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# Valence band offset of GaN/diamond heterojunction measured by X-ray photoelectron spectroscopy

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ABSTRACT

XPS was used to measure the energy discontinuity in the GaN/diamond heterostructure. The valence band offset (VBO) was determined to be $0.38 \pm 0.15$ eV and a type-II heterojunction with a conduction band offset (CBO) of $2.43 \pm 0.15$ eV was obtained.



## 1. Introduction

Gallium nitride (GaN) and its alloys with indium and aluminum nitride are of great interest in recent years due to the successful development of visible and ultraviolet light emitting diodes (LEDs) [1], blue/violet laser diodes [2], and high-power electronic devices [3]. Among this (Al, In, Ga) N semiconductor system, GaN has shown to be a very suitable material for applications in high-frequency, high-power, and/or high-temperature semiconductor devices. However, the full realization of superior properties of GaN is limited by the thermal conductivity of the substrates on which GaN is grown. Commercial substrates for GaN epilayers include sapphire, silicon, and silicon carbide, whose thermal conductivities are between 0.4 and 4 W/K cm. Nowadays, GaN-based electronic devices demonstrate typical power density of 10 W/mm at 10 GHz [4,5]. Further, the state of the art of GaN HEMTs grown on SiC is as high as 32 W/mm [6]. Owing to these high power levels, thermal issues become highly critical. As a material with the highest thermal conductivity (~22 W/K cm at room temperature), diamond substrate could be one of the best candidates for GaN growth. Moreover, diamond has other excellent mechanical and electronic properties, such as high hardness, wide band-gap, chemical inertness, and high optical transparency from ultraviolet to infrared range, which make the GaN/diamond system more attractive. Up to now, the GaN/diamond system, either GaN grown on diamond substrate or diamond grown on GaN, has already been studied by lots of groups [7–12]. As a direct and powerful tool for measuring the VBO of heterojunctions [13–17], X-ray photoelectron spectroscopy (XPS) was used to measure the VBO in GaN/diamond heterojunction in this letter.

## 2. Experiments

To determine the VBO value, three samples were used: a 400 nm-thick GaN layer grown on *c*-plane sapphire substrate, a 2 mm-thick single-crystal diamond synthesized at high temperature and high pressure (HTHP), and a ~5 nm-thick GaN grown on diamond. Both of the GaN films were grown by horizontal low-pressure metal–organic chemical vapor deposition (LP-MOCVD). The crystal structures were characterized using the high-resolution X-ray diffraction (HRXRD) apparatus at Beijing Synchrotron Radiation Facility (BSRF). The incident X-ray beam is monochromized to 0.154791 nm by a Si (1 1 1) monocrystal. According to the XRD results, single-crystal diamond (4 0 0) and wurtzite GaN (0 0 2) were obtained. Both diamond and GaN in our experiment are undoped, while the GaN films are unintentionally *n*-type doped. The XPS measurements were carried out on a PHI Quantera SXM instrument with Al Kα (energy 1486.6 eV) as the X-ray radiation source,

