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ABSTRACT
The surface band bending in Ga-polar $n$-type GaN surfaces, as well as the effect of Si doping levels and \textit{in situ} Ar$^+$ ion processing on band bending, was systematically investigated. To precisely determine the valence band maximum (VBM) of GaN beyond instrumental and material surface environments by XPS, a valence band feature fitting procedure based on photoemission spectra and theoretical densities of states has been developed. Poisson calculation with quadratic depletion approximation on surface potential has been used to model the band bending and further correct the VBM energy. Then, the actual surface band bending was correctly evaluated. Upward band bending of 1.55 $\pm$ 0.03 eV with highly Si doped $n$-GaN, which is about 0.88 eV higher than that of the moderately doped sample, was found. After \textit{in situ} Ar$^+$ plasma treatment, the varying degree of band bending was observed distinctly depending on the Si doping density. The surface components associated with the Ga/N ratio and Ga–O bonding concentration on the $n$-GaN surface have been used to evaluate the contribution to surface band bending.

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I. INTRODUCTION
Surface band bending (BB) is one of the most important properties of wurtzite GaN as it plays an important role in determining the electrical and optical properties of GaN materials and heterostructures.\textsuperscript{1–10} Polarization effects and various surface states in the wurtzite GaN surface are widely recognized as being directly related to the surface band bending (BB).\textsuperscript{1} For the Ga-polar $n$-GaN surface, upward band bending and the electron depletion layer are usually present at the surface.\textsuperscript{1} This is mainly because of the negative bound polarization charge existing on the Ga-polar GaN surface. Large polarization in GaN materials gives rise to bound polarization charges on surfaces, and a distribution of compensating electron states arises to satisfy the charge neutrality. These compensating states, including surface states and internal ionized states (the formation of an internal space-charge layer), affect the internal electric field near the surface and play a crucial role in electric properties of these materials. Commonly, the smaller the net concentration of surface states, the larger the compensation from the internal ionized states and the stronger the band bending is. In many GaN related devices, it is essential to know the extent of surface band bending and gain knowledge of the effects of the surface states.\textsuperscript{1–10} Until now, various surface states related to Ga or N termination, structural defects, adsorbates, and oxidation have been studied to identify their influence on surface band bending.\textsuperscript{1–10} As the primary $n$-type dopant, Si doping density is commonly accompanied by structure defects of Ga vacancies.\textsuperscript{12–17} Although the Si-doped density is supposed to play a decisive role in related device performance, there are rare studies on the electronic surface band and surface structure of $n$-GaN systems focusing on the influence of Si doping levels.\textsuperscript{6,10}
X-ray photoelectron spectroscopy (XPS) is a widely used surface sensitive method for studying electronic properties and determining the surface band bending of III-nitride materials.\textsuperscript{9,12-16} The surface electric field responsible for electron band bending would induce the bending of the valence band and core levels in the space charge region and usually can be explored from angular dependent XPS (ARXPS). In order to determine the band bending at the surface, the method of linear extrapolation on the valence band leading edge has widely been used to measure the valence band maximum (VBM).\textsuperscript{15,16} However, this method usually leads to an underestimation of the VBM to Fermi energy separation due to the spectra broadening.\textsuperscript{17-20} Moreover, the determination of core energies and valence band binding energies at the top surface layer is always influenced by the band bending effect as the photoemission signals constitute integrated intensity contribution from different detection depths and corresponding bending-induced peak shifts.\textsuperscript{21-23} As a result, both effects imply a slightly imprecise surface band bending using this method. Therefore, a more direct and reliable measurement on the band bending preliminarily relies on how to accurately determine the VBM energy position at the surface with the XPS experiments.

In this work, we focused on the surface band bending in Ga-polar n-GaN with different Si doping levels and Ar\textsuperscript{+} ion treatments. The key objective of this investigation was to accurately determine the VBM by fitting a calculated valence band density of states (VB DOS) to valence band spectra from XPS as originally demonstrated by Kraut et al.\textsuperscript{24} and explore the most direct and reliable way to obtain precise band bending. Moreover, we processed the surface VBM correction owing to the complicated XPS measurements with certain detection depth and energy shifts due to the presence of band bending. We further figured out the origins of the surface band bending associated with Si-doping levels by taking the Ga/N ratio and Ga–O components into the analysis.

