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Citation: Chin. Phys. B, 2021, 30 (**6**): 067701. DOI: 10.1088/1674-1056/abdb21
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Band alignment between NiO_x and nonpolar/semipolar GaN planes for selective-area-doped termination structure*

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(Received 8 December 2020; revised manuscript received 8 January 2021; accepted manuscript online 13 January 2021)

Band alignment between NiO_x and nonpolar GaN plane and between NiO_x and semipolar GaN plane are measured by x-ray photoelectron spectroscopy. They demonstrate that the maximum value of the valence band in the unintentional-doped *a*-plane, *m*-plane, and *r*-plane GaN are comparable to each other, which means that all the substrates are of n-type with similar background carrier concentrations. However, the band offset at the NiO_x/GaN interface presents obvious crystalline plane dependency although they are coated with the same NiO_x films. By fitting the Ga 3d spectrum obtained from the NiO_x/GaN interface, we find that relatively high Ga–O content at the interface corresponds to a small band offset. On the one hand, the high Ga–O content on the GaN surface will change the growth mode of NiO_x. On the other hand, the affinity difference between Ga and O forms a dipole which will introduce an extra energy band bending.

Keywords: GaN, NiO_x, band alignment, vertical diode

PACS: 77.84.Bw, 73.30.+y, 73.40.Kp, 52.59.Mv **DOI:** 10.1088/1674-1056/abdb21

1. Introduction

Vertical GaN Schottky barrier diodes (SBDs) are attractive for power-switching application due to their intrinsic low turn-on voltage, high breakdown voltage in small area, no surface trap, and good thermal stability.[1–5] Especially, with the development of low threading dislocation density (10^4 cm^{-2}–10^5 cm^{-2}) free-standing GaN substrate, remarkable progress has been achieved over the past decades. However, the reported average breakdown electric field, which is the breakdown voltage divided by the thickness of the GaN drift layer, for GaN vertical SBD is usually smaller than 1 MV/cm, which is far below the theoretical value of 3 MV/cm.[6] Under reverse bias, the peak electric field in the vertical SBD will crowd at the Schottky contact anode/GaN interface, causing the premature breakdown at the edge of device. Therefore, terminal techniques are suggested as the compromising solutions to suppress the electric field crowding and improve the breakdown voltage.

Several kinds of edge termination techniques,[7–9] such as field plate, beveled MESA, guard ring, and junction barrier Schottky (JBS), have been proposed until now. Among those methods, selective-area-doping method for forming p-type layer plays an important role in guard ring (Fig. 1(a)) and JBS (Fig. 1(b)) structures. The buried p-type region below Schottky anode forms a lateral pn junction and creates a potential barrier to shield the Schottky contact under reverse bias, which is effective in suppressing the electric field crowding. Generally, selective-area-doping for p-type GaN is realized through implantation and trench-filling-regrowth.[10–12] However, high temperature process is necessary for ion implantation to activate the Mg-dopant and remove the implantation damage, which results in the surface decomposition of GaN.[12] While for the regrowth route, the Mg-doped GaN should be grown on *c*-plane at the bottom of trench and on the nonpolar (or semipolar) plane at the sidewalls of trench simultaneously.[11] The discrepancy in growth mode for different planes yields a rough surface with non-uniform distribution of acceptors in p-GaN inside the trench.

Nickel oxide (NiO_x) deposited by sputtering is a natural p-type semiconductor with a critical electric field of approximately 3.5 MV/cm,[13] which is comparable to the critical electric field of GaN. Besides, the relatively low deposition ratio provides a good trench-filling capability along with a flatten surface. Previously, we reported a vertical GaN diode with p-NiO_x serving as planar guard ring termination, which can enhance the breakdown voltage obviously.[14] The band alignment between NiO_x and *c*-plane GaN was measured by x-ray photoelectron spectroscopy (XPS), which plays a crucial role in determining the charge transport across the

*Project supported by the Fund from the Open Project Key Laboratory of Microelectronic Devices and Integrated Technology, China (Grant No. 202006), the Doctoral Research Support Foundation of Shenyang Ligong University, China (Grant No. 1010147000914), and the Science and Technology Program of Ningbo, China (Grant No. 2019B10129).

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heterojunction.[15] Herein, we first determinate the band offset between NiO_x and nonpolar GaN plane and between NiO_x and semipolar GaN plane, which are beneficial to the fabrication of termination structures for vertical GaN diodes.

