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Measurement of valence-band offsets of InAlN/GaN heterostructures grown by metal-organic vapor phase epitaxy

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The valence band offsets, ΔE_v, of In_{0.17}Al_{0.83}N/GaN, In_{0.25}Al_{0.75}N/GaN, and In_{0.30}Al_{0.70}N/GaN heterostructures grown by metal-organic vapor phase epitaxy were evaluated by using x-ray photoelectron spectroscopy (XPS). The dependence of the energy position and the full width at half maximum of the Al 2p spectrum on the exit angle indicated that there was sharp band bending caused by the polarization-induced electric field combined with surface Fermi-level pinning in each ultrathin InAlN layer. The ΔE_v values evaluated without taking into account band bending indicated large discrepancies from the theoretical estimates for all samples. Erroneous results due to band bending were corrected by applying numerical calculations, which led to acceptable results. The evaluated ΔE_v values were 0.2 ± 0.2 eV for In_{0.17}Al_{0.83}N/GaN, 0.1 ± 0.2 eV for In_{0.25}Al_{0.75}N/GaN, and 0.0 ± 0.2 eV for In_{0.30}Al_{0.70}N/GaN. Despite the large decrease of around 1.0 eV in the band gap of InAlN layers according to the increase in the In molar fraction, the decrease in ΔE_v was as small as 0.2 eV. Therefore, the change in band-gap discontinuity was mainly distributed to that in conduction band offset. © 2011 American Institute of Physics.

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I. INTRODUCTION

Group III-nitrides and their alloys are promising materials that should enable excellent high-power, high-frequency, and optoelectronic devices to be fabricated. Their heterostructures can provide a high-density two-dimensional electron gas (2DEG) with a high saturation velocity in wide-gap semiconductors. Lattice-matched In_{x}Al_{1-x}N (x =0.17–0.18)/GaN heterostructures without doping can especially provide a 2DEG with high density exceeding 2 x 10^{13} cm^{-2} due to the difference in spontaneous polarization at the interface. High-performance InAlN/GaN high-electron mobility transistors (HEMTs) have actually been fabricated and reported. If we expand the scope to include nonlattice-matched InAlN/GaN heterostructures, the band gap, E_g, of InAlN can be greatly changed from 6.2 eV (AlN) to 0.67 eV (InN). It has theoretically been predicted that the decrease in the conduction band offset, ΔE_c, according to the increase in the In molar fraction is much larger than decrease in the valence band offset, ΔE_v. This interface property is useful for barrier-height engineering. The large change in ΔE_c according to the molar fraction can be verified by confirming the small change in ΔE_v. However, there have been no reports on measuring the change in ΔE_v by changing the molar fraction.

One of the most useful methods of investigating ΔE_v is by applying x-ray photoelectron spectroscopy (XPS) to the interface between ultrathin InAlN and GaN layers. However, evaluating ΔE_v by using XPS is possibly erroneous due to sharp band bending caused by the spontaneous and piezoelectric polarization in ultrathin InAlN layers. In our preliminary work, the ΔE_v of lattice-matched In_{0.17}Al_{0.83}N/GaN grown by metal-organic vapor phase epitaxy (MOVPE) was evaluated correctly by taking into account band bending due to the polarization-induced electric field combined with surface Fermi-level pinning. In addition to the lattice-matched In_{0.17}Al_{0.83}N/GaN heterostructure, the pseudomorphic heterostructures of In_{0.25}Al_{0.75}N/GaN and In_{0.30}Al_{0.70}N/GaN were also grown and characterized in this work. Erroneous results due to band bending in ultrathin InAlN layers were corrected by applying numerical calculations. Using the measured peak positions of core levels, E_o, of InAlN/GaN heterostructures grown by metal-organic vapor phase epitaxy were evaluated by using x-ray photoelectron spectroscopy (XPS). The dependence of the energy position and the full width at half maximum of the Al 2p spectrum on the exit angle indicated that there was sharp band bending caused by the polarization-induced electric field combined with surface Fermi-level pinning in each ultrathin InAlN layer.