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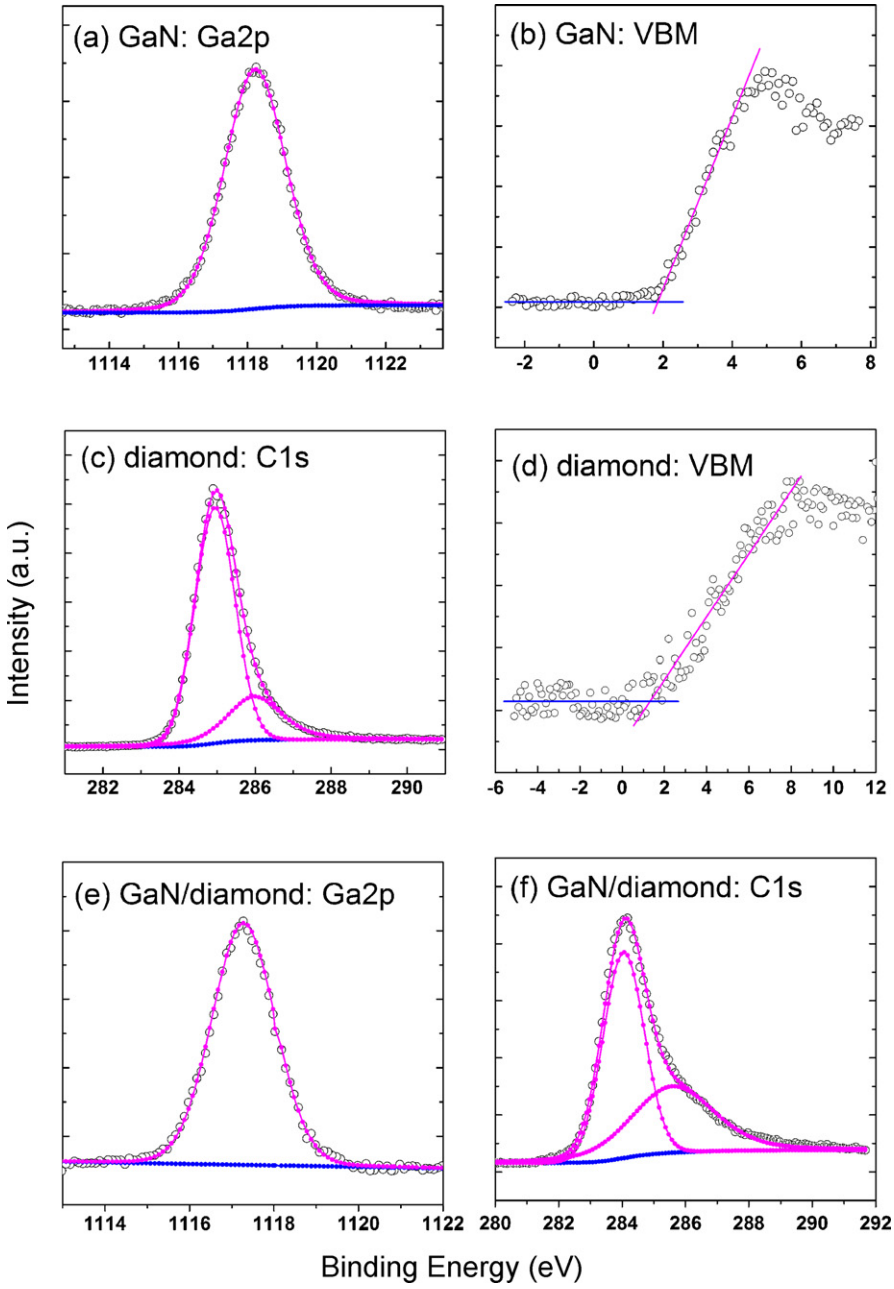


**Fig. 1.** Ga 2p CL spectra for (a) GaN and (e) GaN/diamond, C 1s CL spectra for (c) diamond and (f) GaN/diamond and VB spectra for (b) GaN and (d) diamond. Experimental data points are fitted by Voigt (mixed Lorentzian–Gaussian) line shapes after application of a Shirley background, as summarized in Table 1.

which had been carefully calibrated utilizing work function and Fermi energy level ($E_F$). The total energy resolution of this XPS system is about 0.5 eV and the accuracy of the observed binding energy is within 0.03 eV after careful calibration. In order to compensate the charge effect, the XPS spectra were calibrated by the C 1s peak (284.8 eV). More details can be seen in our previous work [16].

## 3. Results and discussion

According to Kraut et al. [18], the VBO ($\Delta E_v$) can be calculated from the formula

$$\Delta E_V = \Delta E_{CL} - (E^{GaN}_{Ga\,2p} - E^{GaN}_{VBM}) + (E^{diamond}_{C\,1s} - E^{diamond}_{VBM}) \quad (1)$$

where $\Delta E_{CL} = (E^{GaN}_{Ga\,2p} - E^{diamond}_{C\,1s})$ is the energy difference between Ga 2p and C 1s core levels (CLs), which are measured in the GaN/diamond heterojunction. $(E^{GaN}_{Ga\,2p} - E^{GaN}_{VBM})$ and $(E^{diamond}_{C\,1s} - E^{diamond}_{VBM})$ are the GaN and diamond bulk constants respectively, measured from the two corresponding thick films. VBM stands for valence band maximum. The Ga 2p CL peaks, the C 1s CL peaks, and the valence band photoemission are shown in Fig. 1.

To reduce the undesirable effects of surface oxidation and contamination, the samples were cleaned by $Ar^+$ bombardment at a low sputtering to avoid damages to the samples. As seen in Fig. 1, we attribute the single peak located at 1118.25 eV in Fig. 1(a) and that located at 1117.28 eV in Fig. 1(e) to the Ga–N bonding configurations. They are quite symmetric, indicating the uniform bonding state in either thicker GaN or GaN/diamond samples. In the thicker diamond XPS spectrum, the lower-binding energy component (284.9 eV) and the higher-binding energy component (286.00 eV) are considered to be C–C bonding and C–O bonding, respectively [16,19,20], as shown in Fig. 1(c). The VB XPS spectra for the thicker GaN and diamond samples are shown in Fig. 1(b)

