Semiconductors, 2022, Vol. 56, No. 6

Synchrotron radiation photoemission study of the electronic structure of the ultrathin K/AlN interface

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Received February 25, 2022
Revised March 25, 2022
Accepted for publication March 25, 2022

The electronic structure of the clean AlN surface and the ultrathin K/AlN interface has been studied *in situ* by synchrotron-based photoelectron spectroscopy using the photon energies in the range of 100−650 eV. The effect of K adsorption was studied. Changes in the valence band and in the Al $2p$, N $1s$, and K $3p$ core levels spectra have been investigated using K submonolayer deposition. Modification of the surface electronic structure of the AlN caused by K adsorption is found to originate from the local interaction of N surface atoms and K adatoms. As a results the suppression of intrinsic surface state and appearance of a new induced state are observed. It was found the K-induced electron redistribution effect that causes the positive energy shift of N $1s$ surface peak and increasing N-ionicity.

Keywords: III-nitrides, electronic structure, surface states, metal-III-nitride interfaces, photoelectron spectroscopy.

DOI: 10.21883/SC.2022.06.53534.9821a

1. Introduction

Nitrides of III-group are of great importance for the development of heterostructures used in optical and high-power electronic devices. Despite the effective technological progress in the field of the growth of high-quality materials, theoretical and experimental data on the electronic structure of III-nitrides are still insufficient, especially in the case of AlN. This gives rise to the importance of investigating surface states, the formation of interfaces, and zone bending. This is due to the fact that such properties play a key role in nanostructures, nanoheterostructures and in the development of optoelectronic devices [1,2].

III-nitrides are of great interest due to their unique electrical and optical properties. III-nitrides are the most suitable materials for new applications in high-power high-frequency electronic devices, as well as in optoelectronic devices operating in a wide spectral range from IR to UV. High-tech applications in nanoelectronics require comprehensive knowledge of the structural and electronic properties of the bulk and surface of AlN. Changes in surface characteristics can be caused by interactions with adsorbed atoms. The adsorption of K on the AlN surface has not been studied. The electronic structure of the AlN surface has been studied in many aspects [3–5], but information on structure and electronic properties of metal/AlN interface is very limited [6–10]. Recently, the electronic and photoemission properties of metal/$\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{N}$ interfaces, namely Cs/GaN, Ba/GaN, Ba/InGaN, Ba/$\mathrm{Al}_{0.16}\mathrm{Ga}_{0.84}\mathrm{N}$, Ba/$\mathrm{Al}_{0.42}\mathrm{Ga}_{0.58}\mathrm{N}$, have been investigated [11–15].

In this work, the evolution of the electronic structure of the K/AlN interface depending on the K coverage is studied for the first time by photoelectron spectroscopy using synchrotron radiation.

2. Experimental

Photoemission studies were carried out *in situ* in a high vacuum of $5 \cdot 10^{10}$ Torr at room temperature on the experimental RGL-station at Russian-German beamline at BESSY II synchrotron radiation facility (Berlin, Germany). Photoelectron spectroscopy (PES) is a powerful tool for studying the properties of materials and for obtaining the most complete information about the band structure of electronic states due to its high sensitivity to chemical states.

The electronic structure of the clean AlN surface and the ultrathin K/AlN interface has been studied *in situ* by the synchrotron-based photoelectron spectroscopy using the photon energies in the range of 100−650 eV. The AlN samples were grown on 6*H*-SiC/Si(111) substrates by chemical vapor deposition. The samples of AlN were annealed in situ directly in a vacuum at a temperature of about 900 K. Atomically pure potassium was deposited on the sample surface from a standard calibrated source. Step-by-step submonolayer coverage from 0.1 monolayer (ML) to 1.0 ML of K was adsorbed on the clean AlN surface. The effect of K atomic layer desorption was studied. Changes in the surface state and valence band spectra and in the Al $2p$, N 1s, and K 3p core levels spectra have been investigated under the K submonolayer deposition.