II. EXPERIMENTAL

The sample structure used to investigate the interface with XPS is schematically shown in Fig. 1. All the samples were grown on sapphire (0001) substrates by MOVPE without any doping. In_{0.17}Al_{0.83}N/GaN, In_{0.25}Al_{0.75}N/GaN, and In_{0.30}Al_{0.70}N/GaN heterostructures with 2.5 nm-thick InAlN layers were prepared. Here, we have defined the photoelectron exit angle, θ, as the elevation angle indicated in Fig. 1. To measure bulk material constants, thick (around 15 nm) In_{0.17}Al_{0.83}N, In_{0.25}Al_{0.75}N, and In_{0.30}Al_{0.70}N layers on GaN and a 2 μm-thick GaN single layer were also prepared. Tri-
methylgallium was used as a precursor for gallium, trimethylaluminum for aluminum, trimethylindium for indium, and ammonia for nitrogen. The growth temperature was set at 1000 °C for GaN, 820 °C for In$_{0.17}$Al$_{0.83}$N, 780 °C for In$_{0.25}$Al$_{0.75}$N, and 730 °C for In$_{0.30}$Al$_{0.70}$N. The details on the growth conditions are described in Ref. 6. Successful control lapped with the Ga$_3$ was preliminarily confirmed by using a monochromated Al Kα x-ray source (1486.6 eV). The binding energy was calibrated by adjusting the peak positions of the C 1s core levels to 285.0 eV for each sample surface. The morphology of the surfaces was investigated by atomic force microscopy. The surfaces of all the heterostructure samples with the ultrathin InAlN layers were smooth, having monolayer steps, which indicated that the thin InAlN layer had uniform thickness as a result of layer-by-layer growth. The XPS data also indicated this state. Surface oxide layers were removed by pretreating them with hydrofluoric acid.

III. THEORY OF MEASUREMENT

A schematic band diagram for the principle of measuring $\Delta E_V$ at the InAlN/GaN interface is outlined in Fig. 2, where $E_C$ is the conduction-band minimum, $E_V$ is the valence-band maximum (VBM), and $E_F$ indicates Fermi level that is set to the origin of binding energy in XPS measurement. In our preliminary work, we used the In 4$d$ spectrum that overlapped with the Ga 3$d$ and N 2$s$ spectra very closely on both sides. The Al 2$p$ spectrum, however, does not overlap with any other spectra and is therefore more suitable for the $\Delta E_V$ measurement. We therefore used Al 2$p$ in the present work. The $\Delta E_V$ can be estimated from

$$\Delta E_V = \Delta E_{CL} + (E_{Ga}^{3d} - E_{V}^{GaN}) - (E_{InAlN}^{3p} - E_{V}^{InAlN}),$$

where $\Delta E_{CL} = (E_{InAlN}^{3p} - E_{Ga}^{3d})$ is the binding energy difference between the measured Al 2$p$ and Ga 3$d$ core-level spectra of the InAlN (2.5 nm)/GaN sample. The two $(E_{CL}^{material} - E_{material}^{material})$ terms represent the difference in binding energies between the core level and the VBM for GaN and InAlN as bulk material constants. Here, the $E_F$ of InAlN is larger than that of GaN in the range of the molar fraction of the prepared samples. The band alignment is therefore type II when $\Delta E_V < 0$. This method can, however, be applied to a sample in a nearly flat-band situation, with negligible band bending, at the surface to depths of around 10 nm. This situation will be referred to as a “quasiflat-band” situation after this. If there is sharp band bending at the sample surfaces that affects the XPS data, correction is needed for $E_{CL}$.

In pseudomorphic grown wurtzite In$_x$Al$_{1-x}$N (x < 0.32)/GaN heterostructures with Ga-face polarity, the sum of spontaneous polarization, $P_{SP}$, and piezoelectric polarization, $P_{PE}$, in InAlN is larger than $P_{SP}$ in GaN as illustrated in Fig. 3(a). This difference in polarization at the heterointerface produces positive interface charge. Since the Fermi level should be pinned at the InAlN surface, sharp band bending can occur in the InAlN layer. Figures 3(b) and 3(c) show the schematics for the possible surface band bending in the range of the probing depth for samples with thick and ultrathin InAlN layers. Uniform internal electric fields in the outer InAlN layers were calculated for all the samples in the

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**FIG. 1.** (Color online) Sample structure for XPS investigations. Definition of exit angle $\theta$ is also shown.

