<table>
<thead>
<tr>
<th>Title</th>
<th>Band alignment of HfO2/AlN heterojunction investigated by X-ray photoelectron spectroscopy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Author(s)</td>
<td>Ye, Gang; Wang, Hong; Ji, Rong</td>
</tr>
<tr>
<td>Date</td>
<td>2016</td>
</tr>
<tr>
<td>URL</td>
<td><a href="http://hdl.handle.net/10220/40837">http://hdl.handle.net/10220/40837</a></td>
</tr>
<tr>
<td>Rights</td>
<td>© 2016 AIP Publishing LLC. This paper was published in Applied Physics Letters and is made available as an electronic reprint (preprint) with permission of AIP Publishing LLC. The published version is available at: [<a href="http://dx.doi.org/10.1063/1.4947435">http://dx.doi.org/10.1063/1.4947435</a>]. One print or electronic copy may be made for personal use only. Systematic or multiple reproduction, distribution to multiple locations via electronic or other means, duplication of any material in this paper for a fee or for commercial purposes, or modification of the content of the paper is prohibited and is subject to penalties under law.</td>
</tr>
</tbody>
</table>
Band alignment of HfO2/AlN heterojunction investigated by X-ray photoelectron spectroscopy
Gang Ye, Hong Wang, and Rong Ji

View online: http://dx.doi.org/10.1063/1.4947435
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/108/16?ver=pdfcov
Published by the AIP Publishing

Articles you may be interested in
Band alignment of HfO2/multilayer MoS2 interface determined by x-ray photoelectron spectroscopy: Effect of CHF3 treatment

Band alignment of HfO2/In0.18Al0.82N determined by angle-resolved x-ray photoelectron spectroscopy

Band alignment of HfO2/Al0.25Ga0.75N determined by x-ray photoelectron spectroscopy: Effect of SiH4 surface treatment

Determination of MgO/AlN heterojunction band offsets by x-ray photoelectron spectroscopy

Energy gap and band alignment for (HfO2 ) x (Al2O3 ) 1−x on (100) Si
Appl. Phys. Lett. 81, 376 (2002); 10.1063/1.1492024
Band alignment of HfO$_2$/AlN heterojunction investigated by X-ray photoelectron spectroscopy

Gang Ye,$^1$ Hong Wang,$^{1,2, a)}$ and Rong Ji$^3$

$^1$School of Electrical and Electronic Engineering, Nanyang Technological University, Singapore 639798
$^2$CNRS-International-NTU-THALES Research Alliances/UMI 3288, 50 Nanyang Drive, Singapore 637553
$^3$Data Storage Institute, Agency for Science Technology and Research (A-STAR), Singapore 117608

(Received 13 January 2016; accepted 12 April 2016; published online 20 April 2016)

The band alignment between AlN and Atomic-Layer-Deposited (ALD) HfO$_2$ was determined by X-ray photoelectron spectroscopy (XPS). The shift of Al 2$p$ 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. [http://dx.doi.org/10.1063/1.4947435]

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 highest spontaneous polarization$^2$ and largest band gap$^3$ among all the III-nitride semiconductors, AlN can provide the III-nitride based heterostructures with the thinnest barrier thickness to significantly increase the aspect ratio while maintaining a high two-dimensional electron gas (2DEG) density, which makes these structures of great interest for very high frequency high power applications. In recent years, with the significant progress made in growth of high-quality AlN barrier layers on GaN,$^4$ ultrathin AlN/GaN heterojunction-based HEMTs have demonstrated themselves as attractive candidates for high-speed high-power devices.$^{5,6}$ However, due to large surface depletion$^7$ and high gate leakage$^8$ induced by thin AlN barrier layer, further improvement in device performance of AlN/GaN HEMTs is inhibited. The integration of high-$k$ materials as gate dielectric and surface passivation layer is an effective method to overcome the above-mentioned problems.$^8,9$ However, dielectric constant and energy band gap are generally inversely related for high-$k$ materials, and thus a trade-off between these two parameters is necessary. With a high gate dielectric constant ($\sim 25$)$^{10}$ and reasonably large band gap (5.8 eV),$^{11,12}$ HfO$_2$ is a promising candidate among different high-$k$ dielectrics. In order to use high-$k$ dielectrics in AlN/GaN HEMTs, band line-up between gate dielectric and AlN substrate is a critical consideration. However, to date, few experimental results related to band alignment at the HfO$_2$/AlN interface has been reported. X-ray photoelectron spectroscopy (XPS) has been reported to be a direct and powerful tool for measuring the valence band discontinuities ($\Delta E_V$) of heterojunctions with a high accuracy among different measurement methods.$^{13}$ In this letter, $\Delta E_V$ of atomic-layer-deposited (ALD) HfO$_2$ on AlN was measured by high-resolution XPS. In order to eliminate the error brought by surface band bending at AlN surface, angle-resolved XPS measurements combined with numerical calculations were carried out in this work to ensure a better prediction of $\Delta E_V$ at HfO$_2$/AlN interface.$^{14-16}$

