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<td>Author(s)</td>
<td>Ye, Gang; Wang, Hong; Ji, Rong</td>
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Band alignment of HfO$_2$/AlN heterojunction investigated by X-ray photoelectron spectroscopy

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The band alignment between AlN and Atomic-Layer-Deposited (ALD) HfO$_2$ was determined by X-ray photoelectron spectroscopy (XPS). The shift of Al 2p core-levels to lower binding energies with the decrease of take-off angles $\theta$ indicated upward band bending occurred at the AlN surface. Based on the angle-resolved XPS measurements combined with numerical calculations, valence band discontinuity $\Delta E_V$ of 0.4 $\pm$ 0.2 eV at HfO$_2$/AlN interface was determined by taking AlN surface band bending into account. By taking the band gap of HfO$_2$ and AlN as 5.8 eV and 6.2 eV, respectively, a type-II band line-up was found between HfO$_2$ and AlN. Published by AIP Publishing.

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The scaling of gate length is the most natural way to increase the operation frequency of the conventional AlGaN/GaN high electron mobility transistors (HEMTs). However, severe short-channel effects (SCEs) are observed for most of the scaled devices. To mitigate SCEs, a sufficiently high aspect ratio (gate length to barrier thickness) is needed. With the scaled devices, to date, few experimental results related to band alignment at the AlN/GaN interface has been reported. X-ray photoelectron spectroscopy (XPS) has been reported to be a direct and surface band bending into account. By taking the band gap of HfO$_2$ and AlN as 5.8 eV and 6.2 eV, respectively, a type-II band line-up was found between HfO$_2$ and AlN. Published by AIP Publishing.

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The band alignment between AlN and Atomic-Layer-Deposited (ALD) HfO$_2$ was determined by X-ray photoelectron spectroscopy (XPS). The shift of Al 2p core-levels to lower binding energies with the decrease of take-off angles $\theta$ indicated upward band bending occurred at the AlN surface. Based on the angle-resolved XPS measurements combined with numerical calculations, valence band discontinuity $\Delta E_V$ of 0.4 $\pm$ 0.2 eV at HfO$_2$/AlN interface was determined by taking AlN surface band bending into account. By taking the band gap of HfO$_2$ and AlN as 5.8 eV and 6.2 eV, respectively, a type-II band line-up was found between HfO$_2$ and AlN. Published by AIP Publishing.

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where $\lambda_0$ is the inelastic mean free path of photoelectrons. With the decrease of $\theta$ to shorten the probing depth, more sensitive analysis of chemical bonding states near the interface between HfO$_2$ layer and AlN substrate can be obtained.

Fig. 1 shows the Al 2$p$ and Hf 4$f$ spectra obtained at three different take-off angles of 15°, 45°, and 75° for 2 nm thick HfO$_2$/AlN. Al 2$p$ spectrum in Fig. 1(a) could be deconvolved into two components, corresponding to the Al-N and Al-O bonds, while Hf 4$f_{7/2}$ and Hf 4$f_{5/2}$ spin orbit split components are observed for the Hf 4$f$ spectrum as shown in Fig. 1(b). An intensity ratio of 4:3 and a spin orbit splitting around 1.7 eV is considered between Hf 4$f_{5/2}$ and Hf 4$f_{7/2}$ spectrum during fittings. The existence of oxygen related chemical bonding states of Al 2$p$ spectrum could be attributed to the parasitic oxidation of AlN surface after cleaning during ALD process.\(^{17,18}\) It is obvious from Fig. 1(a) that the Al-N bond of Al 2$p$ spectrum shows a trend to shift to lower binding energies with the decrease of $\theta$, which indicates a strong upward band bending occurred at AlN surface. As a polar semiconductor, AlN surface is sensitive to fabrication process. Large polarization combined with possible surface Fermi-level pinning caused by surface defects could bring in sharp surface band bending in AlN.\(^{19}\) Using the core-level binding energy of Al-N bond of Al 2$p$ spectrum and Hf 4$f_{7/2}$ spectrum at a fixed take-off angle $\theta$ shown in Fig. 1, the conventionally used XPS method for the evaluation of valence band discontinuity ($\Delta E_{\text{CL}}$) between HfO$_2$ and AlN is summarized below

\[
\Delta E_{\text{CL}} = \left[ E_{\text{CL}}^{\text{AlN}}(b) - E_{\text{V}}^{\text{AlN}}(b) \right] - \left[ E_{\text{CL}}^{\text{HfO}_2}(b) - E_{\text{V}}^{\text{HfO}_2}(b) \right] - \Delta E_{\text{CL}},
\]