**Table 1**
XPS CL spectra fitting results and VBM positions obtained by linear extrapolation of the leading edge to the extended base line of the VB spectra.

| Sample | State | Binding energy (eV) | Bonding | FWHM (eV) |
|---|---|---|---|---|
| Diamond | C 1s | 284.90 | C–C | 1.21 |
| | | 286.00 | C–O | 1.89 |
| | VBM | 1.32 | | |
| GaN | Ga 2p | 1118.25 | Ga–N | 1.09 |
| | VBM | 1.84 | | |
| GaN/diamond | Ga 2p | 1117.28 | Ga–N | 1.32 |
| | C 1s | 284.07 | C–C | 1.41 |
| | | 285.67 | C–O | 2.68 |

and (f) [16,21,22]. All the peak parameters deduced from Fig. 1 are summarized in Table 1 for clarity.

As illustrated in Table 1, the energy difference between Ga 2p and VBM of the GaN film ($E^{GaN}_{Ga\,2p} - E^{GaN}_{VBM}$) is 1116.41 eV, which is comparable to the results reported by Martin et al. [23]. The VBO values can be calculated by substituting those measured values in Table 1 into Eq. (1). The average GaN/diamond VBO ($\Delta E_v$) is $0.38 \pm 0.15$ eV. The CBO ($\Delta E_C$) is given by the formula $\Delta E_C = (E_g^{diamond} - E_g^{GaN}) - \Delta E_V$. So the band lineup can be determined, with a conduction band offset (CBO) of $2.43 \pm 0.15$ eV, as shown in Fig. 2.

The reliability analysis of the measured result is provided by considering possible factors that could impact the experimental results, such as band bending effect and strain-induced piezoelectric effect [23]. According to Wu et al. [24], the measured binding energy differences in XPS spectra between the cation CLs and the VBM positions are considered to be material constants, which are independent of crystal polarity and band-bending. So the systematic error related to band bending is expected to be much smaller than the average standard deviation of 0.15 eV given above. Due to the large lattice mismatch between GaN and diamond [10], the critical thickness for GaN/diamond is estimated to be less than 1 monolayer, which is much smaller than the thickness of heterojunction GaN overlayer, so it can be approximately treated as completely relaxed. The strain relief mechanisms caused by dense networks of threading defects existing in nitride epitaxial layers [23] also make the strain-induced piezoelectric effect negligible here. Another factor that should be considered when analyzing the XPS data is the spontaneous polarization, which does exist in the strong polar semiconductors. In order to eliminate this influence and obtain a relatively "intrinsic" VBO by XPS, a modification method based on a modified self-consistent calculation has been proposed in our previous work [25]. Moreover, for heterojunctions formed between three semiconductors (A, B, and C), if $\Delta E_v$ (A–B) and $\Delta E_v$ (B–C) are determined, $\Delta E_v$ (A–C) will also be specified, which is called transitive property of $\Delta E_v$ [26]. From the reported experiment data, $\Delta E_v$ (InN-diamond) is $0.39 \pm 0.08$ eV [16], $\Delta E_v$ (InN-GaN) is ~0.78 [24] or ~0.9 eV [27], so $\Delta E_v$ (GaN-diamond) can be deduced to ~0.39 or ~0.51 eV. They are comparable to our calculated result within the experimental errors, which further confirm the reliability of the experimentally obtained VBO value.

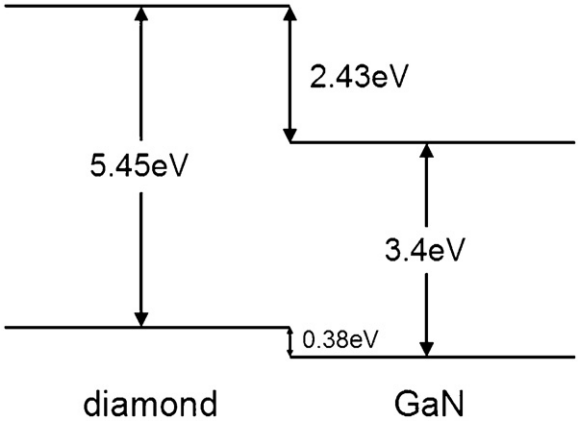


**Fig. 2.** Schematic energy band diagram of GaN/diamond heterojunction. A type-II band heterojunction is formed in the staggered arrangement.

## 4. Conclusion

In summary, the valence band offset of the GaN/diamond heterojunction has been measured by XPS. A type-II band alignment with a valence band offset of $\Delta E_v = 0.38 \pm 0.15$ eV and conduction band offset of $\Delta E_c \sim 2.43$ eV was obtained.

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