Proceedings of the 46th International School and Conference on the Physics of Semiconductors "Jaszowiec" 2017, Szczyrk

Modification of Electronic Structure of *n*-GaN(0001) Surface by N^+-Ion Bombardment

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The electronic structure of *n*-type GaN(0001) surface and its modification by N^+ ion bombardment are presented in this report. The studies were carried out *in situ* in ultrahigh vacuum by ultraviolet photoelectron spectroscopy, X-ray photoelectron spectroscopy, and low-energy electron diffraction. Low-energy N^+ ion bombardment, which was done using an ion gun at an energy of 200 eV, leads to nitriding of the surface. The process changes the surface stoichiometry and, consequently, provides formation of a disordered altered GaN layer. The calculated electron affinity of the clean *n*-GaN surface of 3.4 eV and band bending of 0.2 eV became changed after bombardment to 2.9 eV and 0.8 eV, respectively. The obtained difference in valence band maximum between the clean sample and the bombarded one was 0.6 eV.

DOI: 10.12693/APhysPolA.132.351
PACS/topics: 68.47.Fg, 73.30.+y, 82.80.Pv

1. Introduction

Gallium nitride (GaN) is a semiconductor which has unique physical properties such as the wide and direct band gap, high chemical resistance, a relatively high melting point, good thermal conductivity. The features have opened the door to widespread applications of GaN in modern electronic devices [1–3]. The semiconductor is used as a base for visible and UV lasers, light-emitting diodes, high-temperature and -frequency detectors, and transistors.

In all these devices the electronic structure of GaN has a major impact on their properties. The devices become smaller, and the surface effects such as band bending play a significant role due to their influence on conductivity, recombination velocity, and photochemistry. The preparation stage is crucial to the electronic structure of the surface, and consequently, to properties of the formed device, because the band bending can arise from the state of surface termination and purity. One of the most popular fabrication processes of GaN surfaces in ultrahigh vacuum (UHV) systems is thermal treatment. However, the surface stoichiometry gets altered during annealing, which leads to enriching with gallium as the nitrogen escapes to the vacuum [4]. In order to prevent this phenomenon the nitrogen ion bombardment method can be used.

Herein we present the results of a study of the influence of N^+ ion bombardment of GaN(0001) on the surface stoichiometry and its electronic structure.

2. Experimental details

The treated substrates were GaN samples (UNIPRESS Warsaw), around 5×10 mm^2 in size, terminated with 0.5 μm thick atomically flat homoepitaxial GaN layer, (0001)-oriented, Si-doped ($N_d \approx 10^{18}$ cm^{-3}), grown on the HVPE 100–150 μm thick GaN layer, which in turn was grown in *c*-direction on a GaN ⟨0001⟩-oriented single crystal. Before investigation, the substrates were *ex situ* degreased in isopropanol, next washed in distilled water and dried in air, next mounted on molybdenum plates and disposed in the ultrahigh vacuum (UHV) SPECS surface-analysis system with the base pressure $\leq 10^{-10}$ Torr. The *in situ* experiment procedure included the following stages: (1) degassing the sample at a temperature of 500 °C; (2) annealing sample at 800 °C — in order to remove surface oxides and carbon contamination; (3) nitriding using an ion gun at the energy 200 eV with a current of $I = 6$ μA for 20 min. The state of the samples was characterized by X-ray photoelectron spectroscopy (XPS) using an Mg K_α (1253.6 eV) radiation source, and by ultraviolet photoelectron spectroscopy (UPS) using the He(I) line (21.2 eV) from a DC discharged lamp; additional analyses were carried out by low energy electron diffraction (LEED). Photoelectrons were collected with a hemispherical electron energy analyzer (Phoibos 100, Specs) with 0.1 eV or 0.025 eV steps for core level lines or valence bands, respectively. The position of the Fermi level (E_F) was measured on the clean reference Au sample. The XPS and UPS spectra were analyzed using the Casa XPS software. Heating the samples in UHV was performed by electron bombardment (from the rear side of the molybdenum plate). The temperature was monitored by an emissive-corrected pyrometer. The composition of residual gases in the chamber during experiments was monitored by a quadrupole mass spectrometer. All measurements were done at room temperature.

3. Results and discussion

After degassing and annealing samples, the GaN(0001) surfaces with a very small amount of residual oxygen, but free of carbon were obtained. Annealing changes the LEED pattern, which displays (1×1) structure, from

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weak to strong intensity diffraction spots. Aside from the normal order spots, sextet diffraction spots appear in the hexagonal configuration as was shown in a previous report concerning oxidation of a GaN(0001) surface [5]. The XPS studies show that Ga 3*d* line at 20.8 eV has the full width at half-maximum (FWHM) of 1.7 eV and the N 1*s* peak at 398.3 eV has the FWHM of 1.6 eV. Chemical composition of surface layers reveals the Ga/N ratio of 1.1, which indicates that annealing leads to the formation of the Ga-rich GaN(0001) surface. XPS measurements, after N^+ ion bombardment, show that the Ga 3*d* line shifts toward the lower binding energy to reach 20.3 eV and its FWHM increases to 2.3 eV, while the N 1*s* peak shifts to the position of 387.7 eV, and its FWHM increases to 1.9 eV (see Fig. 1). After the bombardment, the concentration of nitrogen in subsurface layers increases and Ga/N ratio amounts to 0.9. After the nitriding, LEED patterns do not appear which means that the surface is disordered and the altered GaN layer is obtained.