II. EXPERIMENTAL AND COMPUTATIONAL DETAILS

A. GaN growth and XPS analysis

The Ga-polar (0001) GaN wafers with three different Si doping densities were grown by metal-organic chemical vapor deposition (MOCVD) onto a 2-in. \(p\)-type Si(111) substrate with a 1.5 \(\mu\)m undoped GaN buffer layer. From Hall measurement, the doping densities of the three GaN samples were determined to 8 \(\times\) 10\textsuperscript{17} cm\textsuperscript{-3}, 4 \(\times\) 10\textsuperscript{18} cm\textsuperscript{-3} and 1.4 \(\times\) 10\textsuperscript{19} cm\textsuperscript{-3}. Following sonication in acetone and isopropanol, the GaN samples were first cleaned in acid solution (HCl: \(\text{H}_2\text{O}_2: \text{H}_2\text{O} = 1:1:5\)) for 20 min followed by alkaline solution (48\% KOH, 80 \(^\circ\)C) for 15 min. Each step of chemical treatments was followed by rinsing thoroughly in DI water and finally blowing dry with pure N\textsubscript{2} to eliminate any residuals on sample surfaces. All samples were immediately inserted into an ultrahigh vacuum (UHV) sample loading system, which is connected to the X-ray photoelectron spectroscopy with a base pressure of 3 \(\times\) 10\textsuperscript{-9} Pa. The Ar\textsuperscript{+} ion sputter gun is attached to a dual-beam charging compensation system of states (VB DOS) to valence band spectra from XPS as originally demonstrated by Kraut et al.\textsuperscript{24} and the most direct and reliable way to obtain precise band bending. Moreover, we processed the surface VBM correction owing to the complicated XPS measurements with certain detection depth and energy shifts due to the presence of band bending. We further figured out the origins of the surface band bending associated with Si-doping levels by taking the Ga/N ratio and Ga–O components into the analysis.

XPS measurements were carried out in an UHV chamber, equipped with a hemispherical electron energy analyzer (PHI 5000, VersaProbe II, ULVAC-PHI) and a monochromatic Al Ka-X-ray source of 1486.7 eV. The duo-beam charging compensation system is attached to the UHV chamber, focusing on the XPS analysis area of the sample. The XPS analytical area is about 0.1 \(\times\) 0.1 mm\textsuperscript{2}. The XPS spectra were collected with a pass energy and an entrance slit of 58.7 eV and 1.5 mm, respectively. The XPS resolution was determined by fitting the Au4f\textsubscript{7/2} and Au 4f\textsubscript{5/2} core level peak from clean single crystal Au to the convolution of the Voigt spectrometer response function, formed by folding the Gaussian with Lorentzian function following Kraut et al.\textsuperscript{27} The binding energy scale was accurately calibrated so that the Au4f\textsubscript{7/2} peaks and Fermi level binding energies were 84.00 \(\pm\) 0.02 eV and 0.00 \(\pm\) 0.02 eV, respectively. To eliminate the charge effect induced peak shift, we applied the dual-beam neutralization technique for sample compensation during the data collection.

All XPS spectra were analyzed via CasaXPS software. After subtracting the Shirley-type background, the core level peaks were fitted using combined Gaussian and Lorentzian line shapes. Both the core level and VBM were further calibrated against C 1s (284.8 eV). Atomic ratios (\(A_x, x = \text{Ga, N, O}\)) of the GaN surface were calculated from integral peak intensities \(I_x\) of Ga 3d, N 1s, and O 1s, and their corresponding sensitivity factors, \(S_x\), i.e., \(A_x = (I_x/S_x)/\Sigma I/S\).