**FIG. 2.** Schematic band diagram for XPS measurement of $\Delta E_V$.

**FIG. 3.** (Color online) (a) Polarization in pseudomorphic grown wurtzite InAlN/GaN heterostructure with Ga-face polarity. (b) and (c) show possible sharp band bending, in the range of probing, schematically for thick and thin InAlN samples.
range of probing depths and observed surface potentials that will be described later, while the nonuniform electric fields were calculated for GaN layers. Similar results have previously been reported. In XPS measurement, only shallow parts of InAlN layers were probed as shown in Fig. 3(b) for the samples with thick InAlN layers with 2DEG, resulting in no detection of the Ga 3d spectrum from the host GaN layer. The samples with ultrathin InAlN layers were without 2DEG, which was confirmed by the contactless eddy current method. Consequently, the band bending in the GaN layers of the samples with ultrathin InAlN layers would be observed as a slight tilt of the potential or a nearly flat band in the range of the probing depth. For example, Fig. 3(c) indicates the observed result, for the In0.17Al0.83N (2.5 nm)/GaN sample, that will be described in Sec. IV. A normally-off type GaN-based HEMT has recently been fabricated by using an ultrathin In0.17Al0.83N (1 nm)/AlN (1 nm) barrier, which supports our results because the barrier thickness and the sum of interface charges are close to those of the In0.17Al0.83N (2.5 nm)/GaN sample.

In the situations shown in Figs. 3(b) and 3(c), the core levels in the InAlN layer are also bent along with the valence band. As schematically outlined in Fig. 4, the observed spectrum is given by integrating the true spectrum from each depth point along the bent core level. Therefore, sharp band bending results in apparent increases in FWHM of core-level spectra from the InAlN layer. This phenomenon becomes more remarkable by increasing θ to extend the probing depth. Furthermore, the E_CL of the core-level spectra from the GaN layer increases due to the total potential drop in the InAlN layer for the InAlN/GaN heterostructure sample. With the band bending in Fig. 3(c), ΔE_V might be evaluated to have a negative value despite the type-I alignment. Therefore, we have to derive the actual E_CL’s by subtracting increases due to band bending so that we can correctly evaluate ΔE_CL.

The sequence of correction for ΔE_V at the InAlN/GaN heterointerfaces involves three steps

1. The internal electric field in InAlN is extracted. Assuming a uniform internal electric field in the InAlN layer, the band bending for the entire heterostructure including the GaN layer is calculated by solving the Poisson equation using the measured surface Fermi level, E_Fsurf, position as the boundary condition for strong pinning. Then, the apparent E_CL and FWHM due to band bending are calculated for Al 2p and Ga 3d. This procedure is repeated to find the most suitable internal electric field in InAlN that achieves the apparent E_CL and FWHM observed for Al 2p and Ga 3d.

2. E_CL values are corrected for Al 2p and Ga 3d by subtracting the apparent increases due to band bending to correctly evaluate ΔE_CL value.

3. ΔE_V is derived using the corrected ΔE_CL value in Eq. (1).

The details on the calculations to estimate the apparent E_CL and FWHM of core-level spectra due to band bending are as follows. A core-level spectrum as a function of the binding energy, E, from a layer of thickness d is given by

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

(2)

where z, λ, and I_0(E,z) correspond to the depth from the surface, the escape depth of the photoelectrons, and the spectrum generated at each depth point. Here, to do the calculations within a practical time frame and to avoid heavy computation, the I_0(E,z) for one spin orbital is represented by the pseudo-Voigt function given by

