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Band alignment between GaN and ZrO₂ formed by atomic layer deposition

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The band alignment between Ga-face GaN and atomic-layer-deposited ZrO₂ was investigated using X-ray photoelectron spectroscopy (XPS). The dependence of Ga 3d and Zr 3d core-level positions on the take-off angles indicated upward band bending at GaN surface and potential gradient in ZrO₂ layer. Based on angle-resolved XPS measurements combined with numerical calculations, valence band discontinuity ΔE_V of 1 ± 0.2 eV and conduction band discontinuity ΔE_C of 1.2 ± 0.2 eV at ZrO₂/GaN interface were determined by taking GaN surface band bending and potential gradient in ZrO₂ layer into account. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4890470>]

The use of ultrathin high-*k* ZrO₂ as possible gate oxide candidates for GaN-based heterostructure devices such as high electron mobility transistors (HEMTs) has been evaluated recently. Excellent electrical characteristics of GaN metal-insulator-semiconductor (MIS) HEMTs utilizing ZrO₂ as gate dielectrics have been reported.^{1–7} One of the main parameters which have great impact on the properties of GaN-based MIS structures is the band alignment between gate dielectric layer and GaN layer. For example, to maintain low gate leakage and small effective oxide thickness, a large conduction band discontinuity ΔE_C (at least 1 eV) between ZrO₂ dielectric and GaN is required. However, so far, ΔE_C at the ZrO₂/GaN interface has not been experimentally investigated. Among the different methods of determining band alignment, the x-ray photoelectron spectroscopy (XPS), which was first reported by Kraut⁸ on the estimation of valence band discontinuity ΔE_V of Ge/GaAs heterojunctions, is believed to provide high accuracy. In this Letter, ΔE_C at the interface between atomic-layer-deposited (ALD) ZrO₂ and Ga-face GaN was estimated by XPS measurements. Instead of using the conventional XPS measurement with a fixed take-off angle θ , which could be erroneous due to strong band bending at GaN surface and possible potential gradient existed in ZrO₂ dielectric layer, angle resolved XPS measurements combined with numerical calculations^{9–11} were carried out in this work to ensure a better prediction of ΔE_C at ZrO₂/GaN interface.

ZrO₂ with different thickness were deposited on GaN-on-sapphire substrates by using ALD. The un-doped GaN-on-sapphire wafers were grown by Metal Organic Chemical Vapor Deposition (MOCVD) using a commercial reactor. A GaN-on-sapphire and a 30 nm-thick ZrO₂ on GaN were used to obtain GaN and ZrO₂ bulk material properties, respectively. For the investigation of ZrO₂/GaN interface, samples with ~2 nm thick ZrO₂ on GaN surface was used. To deposit the ZrO₂ on GaN, the GaN-on-sapphire wafers were initially degreased for 10 min in acetone and subsequently in isopropyl alcohol (IPA). Before loaded into the ALD chamber,

samples were treated by buffered oxide etchant (BOE) solution to remove surface native oxide and then followed by a rinse in flowing de-ionized (DI) water. ZrO₂ dielectric layer was deposited by a Cambridge Nanotech Savannah ALD system. The tetrakis(diethylamino)-zirconium and H₂O were used as the precursors. Chamber pressure and substrate temperature were set at 0.6 Torr and 250 °C, respectively. During the deposition, sequential 400 ms and 40 ms pulse of H₂O and Zr sources were introduced into the chamber separately. After each pulse of gas, the chamber was purged with N₂ for 6 s to remove excess precursors and by-product gases. The XPS measurements were carried out using a monochromatic Al K α X-ray source of energy 1486.7 eV. The spectra are curve-fitted with a combination of Gaussian and Lorentzian line shapes using a Shirley-type background subtraction. All peaks were referenced to the C 1s peak at 284.6 eV to compensate for any variations in the peak core-level positions due to binding energy (BE) shift caused by surface charging. The schematic structure of the sample used for investigating the ZrO₂/GaN interface is shown in Fig. 1, where the photoelectron take-off angle is also defined as θ . In order to change the photoelectron escape depth (λ), the measurements were conducted under three different take-off angles (15°, 45°, and 75°). The λ can thus be defined as,

FIG. 1. A schematic cross-sectional diagram for GaN with ~2 nm ALD-ZrO₂ dielectric layer. The definition of take-off angle θ is also shown.