B. First principle calculations

The theoretical density of states of GaN was obtained using first principle calculations. Although different exchange-correlation functions qualitatively yield trustworthy electronic structures, the absolute value can differ from several tenths of an electron volt to several electron volts. In order to obtain GaN electronic structure to great accuracy, various exchange-correlation functions are considered and compared: (1) Perdew-Burke-Ernzerhof using Generalized Gradient Approximation (GGA-PBE),\textsuperscript{13,25} (2) relativistic GGA-PBE (PBE relative),\textsuperscript{4} and (3) hybrid functionals of Heyd-Scuseria-Ernzerhof (HSE).\textsuperscript{26} GGA-PBE is used as a benchmark method in a wide variety of condensed matter physics problems and is the most widely used exchange-correlation functional in the modern density functional theory (DFT). However, it suffers from underestimating the bandgap and the binding. The screened hybrid functional, such as HSE06 used in this work, combines the nonlocal Hatree-Fock exchange with the GGA exchange, partially corrects the self-interaction problem of GGA, and is proven to yield the bandgap value\((E_g = 3.4\text{ eV})\) agreed well with experiments for a wide range of bulk materials. In this work, as implemented in the Vienna \textit{ab initio} simulation package (VASP), the mixing parameter of HSE06 was set to 0.30, and all the structures are fully relaxed with the \(k\)-point meshes 5 \(\times\) 5 \(\times\) 3 in HSE06 methods. The cutoff energy of the plane-wave was set to be 450 eV. The convergence criteria for the energy change and maximum force in all calculations were 1.0 \(\times\) 10\textsuperscript{-5} eV and 0.01 eV \(\text{Å}\)\textsuperscript{-1}.

C. Modeling band bending effects on XPS valence band spectra

XPS is one of the most widely used techniques to characterize surface band bending of III-nitride materials; an energy diagram for surface BB calculation directly using the VBM to Fermi energy
separation is shown in Fig. 1, where BB is calculated as follows:

$$BB = E_g - (VBM - E_F)_{surf} - (E_F - E_C), \quad (1)$$

where $E_g$ is the bandgap of GaN, $(VBM - E_F)_{surf}$ is the VBM energy at the GaN surface, and $(E_F - E_C)$ is the gap of conduction band minimum (CBM) to the Fermi level.

In the XPS experiment, $(VBM - E_F)$ was measured at a take-off angle (TOA) with respect to sample surface) of 85°, with the largest photoelectron detection depth ($\lambda$) of 2.6 nm, using the TPP-2M method in NIST’s database. Obviously, the valence band maximum is bent due to surface band bending effects, as shown in Fig. 1. In this case, the observed valence band spectrum is constituted by integrating the true spectrum from each depth point along the bent VBM. Therefore, sharp upward band bending results in apparent increases in $(VBM - E_F)_{XPS}$ relative to the $(VBM - E_F)_{surf}$, as shown in Fig. 1. So we have to derive the actual $(VBM - E_F)_{surf}$ by subtracting VBM increases $(\Delta E_v)$ due to band bending so that we can correctly evaluate the surface BB value,

$$(VBM - E_F)_{surf} = (VBM - E_F)_{XPS} + \Delta E_v. \quad (2)$$

In order to evaluate the correction of the VBM resulting from the band bending effect at the GaN surfaces, a core level XPS spectrum as a function of the binding energy, from a layer of thickness $d$, is given as follows:

$$I_0(E(z), z) = \frac{b}{\pi \eta^2} \int_{-\infty}^{+\infty} e^{-\eta^2} \frac{1}{((b/S)^2 + (E - E_0 - x)^2)} dx, \quad (4)$$

where $S$ and $b$ are related to the Gaussian and Lorentzian broadening in the XPS experiment, $E$ is the binding energy, and $E_0$ denotes the binding energy of the core level.

Thus, when considering quadratic depletion approximation on the surface of n-GaN. In the depletion approximation, the potential, $\Phi(z)$ within a surface depletion region of width $W$, is given by

$$\Phi(z) = \Phi_s(1 - z/W)^2. \quad (5)$$

The surface potential is $\Phi_s = \frac{qN_dW^2}{\epsilon_{GaN}}$, which could stand for assumed BB at the surface, where $q$ is the electronic charge, $N_d$ is the doping density, and $\epsilon_{GaN}$ is the dielectric constant of GaN and here is assigned to 10.4. When surface band bending is not negligible on the scale of the escape depth of photoelectrons, the binding energy of core level $E_0$ should be treated as a function of depth $z$ to be $E_0(z)$,

$$E_0(z) = E_i + e(\Phi_s - \Phi(z)), \quad (6)$$

where $E_i$ is the true photoelectron core level position at the surface.

Combining Eqs. (3)–(6), we could model a core level spectrum for n-GaN dependence on the photoemission detection depth in which we assume the surface electric potential $\Phi_s$. This procedure is repeated to find the most suitable surface potential at the GaN surface that achieves the experimental band bending from the VBM energy of $(VBM - E_F)_{XPS}$. Then, the true value of BB could be derived from the surface potential $\Phi_s$.