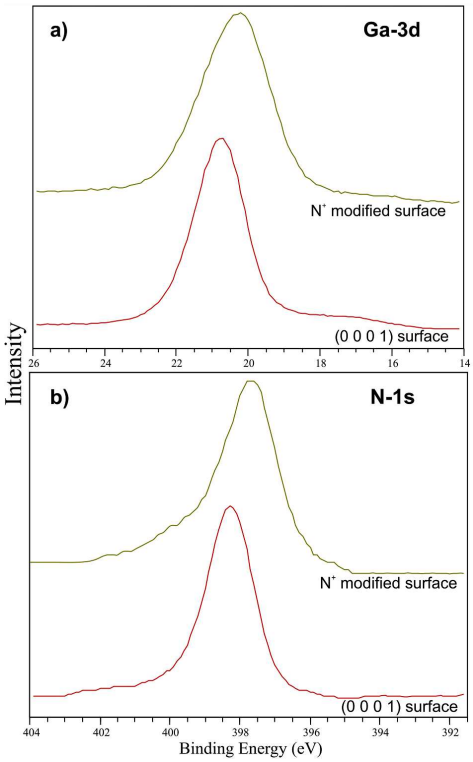

Fig. 1. XPS spectra of (a) the Ga 3*d*, (b) the N-1*s* core level lines before and after the N^+ ion bombardment process.

The UPS spectra for GaN(0001) samples after cleaning in vacuum and after N^+ ion bombardment are shown in Fig. 2. The shape of the valence band of the clean GaN(0001) surface is typical of the *n*-type semiconductor. The position of the valence band maximum (VBM) is at 3.1 eV below the E_F as determined from extrapolation of the line fit to the leading edge of the spectrum. The electron affinity χ of the clean surface calculated

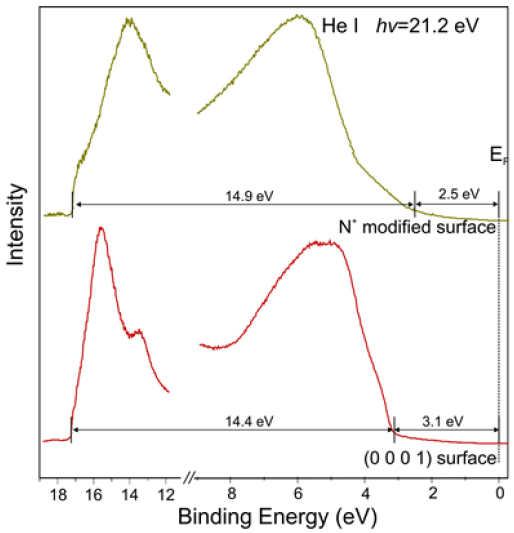

Fig. 2. Photoelectron spectra of valence bands for the clean substrate (a) and after the N^+ ion bombardment process (b).

basing on the relationship $\chi = h\nu - W - E_g$ amounts to 3.4 eV, where $h\nu = 21.2$ eV is the photon energy of He(I); the spectrum width W is the energy difference between the VBM and the cutoff energy of photoemission, equal to 14.4 eV; and E_g is the width of the GaN band gap assumed to be equal to 3.4 eV. The VBM lies 17.7 eV above the Ga 3*d* core level, which is in agreement with the value reported in our previous paper on the formation of Ga–Pd intermetallic compounds at Pd/GaN(0001) interface [6]. The valence band changes under the N^+ ion bombardment; the positions of the cutoff energy and the VBM are shifted. Electron affinity of the modified surface χ_b decreases to 2.9 eV, where W_b was 14.9 eV and the VBM lies 2.5 eV below the E_F and 17.8 eV above the Ga 3*d* core level line.

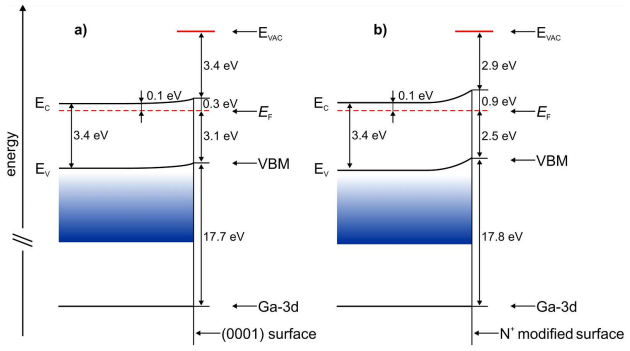

Fig. 3. Schematic energy diagram of the *n*-GaN(0001) surface (a) before and (b) after the N^+ ion bombardment process.

The Fermi level position of the bulk substrate as approximated from the parabolic band model lies 3.3 eV above the VBM. This value enabled us to specify the surface band bending from the following formula:

$(E_F - VBM)_{bulk} - (E_F - VBM)_{surface}$. Accordingly, the upward band bending is 0.2 eV at the clean surface of the n-GaN semiconductor and 0.8 eV at the N^+ ion modified surface. Taking into account the obtained values we elaborated the energy diagrams of the n-GaN before and after the ion bombardment as shown in Fig. 3. Note the small change of the vacuum level relative to E_F in contrast to the position of VBM between the clean n-GaN(0001) surface and the surface after modification.

4. Conclusions

Surface-analysis techniques of UPS, XPS, and LEED were used to study the chemical and electrical properties of the n-GaN(0001) surface before and after the N^+ ion bombardment. Electron affinity for the clean surface is calculated to be 3.4 eV and the upward band bending is 0.2 eV. Diffraction pattern exhibits a highly ordered surface of the (1×1) structure. The N^+ ion bombardment leads to nitriding of the surface, which results in changes in the valence band and the formation of disordered surface layer. Electron affinity for the modified surface is found to be 2.9 eV and the upward band bending to be 0.8 eV. The N^+ ion bombardment results in the change of position of the valence band maximum by 0.6 eV toward the E_F level.

Acknowledgments

The authors thank Dr. Stanisław Surma for helpful discussions and his assistance during preparation of manuscript.

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