(2)

\[
\Delta E_{\text{CL}} = \left[ E_{\text{CL}}^{\text{AlN}}(i) - E_{\text{CL}}^{\text{HfO}_2}(i) \right],
\]

(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 notations (b) and (i), respectively. $\Delta E_{\text{CL}}$ 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. 1. As predicated using Poisson’s equation, the spatially varying electrostatic potential bends all of the energy levels that only depends on the distance from the surface. For bulk AlN, although $E_{\text{CL}}$ and $E_{\text{V}}$ are bent differently at different distance from surface due to the band bending, $E_{\text{CL}}$ and $E_{\text{V}}$ are bent by the same amount at the same distance. Therefore, the difference between $E_{\text{CL}}$ and $E_{\text{V}}$ remains unchanged for AlN regardless of distance. This makes $E_{\text{CL}}(\text{Al-N})-E_{\text{V}}(\text{Al-N})$ independent of band bending. The difference in binding energies between core-level and VBM of bulk AlN and HfO$_2$ is shown in Fig. 2. 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. 2). By using binding energies of Al-N bond and Hf 4$f_{7/2}$ spectra as the core-levels for bulk AlN and thick HfO$_2$ layer, respectively, the corresponding binding energy difference between the core-level and VBM are thus determined to be 70.69 eV ($E_{\text{CL}}^{\text{AlN}}(b) - E_{\text{V}}^{\text{AlN}}(b)$) and 14.06 eV ($E_{\text{CL}}^{\text{HfO}_2}(b) - E_{\text{V}}^{\text{HfO}_2}(b)$).

It should be pointed out that the accurate evaluation of $\Delta E_{\text{CL}}$ at HfO$_2$/GaN interface determined by a fixed take-off angle measurement could be influenced by band bending as indicated in Fig. 3. As shown in Fig. 3, the estimated $\Delta E_{\text{CL}}$
between HfO₂ and AlN is highly relied on the take-off angles and this will lead to uncertainties during the evaluation of \( \Delta E_V \) determined by Eqs. (2) and (3) when the XPS measurement is taken under a fixed take-off angle. If a large band bending at the sample surface that affects \( \Delta E_{CL} \) determination at the interface, correction of \( \Delta E_{CL} \) is necessary.

In brief, for a layer of thickness \( d \), the intensity \( I(E) \) of a core-level spectrum as a function of the binding energy \( E \) can be described by\(^{15,16} \)

\[
I(E) = \int_0^d I_0(E,z) \exp \left( -\frac{z}{L} \right) dz, \tag{4}
\]

where \( z, \lambda, \) and \( I_0(E,z) \) are the depth from the surface, the escape depth of the photoelectrons, and the spectrum generated at each depth point, respectively. For simplicity, \( I_0(E,z) \) for a single spin orbital can be given by the pseudo-Voigt function in the following form:\(^{15} \)

\[
V(E,z) = I_{00} \left[ z \exp \left( -\frac{z}{2} \right) \frac{(E - E_0)^2}{(F/2)^2} \right] \frac{1}{1 + \frac{(E - E_0)^2}{(F/2)^2}}, \tag{5}
\]