III. RESULTS, ANALYSIS, AND DISCUSSION

Figure 2 shows the XPS results for the valence band spectra and the Ga 3d core level of different Si doped GaN measured at near
normal emission. The Ga 3d peaks are deconvoluted into five bonding components. Specifically in Fig. 2, the interphase means an intermediate phase between Ga–N and Ga–O, according to Ref. 30. Commonly, the binding energy of Ga–N referenced to the Fermi level at surface (Ga\textsubscript{d} − E\textsubscript{F})\textsubscript{surf}, after subtracting the (Ga\textsubscript{d} − VBM)\textsubscript{bulk} recognized as an intrinsic property of a given material, was used to determine surface band bending in ARXPS, whereas the surface band bending obtained from the VBM to Fermi level separation (VBM − E\textsubscript{F})\textsubscript{surf} is the most direct and reliable way. 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The methodology of extracting the accurate valence band position using Kraut’s method is demonstrated in Figs. 3(a)–3(d). Comparing the positions of spectral features (such as peak 1 and peak 2 as shown in Fig. 2) with those of a hybrid DFT VB DOS which has been suitably broadened (supplementary material), an extremely good agreement was observed for GaN with an Si-doped density of \(1.4 \times 10^{19} \text{ cm}^{-3}\). The HSE VB DOS broadened because the VB DOS was convolved by a suitable spectrometer response function. It would suggest that the VBM could be precisely determined by fitting the valence-band spectral feature to the broadened theoretically calculated VB-DOS using DFT with suitable functionals. Figure 3(b) shows the accurate determined VBM value \(E_v\) of GaN with three Si-doped densities. When fitting is carried out over the valence band edge \(E_{\text{min}} \sim 5 \text{ eV}\), a fitting interval is ended at energy \(E_{\text{max}} \sim 4 \text{ eV}\), which is below the energy of the first VB peak. \(E_{\text{min}}\) and \(E_{\text{max}}\) are the boundaries of the fitting interval, as shown in Eq. (9). In this case, to obtain a precise VBM, a bare distortion of the VB leading edge spectral from occupied surface states and an accurate prediction on the spectrometer response function are always required. However, the fitting results show that the estimates of VBM depend sensitively on \(E_{\text{max}}\) for the three Si-doped GaN, which implies that the convolved VB DOS could not predict the detailed shape of the XPS VB leading edge. While as shown in Fig. 3(a), the well matching of broadened HSE spectra and XPS VB spectra ensures that we could achieve an accurate determination of the VBM by comparison of the positions of the spectral feature with those of a calculated VB DOS which has suitably been broadened. Therefore, different from band leading edge fitting, we further extend the fitting region to include the valence band feature spectrum. An adjusted fitting maximum energy domain over the first VB peak feature \((E_{\text{max}} = 7.5 \text{ eV})\) is used to achieve the feature fitting. When the fitting interval is ended at the energy \((E_{\text{max}})\) over \(4–7.5 \text{ eV}\), a nearly stable variation of the fitting results \((E_v)\) is observed, confirming that the feature of the first peak in the XPS spectrum matches well with the broadened DOS feature predicted in band structure calculations and an accurate VBM could be determined by using the feature fitting method. Comparing the linear extrapolations in Fig. 2 to the feature fitting results enables us to determine that linear extrapolation underestimates the VBM position by \(-0.4 \text{ eV}\). It is also clearly seen that the estimation of VBM depends sensitively on the fitting region within the VB leading edge. In Figs. 3(c) and 3(d), we show the closer look of the fitting curve and the broadened VB-DOS curve with the corresponding \(E_v\) value in different fitting regions. Meanwhile, the value of figure-of-merit \(\chi^2\) with the same energy region of \(-5 \text{ to } 3 \text{ eV}\) is seen. These comparisons reveal that the leading edge fitting process could be extremely sensitive and might be disturbed by the slight inaccuracy of the Lorentzian broadening or other smaller surface state signals in the valence band edge. The extra signals within the band edge region imply occupied surface states, usually associated with the special surface electronic structure. This surface state signal is further certified by specific in situ Ar s+ ion treatment, as shown in more detail below. However, the precise determination of VBM from the spectral feature fitting demonstrates that this method to extract VBM is robust and does not suffer from relative inaccuracies, especially as the valence-band edge fitting is not suitable. Therefore, we could determine upward surface band bending of \(0.58, 1.21,\) and \(1.10 \text{ eV (±0.03 eV)}\) with three increased Si doped GaN when the bandgap of GaN was assigned to \(3.4 \text{ eV}\) and the separation between the Fermi level and conduction band minimum (CBM) was given to \(0.02, -0.03,\) and \(-0.05 \text{ eV}\), respectively.