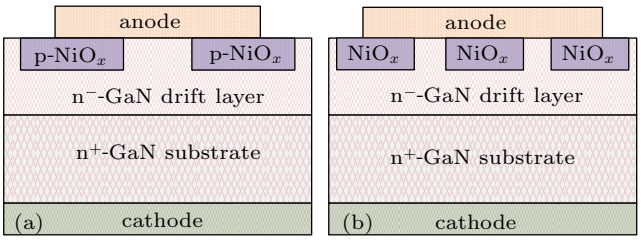


Fig. 1. Schematic view of vertical GaN diode (a) with NiO_x guard ring termination structure, and (b) with junction barrier Schottky termination structure.

2. Experiments and characterization

Three kinds of commercial free-standing GaN substrates (unintentionally doped with an electron concentration of 5×10^{17} cm^{-3}) were adopted for investigation. The surface crystalline planes were *a*-plane, *m*-plane, and *r*-plane, respectively. To measure the band offset, each substrate was cut into three pieces and coated with 0 nm-, 5 nm- and 50 nm-thick NiO_x films, respectively, by radio frequency (RF) magnetron sputtering. A NiO target with a high purity of 99.99 % was used in our experiments. A mixture of argon and oxygen (Ar:O_2 = 10:1) was introduced into the chamber with a pressure of 3 mTorr (1 Torr = 1.33322×10^2 Pa). To eliminate the repeatability concern, we have optimized our experiment procedure. Firstly, the Ar:O_2 ratio presented a relatively low sputtering rate of approximately 0.83 nm/min. Secondly, for the same NiO_x thickness, we placed three kinds of substrates into the chamber simultaneously. The band discontinuity was obtained by an XPS system (Thermo Fisher Scientific) with monochromatized Al $K\alpha$ (1486.60 eV) radiation source. The Fermi level edge and binding energy were calibrated using nickel metal and the C 1s peak of adventitious carbon (at approximately 284.80 eV), respectively. All the core level spectra were analyzed by pseudo-Voigt (mixed Lorentzian and Gaussian) fitting with Shirley background to determine the energy values. In the Kraut method it is assumed that the energy difference between the valence band edge and core level peak of the substrate is unchanged with the over layer. Then, the valence band offset (VBO, ΔE_V) is calculated from the following formula:

$$\Delta E_V = \left(E^{NiO}_{Ni\ 2p} - E^{NiO}_{VBM}\right) - \left(E^{GaN}_{Ga\ 3d} - E^{GaN}_{VBM}\right) - \Delta E_{CL}, \quad (1)$$

where $\left(E^{NiO}_{Ni\ 2p} - E^{NiO}_{VBM}\right)$ was the energy difference between Ni 2p (by fitting the core level spectra with pseudo-Voigt) and valence band maximum (VBM) (intercept between the slope at the leading edge of the valence band spectrum and base line) of the bulk NiO_x film, $(E^{GaN}_{Ga\ 3d} - E^{GaN}_{VBM})$ was the energy difference between Ga 3d and VBM of the bulk GaN film, and $\Delta E_{CL} = (E^{NiO}_{Ni\ 2p} - E^{GaN}_{Ga\ 3d})$ was the energy difference between Ni 2p and Ga 3d at the NiO_x/GaN interface. Then, the conduction band offset (CBO), ΔE_c, could be estimated from

$$\Delta E_c = \Delta E_V + E^{NiO}_g - E^{GaN}_g. \quad (2)$$

Based on our previous work, the band gaps of NiO_x and GaN were 2.80 eV and 3.40 eV at room temperature, respectively,[16]

3. Results and discussion

3.1. Band alignment between NiO_x and *a*-plane GaN

Figure 2 shows the Ga 3d core level spectrum as well as the valence band spectrum of *a*-plane GaN substrate without NiO_x. A VBM value of approximately 2.65 eV is obtained from the valence band spectrum, which is consistent with the n-type conductivity for the unintentional-doped GaN substrate. Besides, in the Ga 3d spectrum, three peaks corresponding to the N 2s (around 17.79 eV), Ga–N (around 20.38 eV), and Ga–O (around 21.22 eV) are fitted.[16,17] Therefore, the energy difference of $(E^{GaN}_{Ga\ 3d} - E^{GaN}_{VBM})$ is calculated to be 17.73 eV.