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

(3)

where I_{00}, α, I_0, and F are the intensity, the ratio of the Gaussian function, the binding energy of the core level, and the actual FWHM. When surface band bending is not negligible on the scale of the escape depth of photoelectrons, E_0 should be treated as a function of depth z to be E_0(z). The F was assumed to be a sample dependent constant. The α was fixed to 0.73 for both Al 2p and Ga 3d spectra. For Al 2p and Ga 3d spectra, I_0(E,z) is given by a weighted combination of two pseudo-Voigt-function components taking into account the spin-orbit splitting of 0.41 eV for Al 2p and
0.44 eV for Ga 3d. Furthermore, \( \lambda \) can be changed by changing \( \theta \) according to

\[
\lambda = \lambda_0 \sin \theta,
\]

where \( \lambda_0 \) indicates the inelastic mean free path of a photoelectron. The value of \( \lambda_0 \) was calculated using a previously reported equation\(^\text{17,18} \) that was demonstrated to fit the experimental data for several materials including GaN.\(^\text{19} \) The \( \lambda_0 \) of Al 2p spectrum before and after HF treatment was calculated to be 2.87 nm for In\(_{0.17}\)Al\(_{0.83}\)N, 2.79 nm for In\(_{0.25}\)Al\(_{0.75}\)N, and 2.76 nm for In\(_{0.30}\)Al\(_{0.70}\)N. The \( \lambda_0 \) of Ga 3d spectrum was calculated to be 2.58 nm for GaN, 2.95 nm for In\(_{0.17}\)Al\(_{0.83}\)N, 2.88 nm for In\(_{0.25}\)Al\(_{0.75}\)N, and 2.84 nm for In\(_{0.30}\)Al\(_{0.70}\)N.

\[\text{IV. RESULTS AND DISCUSSION}\]

**A. Measurement of bulk material constants**

We found that HF treatment efficiently removed oxides from the InAlN and GaN surfaces. Figure 5 shows the O 1s spectra before and after HF treatment for In\(_{0.17}\)Al\(_{0.83}\)N at \( \theta = 45^\circ \), In\(_2\)O component appear at 530.2 eV (Ref. 20) and that for Al\(_2\)O component at 531.6 eV.\(^\text{21} \) The spectral intensity at these binding energies drastically decreased after HF treatment leaving only a faint component assigned to O–H bonding.\(^\text{22} \) Similar results were also obtained for the In\(_{0.30}\)Al\(_{0.70}\)N layer to maintain good bulk quality. We also found that the thickness needed to investigate the surface sensitive angle of \( \theta = 45^\circ \) or 75\(^\circ \), even though they were detected at the surface sensitive angle of \( \theta = 15^\circ \).

The Ga 3d and VBM spectra observed at \( \theta = 45^\circ \) for the HF-treated thick GaN layer on a sapphire substrate are shown in Fig. 6. The efficiency of HF treatment can also be seen here. The shape of the Ga 3d spectrum was identical to that obtained for the GaN (2 × 2) clean surface grown by molecular beam epitaxy, which indicated that the surface was nearly oxide free. The VBM position was determined by linear extrapolation of the low binding energy edge of the valence band spectrum. The value of \( (E_{\text{Ga 3d}} - E_{\text{VBM}}) \) was evaluated to be 17.10 ± 0.07 eV. The same value was also obtained for the thick GaN layer on a SiC substrate.