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FIG. 2. The measured (open circles) and fitted (lines) XPS Ga 3d (a) core-level spectra and Zr 3d (b) core-level spectra for 2 nm thick ZrO₂/GaN obtained at different take-off angles θ .

$$\lambda = \lambda_0 \sin \theta, \quad (1)$$

where λ_0 is the inelastic mean free path of photoelectrons.

Fig. 2 shows the Ga 3d and Zr 3d spectra obtained at different take-off angles for 2 nm thick ZrO₂/GaN sample. Ga 3d spectrum in Fig. 2(a) could be deconvolved into two components, corresponding to the Ga-N and Ga-O bonds, while Zr 3d_{5/2} and Zr 3d_{3/2} spin orbit split components are observed for Zr 3d spectrum as shown in Fig. 2(b). It can be seen that the Ga-N bond component of Ga 3d spectrum showed a trend to shift to lower binding energies with the

FIG. 4. A schematic band diagram showing the effect of the upward band bending at GaN surface on the evaluation of valence band discontinuity ΔE_V at ZrO₂/GaN interface by using angle-resolved XPS measurements. The potential gradient in ZrO₂ layer will bring in similar effect on the evaluation of ΔE_V . $q\Delta V_{ZrO_2}$ is the potential drop in ZrO₂ oxide layer.

decrease in θ , which indicates that there is strong upward band bending occurred at GaN surface. As a polar semiconductor, GaN surface is sensitive to fabrication process. Large polarization combined with possible surface Fermi-level pinning caused by surface defects and contaminations will bring

FIG. 3. (a) Ga 3d core-level and valence band spectra (VB) for bulk GaN. The difference between Ga 3d core-level (Ga-N bond) and VBM is 17.34 eV. (b) Zr 3d core-level and VB for bulk ALD-ZrO₂. The difference between Zr 3d core-level (Zr 3d_{5/2}) and VBM is 179.43 eV. The VBM is extrapolated from the intersection point between the leading edge of the valence band spectrum and the base line.

FIG. 5. Dependence of measured (open squares) and simulated (solid lines) BEs on take-off angles θ for (a) Ga-N bond from the GaN substrate layer and (b) Zr 3d_{5/2} from 2 nm-thick ZrO₂ dielectric layer.

TABLE I. Summary of parameters for band alignment between ALD-ZrO₂ and Ga-face GaN.

GaN ($E_{CL} - E_V$) _{bulk} (eV)	ZrO ₂ ($E_{CL} - E_V$) _{bulk} (eV)	$E_{CL}^{GaN}(i)$ at $\theta = 0^\circ$ (eV)	$E_{CL}^{ZrO_2}(i)$ at $\theta = 0^\circ$ (eV)	$q\Delta V_{ZrO_2}$ (eV)	GaN E_g (eV)	ZrO ₂ E_g (eV)	ΔE_V (eV)	ΔE_C (eV)
17.34	179.43	19.19	181.87	-0.4	3.4	5.6 ^a	1.0	1.2

^aRefs. 16 and 17.

in sharp surface band bending in GaN.^{12,13} Similar to Ga 3*d*, a shift of spectrum to lower binding energies with the decrease of θ is also observed for Zr 3*d*. This implies the existence of potential gradient in ZrO₂ oxide layer. Using the energy difference between Ga-N bond component of Ga 3*d* spectrum and Zr 3*d*_{5/2} spectrum at a fixed take-off angle θ shown in Fig. 2, the conventionally used XPS method for the evaluation of valence band discontinuity (ΔE_V) between ZrO₂ and GaN is summarized below⁸

$$\Delta E_V = [E_{CL}^{GaN}(b) - E_V^{GaN}(b)] - [E_{CL}^{ZrO_2}(b) - E_V^{ZrO_2}(b)] - \Delta E_{CL}, \quad (2)$$