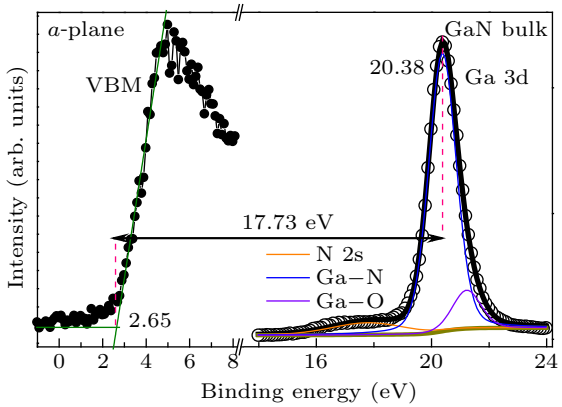


Fig. 2. Ga 3d and valence band spectrum for *a*-plane bulk GaN without NiO_x layer.

The core level spectra of Ni 2p and valence band spectrum for 50-nm NiO_x on *a*-plane GaN are shown in Fig. 3. The obtained XPS signals are comparable to those of the NiO_x bulk material, which means that a thickness of 50 nm is effective in eliminating the effect of GaN wafer. The VBM value of NiO_x measured from the valence band spectra by using linear fitting is approximately 0.69 eV, implying the p-type conductivity characteristics. Besides, the Ni 2p spectrum is fitted to three peaks around 854.09 eV, 855.70 eV, with a satellite peak at 861.04 eV. The former two peaks are assigned to Ni^{2+} and Ni^{3+} bonds as reported in previous work, implying that the grown film contains both NiO phase and Ni_2O_3 phase. The satellite peak is usually attributed to various possible originations such as multi-electron excitation, multiple

splitting or surface plasmon loss, but the root mechanism is still unclear.[21] The energy difference of $\left(E^{\mathrm{NiO}}_{\mathrm{Ni\ 2p}} - E^{\mathrm{NiO}}_{\mathrm{VBM}}\right)$ is then calculated to be 853.40 eV, which is in good agreement with the result reported previously.[22]

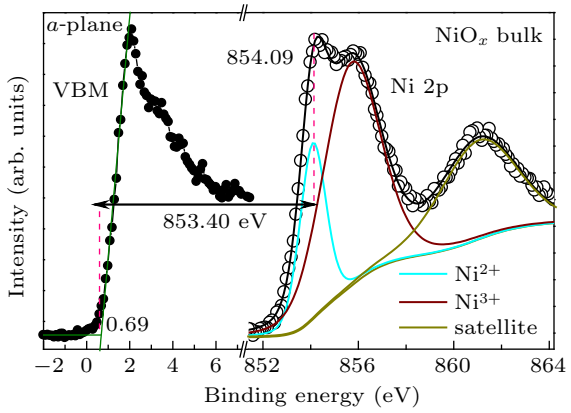


Fig. 3. Ni 2p and valence band spectrum for the 50-nm NiO_x deposited on a-plane bulk GaN.

The core level energy difference $\Delta E_{\mathrm{CL}} = (E^{\mathrm{NiO}}_{\mathrm{Ni\ 2p}} - E^{\mathrm{GaN}}_{\mathrm{Ga\ 3d}})$ is determined from the sample that possesses a thin NiO_x (approximately 5 nm) on a-plane GaN. As shown in Fig. 4, Ni 2p and Ga 3d core levels are detected from the top NiO_x and the beneath GaN, respectively. It worth noting that the relatively thick NiO_x layer hindrances the detection of Ga 3d core level and causes a weak intensity. Fortunately, all the N 2s (around 17.42 eV), Ga–N (around 20.11 eV), and Ga–O (around 21.28 eV) peaks are observed. Besides, Ni 2p core level signal is fitted to three features at 853.88, 855.41, and 860.79 eV, which are related to the Ni^{2+}, Ni^{3+}, and satellite peaks, respectively. Therefore, the energy difference between Ga 3d and Ni 2p is then calculated to be 833.77 eV. The ΔE_{V} and ΔE_{c} can be calculated to be 1.90 eV and 1.30 eV, implying a type-II band alignment.