Clearly, for higher Si-doped density, the Ga polar \(n\)-GaN presents a smaller separation of VBM to Fermi energy and more upward surface band bending. In this case, we have to consider the overestimation of the VBM value by XPS valence band measurements with upward band bending, as shown in Fig. 1. Ignoring any chemical shift, the observed XPS VB spectrum can be seen as integrating the bulk spectrum taken from each depth (exponentially reducing in intensity) along with the energy shift due to upward surface band bending. Therefore, the experimental photoelectron intensity peak is expected to shift to higher energy and the surface VBM to Fermi level separation is overestimated, as shown in the inset of Fig. 4.

According to Eqs. (3)–(6) as shown above, we have modeled the XPS measured spectra for the largest photoelectron detection depth (~8 nm for GaN material) with the quadratic depletion approximation. Then, we tested several different surface potential until the model value of surface band bending was in agreement with that derived from the fitting VBM value. A VBM correction by \(-0.45 \text{ eV}\) was determined for high Si-doped density GaN of \(1.4 \times 10^{19} \text{ cm}^{-3}\), derived from the best match to the model core level position with ~8 nm detection depth (supplementary material). In Fig. 4, we show the Poisson calculations of the band profile assuming an upward surface band bending of \(1.10 \text{ eV}\) determined from XPS and of \(1.55 \text{ eV}\) after VBM correction. The corrected band bending of \(1.55 \text{ eV}\) for high Si-doped \(n\)-GaN is in good agreement with the value of \(1.47 \text{ eV}\) measured by Barbet et al. for an Si-doped density of \(1.0 \times 10^{19} \text{ cm}^{-3}\) when using a more surface sensitive technique of Kelvin force microscopy. Moreover, as shown in Table I, a constant energy separation \(E_s^{\text{GaN}} - E_{\text{F}}^{\text{GaN}}\) between the Ga–N bonding and the VBM as

![FIG. 4](https://example.com/figure4.png)
### Table I. Energies relevant to the determination of surface band bending and the Fermi level pinning position relative to the CBM in n-GaN surface with three Si-doped densities.

| Doping density (cm$^{-3}$) | $E_V$ (feature fitting) (eV) | $E_{CL}$ ($E_{CL} - E_V$) (eV) | $E_F$ ($E_F - E_C$) (VBM correction) (eV) | $\Delta E_V$ (surface band bending after VBM correction) (eV) | Fermi level position (relative to CBM) (eV) |
|---------------------------|-----------------------------|-------------------------------|-------------------------------------|-------------------------------------|-------------------------------------|
| $8 \times 10^{17}$        | 2.79 ± 0.03                 | 20.04                         | 17.25                               | −0.03                               | −0.09                               | 0.67                                 | 0.70 |
| $4 \times 10^{18}$        | 2.21 ± 0.03                 | 19.46                         | 17.25                               | 0.02                                 | −0.26                               | 1.48                                 | 1.46 |
| $1.4 \times 10^{19}$      | 2.35 ± 0.03                 | 19.64                         | 17.29                               | 0.05                                 | −0.45                               | 1.55                                 | 1.50 |

17.25–17.29 eV has been derived from the Ga 3d and VBM value for the three different Si-doped samples. This value differs substantially from that determined earlier using band edge fitting to determine the VBM ($E_{GaN}^{3d} - E_{GaN}^{V} = 17.76$ eV), possibly because of the presence of uncertainty spectra broadening or extra surface state signals in the band edge. As shown in Table I, the observed amplitude of upward band bending indicates that the Si doping level would influence the GaN surface electronic property and band bending is extreme for the highly Si-doped GaN sample. As a result, the overestimation of the VBM to Fermi-level separation and underestimation of the Fermi level position relative to CBM by XPS due to the band bending effect will be more severe for the higher Si-doped case.