where \( I_{00}, \alpha, E_0, \) and \( F \) are the intensity, the ratio of the Gaussian function, the binding energy of the core-level, and the actual full width at half maximum (FWHM), respectively. If surface band bending cannot be ignored on the scale of the escape depth of photoelectrons, \( E_0 \) should be treated as a function of depth \( z \). The \( F \) is assumed to be a sample dependent constant. While the \( \alpha \) is fixed to 0.73 for Al 2p, \( I_0(E,z) \) is given by a weighted combination of two pseudo-Voigt-function components by taking the spin-orbit splitting of 0.41 eV for Al 2p.\(^{15,16} \) As schematically outlined in Fig. 4, the observed spectrum is obtained by integrating the true spectrum from each depth point along the bent core-levels through Eq. (4). Therefore, surface upward band bending in AlN results in the increase of \( E_{CL} \) and FWHM with the increase of \( \theta \) to extend the probing depth. For the correction of the measured \( \Delta E_{CL} \), in order to obtain the dependence of apparent binding energy values \( E_{CL} \) on the take-off angles, numerical calculations considering the effect of surface band bending in AlN on the core-level spectra are conducted. Assuming that the internal electric field in the AlN substrate layer is uniform, the internal electric field can be obtained by fitting the apparent binding energy and FWHM.\(^{15,16} \) The dependence of measured and simulated binding energies on the take-off angles \( \theta \) for Al-N bond of 2 nm-thick HfO₂/AlN is illustrated in Fig. 5. To obtain a more accurate \( \Delta E_{CL} \) at HfO₂/AlN interface, binding energies \( E_{CL} \) for Al-N bond at \( \theta = 0^\circ \) obtained from simulated binding energy curves should be considered, and Eq. (3) can be written as

\[
\Delta E_{CL} = E_{CL}^{GaN}(i) - E_{CL}^{HfO2}(i). \tag{6}
\]

Combining Eqs. (2) and (6), a \( \Delta E_V \) of 0.4 eV at HfO₂/AlN interface is thus estimated with a total error of ±0.2 eV. A summary for the band alignment between AlN and ALD-HfO₂ is given in Table I, and a type-II band line-up with the conduction band discontinuity \( \Delta E_C \) of 0.8 eV is obtained for HfO₂/AlN heterojunction (Fig. 6). Since the dielectric constant and band gap energy are inversely related, the sacrifice

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**FIG. 3.** Schematic band diagram showing the effect of the upward band bending at AlN surface on the evaluation of valence band discontinuity \( \Delta E_V \) at HfO₂/AlN interface by using angle-resolved XPS measurements.

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**FIG. 4.** A schematic diagram describing the change in the spectral shape of the core-levels due to surface band bending.

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**FIG. 5.** Dependence of measured (open squares) and simulated (solid lines) binding energies (BEs) of Al-N bond on take-off angles \( \theta \) for 2 nm ALD-HfO₂ on AlN.
of barrier height between high-$k$ insulators and the AlN barrier layer is inevitable to keep reasonably large gate controllability over the channel. Furthermore, for AlN/GaN HEMTs, gate leakage is mainly caused by a limited AlN barrier thickness. Thus, the insertion of a dielectric between the gate metal and the barrier layer could also be beneficial to suppress gate leakage.

In conclusion, the band alignment between ALD-HfO$_2$ and AlN was experimentally evaluated by using XPS measurements. The core-level $E_{\text{CL}}$ of the Al 2$p$ decreased with the decrease in take-off angles, which indicates that upward band bending occurred at AlN surface. A type-II band alignment with $\Delta E_V$ of 0.4 eV at HfO$_2$/AlN interface was determined by taking into account the AlN surface band bending using the angle-resolved XPS measurements combined with numerical calculations.

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### TABLE I. Summary of parameters for band alignment between ALD-HfO$_2$ and AlN.

<table>
<thead>
<tr>
<th>AlN ($E_{\text{CL}} - E_{\text{V}}$)$_{\text{bulk}}$ (eV)</th>
<th>HfO$<em>2$ ($E</em>{\text{CL}} - E_{\text{V}}$)$_{\text{bulk}}$ (eV)</th>
<th>$E_{\text{CL}}(i)$ at $\theta = 0^\circ$ (eV)</th>
<th>$E_{\text{CL}}(i)$ (eV)</th>
<th>AlN $E_g$ (eV)</th>
<th>HfO$_2$ $E_g$ (eV)</th>
<th>$\Delta E_V$ (eV)</th>
<th>$\Delta E_C$ (eV)</th>
</tr>
</thead>
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<tr>
<td>70.69</td>
<td>14.06</td>
<td>72.94</td>
<td>16.68</td>
<td>6.2</td>
<td>5.8</td>
<td>0.4</td>
<td>0.8</td>
</tr>
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</table>

![FIG. 6. A type-II band alignment is obtained between ALD-HfO$_2$ and AlN.](image-url)