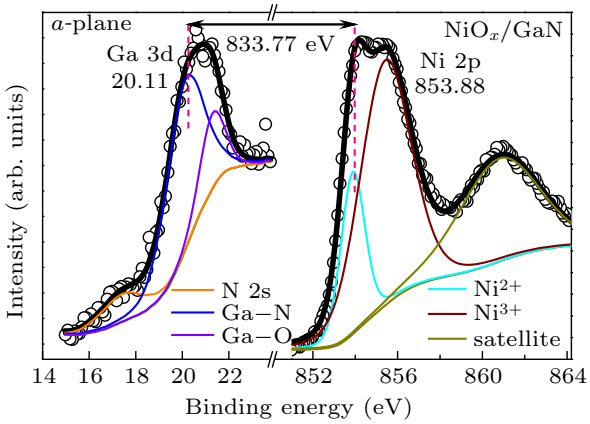


Fig. 4. Core level energy difference between Ga 3d energy levels of thin NiO_x on a-plane GaN.

Table 1. Summary of band alignments between NiO_x and different GaN planes.

Substrate	Core levels		GaN bulk	NiO_x (50 nm)	NiO_x (5 nm)	VBO	CBO
	Ga 3d	Ga–N	20.38	/	20.11		
a-plane	Ni 2p	Ni–O	/	854.09	853.88	1.90	1.30
	VBM		2.65	0.69	/		
	Ga 3d	Ga–N	20.12	/	19.63		
m-plane	Ni 2p	Ni–O	/	853.67	853.90	1.00	0.40
	VBM		2.64	0.92	/		
	Ga 3d	Ga–N	20.17	/	19.89		
r-plane	Ni 2p	Ni–O	/	853.96	853.98	1.52	0.92
	VBM		2.60	0.78	/		

3.2. Band alignment between NiO_x and m-plane GaN

Similarly, the VBM value of the m-plane GaN bulk material is approximately 2.64 eV, which is obtained from the valence band spectrum (Fig. 2). The Ga 3d core level spectrum also contains three peaks of N 2s (around 17.52 eV), Ga–N (around 20.12 eV), and Ga–O (around 20.51 eV). Then, the energy difference of $(E^{\mathrm{GaN}}_{\mathrm{Ga\ 3d}} - E^{\mathrm{GaN}}_{\mathrm{VBM}})$ for m-plane is calculated to be 17.48 eV. From the valence band spectrum of 50-nm NiO_x on m-plane GaN, the VBM value is deduced to be approximately 0.92 eV. This value is larger than that of the NiO_x material grown on a-plane GaN, which may be ascribed to the different growth modes. The core level of Ni 2p spectrum is fitted to three peaks around 853.67, 855.27, and 860.66 eV, respectively. The energy difference of $\left(E^{\mathrm{NiO}}_{\mathrm{Ni\ 2p}} - E^{\mathrm{NiO}}_{\mathrm{VBM}}\right)$ is then calculated to be 852.75 eV. Finally, from the thin NiO_x on m-plane GaN sample, N 2s (around 17.21 eV), Ga–N (around 19.63 eV), and Ga–O (around 21.72 eV) peak are observed in

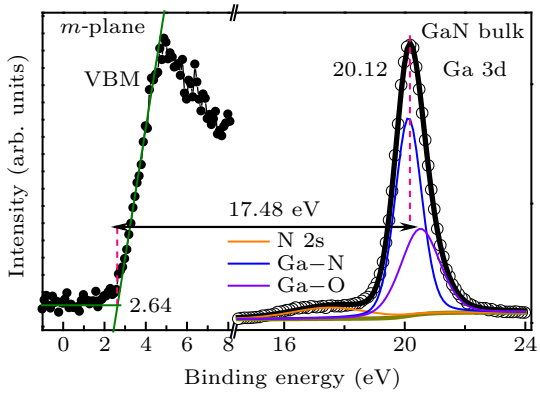


Fig. 5. Ga 3d and valence band spectrum for m-plane bulk GaN without NiO_x layer.

the Ga 3d spectrum. Besides, three features at 853.90, 855.44, and 860.75 eV are observed in the Ni 2p spectrum. Then, the core level energy difference $\Delta E_{\mathrm{CL}} = (E^{\mathrm{NiO}}_{\mathrm{Ni\ 2p}} - E^{\mathrm{GaN}}_{\mathrm{Ga\ 3d}})$ is determined to be 834.27 eV. The ΔE_{V} and ΔE_{c} can be calculated to be 1.00 and 0.40 eV, respectively.