3. Results

Fig. 1 shows the normal photoemission spectra in the valence band region for the clean AlN surface (*1*) and for the K/AlN interface at the different K submonolayer coverages: *2* — 0.2 ML, *3* — 0.5 ML, and *4* — 0.9 ML. The excitation energy $h\nu$ is 100 eV. The energy position of the E_{VBM} at the surface is determined by extrapolating a linear fit to the leading edge of the spectrum of the valence band (VB). For the clean AlN surface the spectrum is characterized by the weakly structured band in the binding energy region of $-3-12$ eV below E_{VBM} with major VB maximum at ~ 4.0 eV. The shape and the bandwidth of the valence band spectrum coincide well with the GaN and AlGaN photoemission results reported earlier [11–15]. It can be seen that a K 3p peak appears in the spectrum at binding energy of ~ 15.3 eV and increases upon the adsorption of potassium.

Fig. 2 shows the decomposition of the spectra in the valence band region for the clean AlN surface (*a*) and for the K/AlN interface (*b*) with potassium coverage of 0.9 ML. It is seen that the adsorption of K on the AlN surface modifies the spectrum. Sharp changes are observed in the valence band region, which are manifested in a decrease in the initial intensity and the formation of a new ISS peak. Decomposition is performed by dividing the spectrum into individual peaks using Gaussian and asymmetric Gaussian functions. The A and B peaks at the binding energies of 2.9 and 5.8 eV correspond to photoemission from the valence band. The S1 peak at the binding energy of -0.2 eV can be attributed to intrinsic surface states [11]. During the adsorption of potassium, the intensity of the S1 peak is significantly reduced. The intensity of B peak also decreases with increasing potassium coverage. A new ISS peak was found at the energy of 6.6 eV with a K 0.9 ML coverage. This can be caused by the surface state caused by the adsorption of K. Similar data on the induced surface states near EVBM were obtained for the Cs/GaN, Ba/GaN, Ba/InGaN, Ba/$\mathrm{Al_{0.16}Ga_{0.84}N}$, Ba/$\mathrm{Al_{0.42}Ga_{0.58}N}$ interfaces [11–15].

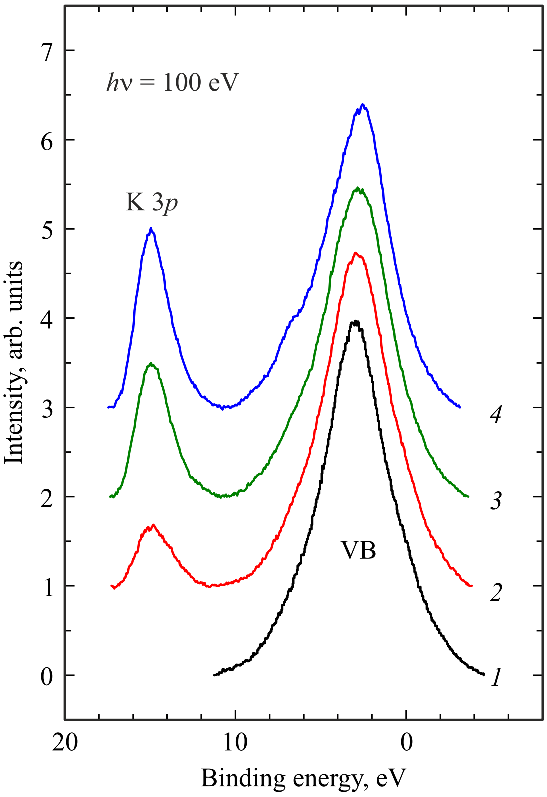

Figure 1. The photoemission spectra from the valence band region for the clean AlN surface (*1*) and for the K/AlN interface at the different K coverage: *2* — 0.2 ML, *3* — 0.5 ML, and *4* — 0.9 ML.