The surface band strongly bends upward for high Si-doped n-GaN samples, implying that negatively charged surface states (e.g., Ga vacancy detects, $V_{Ga}$) might enhance the extent of surface electron depletion and induce more internal ionized states. Moreover, it has been shown that Ga vacancy has relatively low formation energy in n-type GaN and usually acts as a compensating center to form an acceptor-type defect.$^{11–13}$ Typically, for n-type GaN, the increase in Si-doped density usually leads to the increase in the concentration of the Ga vacancy. Otherwise, the Ar$^+$ ion beam bombardment has been studied for cleaning the C and O contaminants at the GaN surface and found preferential sputtering of N, leading to the monotonic increase in the Ga/N ratio.$^{32}$ In order to explore surface band bending of n-GaN dependence on the surface structures and further identify the microscopic nature of the Si doping density influence on surface band bending, we carried out in situ Ar$^+$ ion beam bombardment on the three Si-doped GaN to clean the C and O contaminants from the GaN surface. Valence band spectra and the atomic composition of Ga, N, and O are analyzed to examine the effects of Ar$^+$ surface treatment.

Focusing now on Fig. 5(a), it is apparent that after different Ar$^+$ treatment times, the first peak shifts to upper binding energy for high Si-doped GaN, while the inverse trend is observed for low Si-doped GaN. This difference implies that there exist different surface structure properties on n-GaN surface, leading to discrepant correlation associated with the band bending and Si-doping density. In addition, there is a substantially weaker feature in the

![Fig. 5](https://example.com/fig5.png)
valence band tail of about \( \sim 0.5 \) eV below \( E_v \), which may imply that enhanced surface states exist in these energy regions. These surface state signals would further result in a deteriorative VBM value through band edge fitting (not shown here) or linear extrapolation methods.\(^7\) Figures 5(b) and 5(c) show the feature fitting results in the case of high Si-doped GaN after 30 s \( \text{Ar}^+ \) treatment as \( E_{\text{max}} = 4.5 \) eV and \( E_{\text{max}} = 12.5 \) eV. For both cases, a relatively stable VBM value (2.45–2.47 eV) is observed, barely influenced by the surface state signals near the valence band edge. These results demonstrate that VBM determination by the feature fitting method would not be disturbed by VB DOS inaccuracies associated with the contribution from the surface state. Therefore, for the \( n \)-GaN surface after the \( \text{Ar}^+ \) ion is processed, surface band bending would be determined by the accurate VBM relative to the Fermi level value from feature fitting after the band bending correction (as discussed above).

The correlation between the accurately expected band bending and the Ga/N ratio and O–Ga concentration determined from XPS measurements for various doped GaN after \( \text{Ar}^+ \) treatment is shown in Figs. 6(a) and 6(b). The Ga–N components are from Ga 3d spectra, N–Ga components are from the N 1s, and O–Ga components are from the O 1s spectra (supplementary material). Apparently, the higher Si-doped GaN surface shows a lower Ga/N ratio, indicating more likely the presence of near surface acceptor-type Ga-vacancies. These acceptor-type states may partly account for the increased upward band bending for high-doped \( n \)-GaN. The native defect level related to Ga vacancy in GaN could generate a deep acceptor state at shallower energy position.\(^11\) While for the most relevant Ga-polar GaN surface, various surface states such as gallium adatom, nitrogen adatom, gallium vacancy, gallium vacancy structures in a clean surface, and also oxidized and/or metal-rich surfaces would exist, depending on the surface preparation and stoichiometry. Also the energy level of Ga vacancy at the GaN surface is always different from the native defect level in the GaN bulk.\(^12\) For surface states of Ga vacancy, the energy location is about 0.3 and 1.4 eV above the VBM, as shown in Ref. 34. After \( \text{Ar}^+ \) treatment, it is noticed that the Ga/N ratio is increased, suggesting that the \( \text{Ar}^+ \) ion bombardment appears to preferential sputter N and change the near-surface stoichiometry, especially for high-doped GaN, which indicates a slightly decreased upward band bending. However, for low Si-doped GaN, \( \text{Ar}^+ \) ion treatment is found to induce a small loss of N and an increased upward band bending, which appears to be associated with the increased Ga/N ratio.