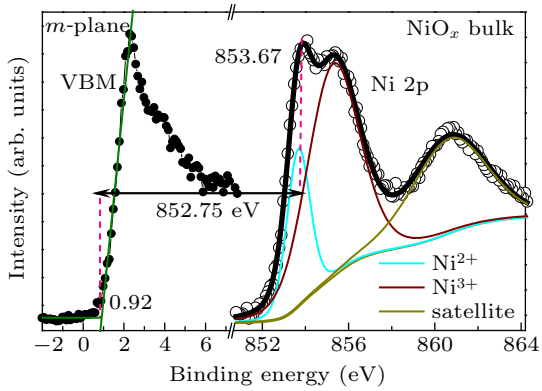


Fig. 6. Ni 2p and valence band spectrum for 50-nm NiO_x deposited on *m*-plane GaN.

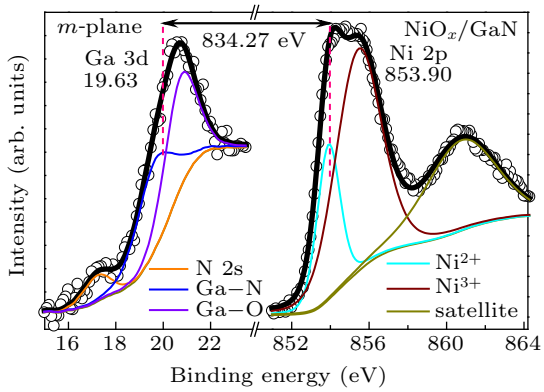


Fig. 7. Core level energy difference between Ga 3d energy levels of 5-nm NiO_x on *m*-plane GaN.

3.3. Band alignment between NiO_x and *r*-plane GaN

By using the same method, the VBM value of the *r*-plane GaN bulk material is approximately 2.60 eV, which is obtained from the valence band spectrum (Fig. 8). The Ga 3d core level spectrum also contains three peaks of the N 2s (around 17.56 eV), Ga–N (around 20.17 eV), and Ga–O (around 20.55 eV). Then, the energy difference of $(E^{\mathrm{GaN}}_{\mathrm{Ga\ 3d}} - E^{\mathrm{GaN}}_{\mathrm{VBM}})$ for *m*-plane is calculated to be 17.57 eV. From the valence band spectrum of 50-nm NiO_x on *r*-plane GaN, the VBM value is deduced to be approximately 0.78 eV. This value is larger than that of the NiO_x material grown on *a*-plane GaN, which may be ascribed to the different growth modes. The core level of Ni 2p spectrum is fitted to three peaks around 853.96, 855.58, and 860.94 eV, respectively. The energy difference of $\left(E^{\mathrm{NiO}}_{\mathrm{Ni\ 2p}} - E^{\mathrm{NiO}}_{\mathrm{VBM}}\right)$ is then calculated to be 853.18 eV. Finally, from the thin NiO_x on *m*-plane GaN sample, N 2s (around 17.37 eV), Ga–N (around 19.89 eV), and Ga–O (around 20.86 eV) peaks are observed in the Ga 3d spectrum. Besides, three features at 853.98, 855.52, and 860.89 eV are observed in the Ni 2p spectrum. Then, the core level energy difference $\Delta E_{\mathrm{CL}} = (E^{\mathrm{NiO}}_{\mathrm{Ni\ 2p}} - E^{\mathrm{GaN}}_{\mathrm{Ga\ 3d}})$ is determined to be 834.09 eV. The ΔE_{V} and ΔE_{c} can be calculated to be 1.52 eV and 0.92 eV, respectively.

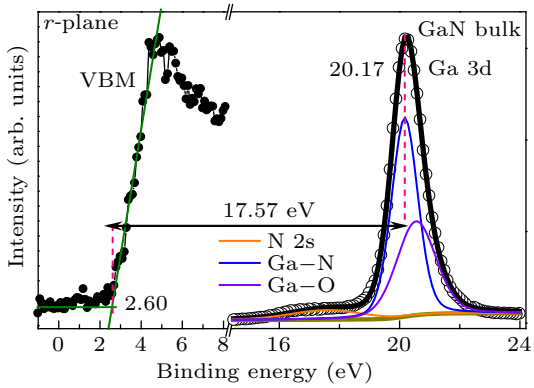


Fig. 8. Ga 3d and valence band spectrum for *r*-plane bulk GaN without NiO_x layer.