$$\Delta E_{CL} = [E_{CL}^{GaN}(i) - E_{CL}^{ZrO_2}(i)], \quad (3)$$

where the subscripts CL and V denote the binding energy for the “core-level” and “valence band maximum (VBM)”, respectively. The bulk and interface binding energies are indicated by the notation (b) and (i), respectively. ΔE_{CL} is the binding energy difference between core-level positions from each side of the interface at a fixed take-off angle XPS measurement shown in Fig. 2. Predicted by Poisson’s equation, the amount of band bending, which is caused by the spatially varying electrostatic potential, is only depending on the distance from the surface.¹⁴ Therefore, the quantities ($E_{CL} - E_V$) for bulk GaN and ZrO₂ should be independent of band bending. The difference of binding energy between core-level and VBM of bulk GaN and ZrO₂ are shown in Fig. 3. The VBM of each sample is determined by extrapolating the leading edge of the valence band spectrum to the base line (the cross-over points in Fig. 3).¹⁵ Using binding energies of Ga-N bond and Zr 3*d*_{5/2} spectra as the core-levels for bulk GaN and ZrO₂, respectively, the corresponding binding energy differences between the core-level and VBM are thus determined to be 17.34 eV and 179.43 eV. It should be pointed out that, the accurate evaluation of ΔE_{CL} at ZrO₂/GaN interface could be influenced by band bending as indicated in Fig. 4. As shown in Fig. 4, the estimated ΔE_{CL} between ZrO₂ and GaN is highly relied on take-off angles and this will lead to uncertainties during the evaluation of ΔE_V . If there is a large band bending at the sample surface that affects the XPS results, correction is necessary for ΔE_{CL} . For the correction, to obtain the dependence of apparent binding energies E_{CL} on the take-off angles θ , numerical calculation on the effect of the surface bending at GaN surface and potential gradient in ZrO₂ layer on the core-level spectra will be considered. Details of the principle and calculation method can be found in Ref. 10.

The dependence of measured and simulated BEs on take-off angles θ for Ga-N bond from the GaN layer and Zr 3*d*_{5/2} spectra from a 2 nm-thick ZrO₂ on GaN are shown in Fig. 5. An internal potential drop of -400 meV in ZrO₂

layer, which provides a best fit between the measured and simulated binding energies, is obtained. The negative sign of the potential drop indicated that potential goes down in the ZrO₂ layer as the depth increases. To obtain a more accurate ΔE_{CL} at ZrO₂/GaN interface, binding energies E_{CL} for both Ga-N bond and Zr 3*d*_{5/2} spectra at $\theta = 0^\circ$ obtained from simulated binding energy curves as well as potential drop in ZrO₂ layer are considered, and Eq. (3) can be written as:

$$\Delta E_{CL} = [E_{CL}^{GaN}(i) - E_{CL}^{ZrO_2}(i)]_{\theta=0^\circ} + q\Delta V_{ZrO_2}, \quad (4)$$

where q is the elementary charge and $q\Delta V_{ZrO_2}$ is the potential drop in ZrO₂ layer. Combining Eqs. (2) and (4), a ΔE_V of 1 eV and ΔE_C of 1.2 eV at ZrO₂/GaN interface are, thus, estimated with a total error of ± 0.2 eV.¹⁰ A summary for the band alignment between GaN and ALD-ZrO₂ is given in Table I.

In conclusion, the band alignment between ALD-ZrO₂ and Ga-face GaN was experimentally evaluated by using XPS measurements. The core-level E_{CL} of the Ga 3*d* and Zr 3*d* decreased with the decrease of take-off angles suggesting a strong band bending occurred at GaN surface as well as the existence of potential gradient in ZrO₂ layer. ΔE_V of 1 eV and ΔE_C of 1.2 eV at ZrO₂/GaN interface were determined by taking into account of GaN surface band bending and gradient potential in ZrO₂ layer using angle-resolved XPS measurements combined with numerical calculations. The results suggest that ZrO₂ could serve as an excellent high- k insulator for both p and n-type carriers in GaN-based devices.

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