On the other hand, oxygen coverage on the GaN surface has been found to strongly influence the Fermi pinning position and surface band bending. Both larger band bending and smaller band bending have been observed at the Ga-polar \( n \)-GaN(0001) surface due to the oxygen chemisorption contamination or oxidation.\(^4\)\(^,\)\(^8\)\(^,\)\(^9\)\(^,\)\(^10\)\(^,\)\(^13\) Specifically, correlation of Ga–O concentrations and surface band bending at the Si-doped GaN surface is shown in Fig. 6(b). Apparently, more Ga–O components are observed on the low-doped GaN surface. Compared to high doped GaN, relatively more Ga–O bonding coverage appears to be one of the causes of small upward band bending for low Si-doped GaN, which suggests that oxygen coverage might passivate surface defect from the Ga-vacancy and reduce the upward band bending. After \( \text{Ar}^+ \) ion treatment, a significant decrease in the Ga–O concentration and increased upward band bending are observed, which further demonstrates that smaller band bending appears in the oxidized and contaminated GaN with the low Si-doped level. In contrast to these results, even though the Ga–O component is reduced with \( \text{Ar}^+ \) ion treatment, the upward band bending does not show a corresponding increase for higher doping GaN. It is suggested that the Fermi level position is governed by the relatively small Ga/N ratio and might be attributed to the Ga-vacancy surface defect. Furthermore, the Si-doped density likely induces a change in the material stress field as the \( n \)-GaN grows on the Si substrate. So a combined polarization effect should be explored on surface band bending of \( n \)-GaN when depending on Si-doped density in the future.

For the Ga-polar \( n \)-GaN surface, upward band bending is always observed. This is mainly because of the negative bound polarization charge existing on the Ga-polar GaN faces, which have been indicated by previous studies.\(^4\)\(^,\)\(^9\)\(^,\)\(^10\) Large polarization in GaN materials induces bound polarization charges on surfaces, which results in a distribution of compensating electron states to satisfy the charge neutrality.\(^4\) These compensating states, including internal ionized states and surface states, affect the internal electric field near the surface and play a crucial role in electric properties of these materials. The surface states can be surface vacancies, dangling bonds, structural defects, surface oxides, or adsorbates, which intimately depend on the specific deposition and processing conditions. However, identifying these states is always difficult. In this situation, we could not exactly know the surface structural defects on the GaN surface. By analyzing the XPS spectra of the GaN surface with different Si-doping densities, different

![FIG. 6. Correlation of surface band bending to the Ga/N ratio (a) and Ga–O% components (b) at the \( n \)-GaN surface with different \( \text{Ar}^+ \) ion treatments. The Ga/N ratio of the low doped GaN surface without \( \text{Ar}^+ \) treatment was set as 1 for reference with the values of other samples normalized to it.](image-url)
Ga/N ratios and oxidation components were observed to be dependent on the Si-doped density and Ar⁺ processing. Then, a rough prediction was made related to surface states of the Ga vacancy and surface oxides. Besides, we could not exclude other surface state effects (such as the continuously distributed surface states) influencing the band bending, but these effects are not discussed in this paper.

IV. CONCLUSION

In conclusion, we have achieved accurate determination of the VBM from XPS VB spectra combined with hybrid DFT valence band calculations. Distinct upward surface band bending in the Ga-polar n-GaN surface with different Si-doped levels and Ar⁺ ion treatment was derived after VBM band bending correction. Our results showed that the Fermi level pinned over the available doping density and showed 0.67 ± 0.03 eV and 1.55 ± 0.03 eV upward surface band bending for low and high Si-doped GaN, respectively. After in situ Ar⁺ ion treatment, different varying trends for band bending were observed to be dependent on the doping density. Large upward bending for high Si-doped n-GaN might contribute to a relatively small Ga/N ratio and more Ga-vacancies. This is in sharp contrast to the low doped one, with suppressed band bending and strong oxidation surface associated with a large Ga/N ratio. This work may provide helpful insights into understanding the physical mechanism that influences the band bending on the n-GaN surface and further aids in the issues of metal contact formation on different Si-doped n-GaN surfaces.

SUPPLEMENTARY MATERIAL

See the supplementary material for information on fitting, modeling, and analysis of the photoemission data.

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