Commercially obtained 2 $\mu$m unintentionally doped (UID) AlN-on-sapphire substrates grown by Metal Organic Chemical Vapor Deposition (MOCVD) were utilized in this work. An AlN-on-sapphire and a 30 nm-thick HfO$_2$ on AlN were used to obtain AlN and HfO$_2$ bulk material properties, respectively. For the investigation of HfO$_2$/AlN interface, sample with $\sim$2 nm thick HfO$_2$ on AlN surface was used. To deposit the HfO$_2$ on AlN, the wafers were initially degreased in acetone and subsequently rinsed by isopropyl alcohol (IPA) for 10 min. Samples were dipped into buffered oxidant etchant (BOE) solution to remove surface native oxide and followed by a rinse in de-ionized (DI) water prior to ALD deposition. The ALD process was carried out at a pressure of 0.6 Torr and a substrate temperature of 250 °C with tetrakis-(dimethylamido)-hafnium as the metal precursor and H$_2$O as the oxidant. During the deposition, sequential 400 ms and 40 ms pulse of H$_2$O and Hf sources were introduced into the chamber separately. After each pulse, the chamber was purged with N$_2$ for 6 s to remove excess precursors and by-product gases. The growth rate for HfO$_2$ was around 0.1 nm per ALD cycle. The XPS measurements were carried out using a monochromatic Al K$_z$ 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 take-off angle $\theta$ defined as the elevation angle with respect to the sample surface was changed to vary the photoelectron escape depth $\lambda$ according to

$$\lambda = \lambda_0 \sin \theta,$$

1Electronic mail: ewanghong@ntu.edu.sg

0003-6951/2016/108(16)/162103/4/$30.00$
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 deconvoluted into two components, corresponding to the Al-N and Al-O bonds, while Hf 4$f_{5/2}$ and Hf 4$f_{7/2}$ 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$f$.

The bulk and interface binding energies are determined below

\[ \Delta E_V = [E_{V}^{\text{AlN}}(b) - E_{V}^{\text{AlN}}(i)] - [E_{V}^{\text{HfO}_2}(b) - E_{V}^{\text{HfO}_2}(i)] - \Delta E_{CL} \]

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

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. $\Delta E_{CL}$ 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 $E_{CL}$ and $E_V$ are bent differently at different distance from surface due to the band bending, $E_{CL}$ and $E_V$ are bent by the same amount at the same distance. Therefore, the difference between $E_{CL}$ and $E_V$ remains unchanged for AlN regardless of distance. This makes $E_{CL}(\text{Al-N})-E_V(\text{Al-N})$ 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 ($E_{V}^{\text{AlN}}(b) - E_{V}^{\text{AlN}}(i)$) and 14.06 eV ($E_{CL}^{\text{HfO}_2}(b) - E_{V}^{\text{HfO}_2}(i)$).

It should be pointed out that the accurate evaluation of $\Delta E_{CL}$ 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 $\Delta E_{CL}$
between HfO$_2$ 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 affects the observed spectrum is obtained by integrating the true core-level spectrum as a function of the binding energy $E$.

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\textsuperscript{15,16}

\begin{equation}
I(E) = \int_0^d I_0(E,z) \exp \left(-\frac{z}{\lambda}\right) dz,
\end{equation}

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:\textsuperscript{15}

\begin{equation}
V(E,z) = I_{00} \left[ x \exp \left\{ -\ln 2 \left( \frac{E - E_0}{F/2} \right)^2 \right\} + (1-x) \frac{1}{1 + \left( \frac{E - E_0}{F/2} \right)^2} \right],
\end{equation}

where $I_{00}$, $x$, $E_0$, 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 $x$ 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.\textsuperscript{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 incensement of $\theta$ to extend the probing depth $\lambda$. 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.\textsuperscript{15,16} The dependence of measured and simulated binding energies on the take-off angles $\theta$ for Al-N bond of 2 nm-thick HfO$_2$/AlN is illustrated in Fig. 5. To obtain a more accurate $\Delta E_{CL}$ at HfO$_2$/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

\begin{equation}
\Delta E_{CL} = E_{CL}^{GaN}(\theta = 0^\circ) - E_{CL}^{HfO_2}(i),
\end{equation}

Combining Eqs. (2) and (6), a $\Delta E_v$ of 0.4 eV at HfO$_2$/AlN interface is thus estimated with a total error of ±0.2 eV. A summary for the band alignment between AlN and ALD-HfO$_2$ is given in Table I, and a type-II band line-up with the conduction band discontinuity $\Delta C$ of 0.8 eV is obtained for HfO$_2$/AlN heterojunction (Fig. 6). Since the dielectric constant and band gap energy are inversely related, the sacrifice

![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 HfO$_2$/AlN interface by using angle-resolved XPS measurements.](Image 72x552 to 276x755)

![FIG. 4. A schematic diagram describing the change in the spectral shape of the core-levels due to surface band bending.](Image 330x77 to 546x236)

![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-HfO$_2$ on AlN.](Image 336x643 to 540x755)
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.

This work was partially supported by NTU-A*Star Silicon Technologies, Centre of Excellence Grant No. 1123510003 and the National Research Foundation of Singapore (NRF-CRP12-2013-04).

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

<table>
<thead>
<tr>
<th>AlN ($E_{\text{CL}} - E_{\text{V bulk}}$ (eV))</th>
<th>HfO$<em>2$ ($E</em>{\text{CL}} - E_{\text{V bulk}}$ (eV))</th>
<th>$E^{\text{ABN}}_{\text{CL}}(i)$ at $\theta = 0^\circ$ (eV)</th>
<th>$E^{\text{HfO2}}_{\text{CL}}(i)$ (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>
<tbody>
<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>
</tbody>
</table>

FIG. 6. A type-II band alignment is obtained between ALD-HfO$_2$ and AlN.