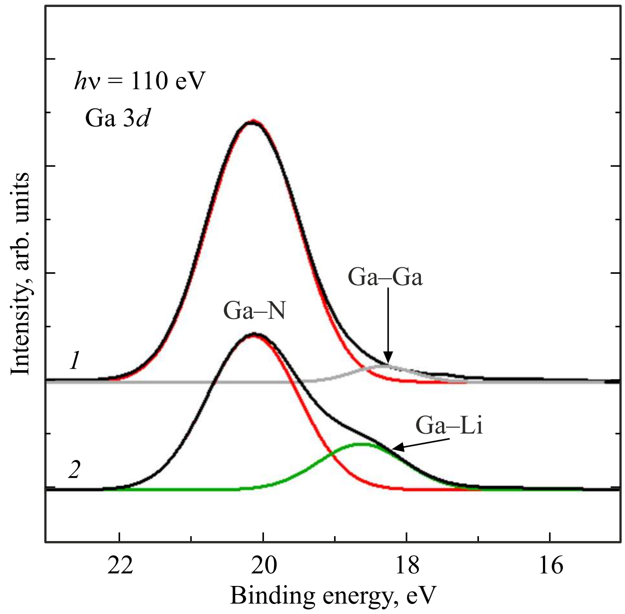

Figure 3. Photoemission spectra of the core level of Ga 3*d* for a clean GaN/Si(111) surface (*1*) and the Li/GaN/Si(111) interface with a monolayer coating of Li (*2*) at the excitation energy $h\nu = 110$ eV.

The obtained values practically coincide with the literature data [22,23].

During Li adsorption, the intensity of the core level of Ga 3*d* decreases (Fig. 3, curve *2*). The main peak corresponding to the Ga-N bond is suppressed by 40%. An additional peak is observed at the binding energy of 18.6 eV. The shift towards a lower binding energy is characteristic of a metallic bond and corresponds to a redistribution of the electron density at the interface. It can be assumed that the new peak corresponds to the Ga-Li bond.

Photoemission spectra from the core level of N 1*s* for the clean GaN/Si(111) surface and the Li/GaN/Si(111) interface at an excitation energy of 455 eV were investigated (photoemission spectra are not given). The results show that the shape of the spectrum practically does not change during Li adsorption. There is a decrease in the intensity of the peak of N 1*s* by 40% with 1 ML Li coating. Since the greatest changes occur in the spectrum of the core level of Ga 3*d* compared to the spectrum of the core level of N 1*s*, the GaN/Si(111) sample has a predominantly Ga-polar surface. This data is confirmed by the results of the study of the polarity of this sample [20]. It should also be noted that the polarity of the sample differs from the polarity of the GaN sample grown on a hybrid substrate SiC/Si(111) in the same growth process [19].

4. Conclusion

The epitaxial GaN layer was grown by molecular beam epitaxy with plasma activation of nitrogen on a Si(111) substrate. The electronic structure of the GaN/Si(111) surface and the Li/GaN/Si(111) interface with a monolayer coating of Li has been investigated. The evolution of the spectra of surface states and the spectra of core levels with the growth of the Li coating demonstrates the adsorption activity of Ga-dangling bonds on the GaN surface. The GaN sample has a predominantly Ga-polar surface. For a clean GaN surface, three features associated with the hybridized states A, C and B at binding energies of ~ 1.9, ~ 4.2, ~ 6.5 eV are found relative to the maximum of the valence band on the surface, respectively. The position of the intrinsic surface state of SS at a binding energy of 7.5 eV, which is suppressed with a 1 ML Li coating, is established. The adsorption of lithium leads to the appearance of a new induced surface state of ISS at a binding energy of 3.3 eV. A slight suppression of the A, B and C states was detected due to the adsorption of Li. It can be assumed that during the adsorption of Li, the saturation of the Ga-dangling bonds occurs, which leads to the suppression of intrinsic surface states, as well as to the semiconductor character of the Li/GaN interface.