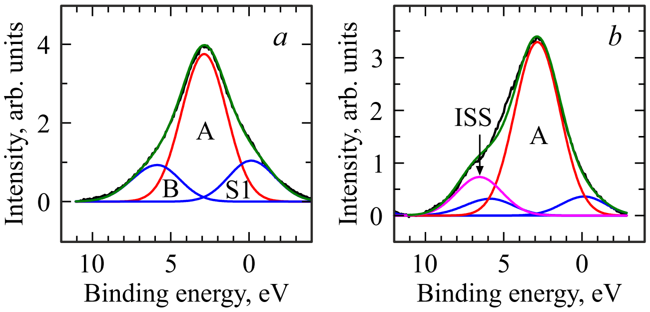

Figure 2. The decomposition of the spectra in the valence band region for the clean AlN surface (*a*) and for the K/AlN interface (*b*) with the potassium coverage of 0.9 ML. The excitation energy $h\nu = 100$ eV.

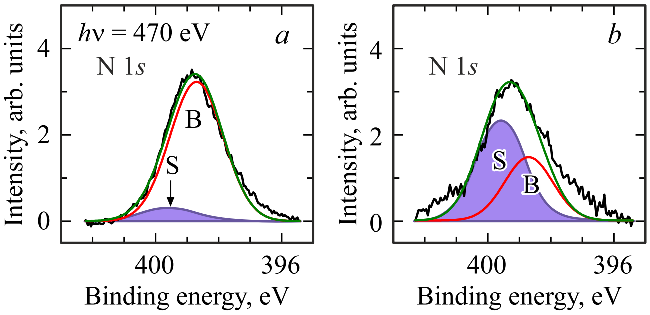

Figure 3. The photoemission spectra of the N 1s core level for the clean AlN surface (*a*) and for the K/AlN interface at the K coverage of 0.9 ML (*b*). The excitation energy $h\nu = 470$ eV.

Fig. 3 shows the photoemission spectra from the N 1s core level for the clean AlN surface and the K/AlN interface. The excitation energy is 470 eV. The study of the photoemission spectra indicates that the shape of the core level changes insignificantly upon adsorption of K. There is a decrease in the intensity of the N 1s peak by of ~ 1.6 and 2 times at the K coverage is 0.5 ML and

0.9 ML, respectively. The intensity of the Al $2p$ peak decreased by ~ 1.2 times at 0.9 ML K coverage (spectrum not shown). Since the photoemission intensity of the N $1s$ core level decreased more than Al $2p$, it can be assumed that the AlN sample has a predominantly N-polar surface. Decomposition is performed by dividing the spectrum into individual peaks using Gaussian and asymmetric Gaussian functions. The difference in the positions of the S and B peaks in the decomposition of the spectrum of the N $1s$ core level is ~ 0.7 eV. This shift of the peak towards higher binding energies was found that is originated from charge transfer with increasing the N-ionicity.

4. Conclusions

In summaries, firstly, the formation of the ultrathin K/AlN interface has been firstly studied *in situ* by synchrotron-based photoelectron spectroscopy. The evolution of both the surface states and core level spectra with increasing the K coverage demonstrates the adsorption capacity of the dangling bonds of the AlN surface. Secondly, the intrinsic surface state S1 at the binding energies of -0.2 eV is found for the clean AlN surface. The suppression of the intrinsic surface state S1 due to the K adsorption is revealed. The K induced surface state ISS is found at the binding energy of 6.6 eV. Thirdly, due to the K adsorption the increasing of the additional surface peak S of the N $1s$ core level spectrum is revealed. The positive shift of the peak S toward higher binding energy is originated from charge transfer with increasing the N-ionicity. The intensity increase of the peak S is caused to the K adsorption providing the interaction of the N nearest surface atoms with the K adatoms.

Acknowledgment

The authors thank Synchrotron BESSY II and Russian-German Beamline, Synchrotron BESSY II, Helmholtz Zentrum, Berlin for providing the facilities to perform the experiments and for help during experiments. The authors thank M.N. Lapushkin and P.A. Dementev for help in the preparation of the experiments.

Ethics declarations

The authors declare that they have no conflict of interest.

Data availability statement

All data generated or analyzed during this study are included in this published article and are available from the corresponding author on reasonable request.

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