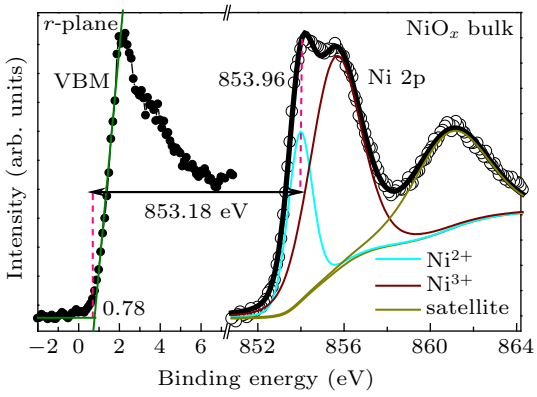


Fig. 9. Ni 2p and valence band spectrum for 50-nm NiO_x deposited on *r*-plane GaN.

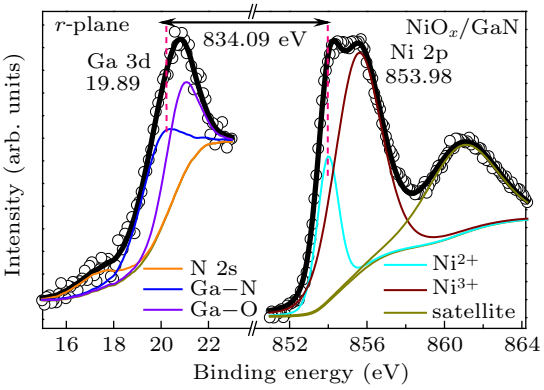


Fig. 10. Core level energy difference between Ga 3d energy levels of 5-nm NiO_x on *r*-plane GaN.

As summarized in Table 1, the valence band maximum values of the *a*-plane, *m*-plane, and *r*-plane GaN substrates are comparable to each other (approximately 2.65 eV), implying that the unintentional-doped substrates are of n-type with similar background electron concentration. However, the band offset at NiO_x/GaN interface presents obvious crystalline plane dependency although it is coated with the same NiO_x film. The polarization of GaN usually generates the charge on the surface and causes the band to bend. In our experiments, the *a*-plane and the *m*-plane are nonpolar GaN planes while the

r-plane is semipolar plane. Therefore, the band alignment of NiO_x/*a*-plane or NiO_x/*m*-plane should not be affected by the polarization charge. While for the *r*-plane, the negative charge on surface generates a band bending upward and reduces the band offset. None of those results is consistent with the XPS result as shown in Table 1. To understand the mechanism of this discrepancy, we fit the Ga 3d spectrum of the sample with 5-nm NiO_x on GaN substrate. It demonstrates that the Ga–O/Ga–N ratio of *a*-plane, *r*-plane, and *m*-plane GaN substrates are approximately 0.29, 0.78, and 1.07, respectively. Combining the variation trend of the band offsets, we assume that a relatively high Ga–O content at the interface corresponds to a small band offset.[23] On the one hand, the high Ga–O content on GaN surface will change the growth mode of NiO_x, resulting in a large VBM value. On the other hand, the large affinity of O than that of Ga will attract electron and generate a dipole at the interface, resulting in an extra energy band bending and the band offsets decreasing.

4. Conclusions

In this work, the band discontinuities between NiO_x and nonpolar GaN plane and between NiO_x and semipolar GaN plane are obtained by XPS with a Kraut method. The NiO_x thin film deposited by sputtering presents a band gap of approximately 2.7 eV as well as a small amount of Ni_2O_3. Based on core-level binding energy and valence band maximum value, a type-II band alignment is formed at the interface between NiO_x and nonpolar GaN plane and between NiO_x and semipolar GaN plane. The VBO (CBO) values present obvious plane dependency and are 1.90 (1.30) , 1.00 (0.40), and 1.52 (0.92) eV for the *a*-plane, *m*-plane, and *r*-plane GaN, respectively. By fitting the Ga 3d spectrum obtained from NiO_x/GaN interface, we find that relatively high Ga–O content at the interface corresponds to a small band offset. These results are beneficial to the selective-area-doped termination structure design of vertical GaN Schottky barrier diodes.

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