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Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] M.S. Shur, R. Gaska, A. Khan. Mater. Sci. Forum, **353–356**, 807 (2001).
[2] T.J. Flack, B.N. Pushpakaran, S.B. Bayne. J. Electron. Mater., **45**, 2673 (2016).
[3] G. Li, W. Wang, W. Yang, Y. Lin, H. Wang, Z. Lin, S. Zhou. Rep. Progr. Phys., **79**, 056501 (2016).
[4] W.R.L. Lambrecht, B. Segall, S. Strite, G. Martin, A. Agarwal, H. Morkoç, A. Rockett. Phys. Rev. B, **50**, 14155 (1994).
[5] T. Strasser, C. Solterbeck, F. Starrost, W. Schattke. Phys. Rev. B, **60**, 11577 (1999).
[6] G.V. Benemanskaya, M.N. Lapushkin, S.N. Timoshnev. Surf. Sci., **603**, 2474 (2009).
[7] D. Yujie, C. Benkang, W. Xiaohui, Z. Junju, L. Biao, W. Meishan. Appl. Surf. Sci., **258**, 7425 (2012).
[8] M. Lozac, S. Ueda, S. Liu, H. Yoshikawa, S. Liwen, X. Wang, B. Shen, K. Sakoda, K. Kobayashi, M. Sumiya. Sci. Technol. Adv. Mater., **14**, 015007 (2013).
[9] A. Eisenhardt, S. Krischok, M. Himmerlich. Appl. Phys. Lett., **102**, 231602 (2013).
[10] D. Skuridina, D.V. Dinh, B. Lacroix, P. Ruterana, M. Hoffmann, Z. Sitar, M. Pristovsek, M. Kneissl, P. Vogt. J. Appl. Phys., **114**, 173503 (2013).
[11] R. Wasielewski, M. Grodzicki, J. Sito, K. Lament, P. Mazur, A. Ciszewski. Acta Phys. Polon. A, **132**, 354 (2017).
[12] M. Grodzicki, P. Mazur, S. Zuber, J. Pers, J. Brona, A. Ciszewski. Appl. Surf. Sci., **304**, 24 (2014).
[13] M. Grodzicki, P. Mazur, J. Pers, J. Brona, S. Zuber, A. Ciszewski. Appl. Phys. A, **120**, 1443 (2015).
[14] C.I. Wu, A. Kahn. Appl. Surf. Sci., **162–163**, 250 (2000).
[15] F. Machuca, Y. Sun, Z. Liu, K. Ioakeimidi, P. Pianetta, R.F.W. Pease. J. Vac. Sci. Technol. B, **18**, 3042 (2000).
[16] T.U. Kampen, M. Eyckeler, W. Moench. Appl. Surf. Sci., **123–124**, 28 (1998).
[17] G.V. Benemanskaya, S.A. Kukushkin, P.A. Dementev, M.N. Lapushkin, S.N. Timoshnev, D.V. Smirnov. Solid State Commun., **271**, 6 (2018).
[18] G.V. Benemanskaya, S.N. Timoshnev, S.V. Ivanov, G.E. Frank-Kamenetskaya, D.E. Marchenko, G.N. Iluridze. JETP, **118**, 600 (2014).
[19] S.N. Timoshnev, A.M. Mizerov, G.V. Benemanskaya, S.A. Kukushkin, A.D. Buravlev. Phys. Solid State, **61**, 2282 (2019).
[20] K.Yu. Shubina, T.N. Berezovskaya, D.V. Mokhov, A.M. Mizerov, E.V. Nikitina. Pis'ma ZhTF, **43**, 47 (2017) (in Russian).
[21] S.A. Kukushkin, A.M. Mizerov, A.V. Osipov, A.V. Redkov, S.N. Timoshnev. Thin Sol. Films, **646**, 158 (2018).
[22] S.M. Widstrand, K.O. Magnusson, L.S.O. Johansson, E. Moons, M. Gurnett, M. Oshima. MRS Internet J. Nitride Semicond. Res., **10**, 1 (2005).
[23] M. Grodzicki, J.-G. Rousset, P. Ciechanowicz, E. Piskorska-Hommel, D. Hommel. Appl. Surf. Sci., **493**, 384 (2019).
[24] G.V. Benemanskaya, M.N. Lapushkin, D.E. Marchenko, S.N. Timoshnev. Techn. Phys. Lett., **44**, 247 (2018).
[25] S. Timoshnev, G. Benemanskaya, G. Iluridze, T. Minashvili. Surf. Interface Anal., **52**, 620 (2020).