Figures 7(a) and 7(b) show the Al 2p and VBM spectra obtained at three different \( \theta \)s for the thick In\(_{0.17}\)Al\(_{0.83}\)N samples. No oxide components were detected for Al 2p spectra at \( \theta = 45^\circ \) or 75\(^\circ \), even though they were detected at the surface sensitive angle of \( \theta = 15^\circ \). It can be seen that the Al 2p spectrum shifts to higher binding energies with the increase in \( \theta \), which indicates that there was sharp band bending in the In\(_{0.17}\)Al\(_{0.83}\)N layer. We also found that the FWHM of the Al 2p spectrum increased with \( \theta \). The results are summarized in Table I with the values calculated by assuming internal electric field of 1.2 MV/cm in the In\(_{0.17}\)Al\(_{0.83}\)N layer. Note that the corrected VBM position in Table I is close to that reported for In\(_{0.16}\)Al\(_{0.84}\)N.\(^\text{23} \) Consequently, the bulk material constant \( (E_{\text{InAlN}} - E_{\text{VBM}}) \) was determined to be 71.10 ± 0.07 eV for In\(_{0.17}\)Al\(_{0.83}\)N. The same value was also obtained for the thick In\(_{0.25}\)Al\(_{0.75}\)N layer by applying the same method. However, applying the same method to the thick In\(_{0.30}\)Al\(_{0.70}\)N layer did not lead to an acceptable result. The thickness needed to investigate the bulk material constant was probably too large for the In\(_{0.30}\)Al\(_{0.70}\)N layer to maintain good bulk quality. Precise evaluation of the critical thickness was beyond the scope of this work. Therefore, the value of \( (E_{\text{InAlN}} - E_{\text{VBM}}) \) for In\(_{0.30}\)Al\(_{0.70}\)N was extrapolated from the results of two other samples to be 71.10 eV.

**B. Measurement of band offsets**

To determine \( \Delta E_V \), the \( \Delta E_{\text{CL}} \) between Al 2p and Ga 3d spectra was measured for each heterostructure with the thin
InAlN top layer. The spectra we obtained are shown in Fig. 8 for the lattice-matched \( \text{In}_{0.17}\text{Al}_{0.83}\text{N} \)\(/\text{GaN} \) heterostructure, in Fig. 9 for the pseudomorphic \( \text{In}_{0.25}\text{Al}_{0.75}\text{N} \)\(/\text{GaN} \) heterostructure, and in Fig. 10 for the pseudomorphic \( \text{In}_{0.30}\text{Al}_{0.70}\text{N} \)\(/\text{GaN} \) heterostructure. The measured values of \( \Delta E_{\text{CL}} \) and \( \Delta E_{\text{V}} \) without correction have been summarized in Table II. Using the previously mentioned bulk constant values, all the \( \Delta E_{\text{V}} \) values were evaluated to be negative and were not independent of \( \theta \). The evaluated \( \Delta E_{\text{V}} \) values in Table II are also plotted in Fig. 11 to compare them with the calculated values according to Refs. 11 and 12. The \( \Delta E_{\text{V}} \) values without correction deviated from the calculated values and indicated type-II alignments for all the samples despite the prediction of type-I alignments. In addition, the \( E_{\text{CL}} \) and FWHM of the Al \( 2p \) spectra for \( \text{In}_{0.17}\text{Al}_{0.83}\text{N} \)\(/\text{GaN} \) and \( \text{In}_{0.25}\text{Al}_{0.75}\text{N} \)\(/\text{GaN} \) interfaces increased with increasing \( \theta \) as summarized in Table III. These results indicate that there was sharp band bending in the ultrathin InAlN layers again. Here, the detected internal electric field decreased according to the increase in the In molar fraction. The observed trend is in agreement with the theoretical estimates.9

For the \( \text{In}_{0.25}\text{Al}_{0.75}\text{N} \)\(/\text{GaN} \) samples, increases in the \( E_{\text{CL}} \) and FWHM of the Al \( 2p \) spectra were sufficiently large to extract the internal electric field in the InAlN layers. The previously mentioned calculation reproduced the observed phenomenon for Al \( 2p \) in the range of experimental error as is also summarized in Table III. The assumed internal electric fields were 3.2 MV/cm for \( \text{In}_{0.17}\text{Al}_{0.83}\text{N} \) layer and 2.4 MV/cm for \( \text{In}_{0.25}\text{Al}_{0.75}\text{N} \) layer. For Ga \( 3d \) spectra, we found that the apparent shift in \( E_{\text{Ga3d}} \) due to band bending in GaN was a few tens of millielectron volts for the \( \text{In}_{0.17}\text{Al}_{0.83}\text{N} \)\(/\text{GaN} \) sample and negligible for the other samples. The corrected \( \Delta E_{\text{V}} \) values were 0.2 eV for \( \text{In}_{0.17}\text{Al}_{0.83}\text{N} \)\(/\text{GaN} \) and 0.1 eV for \( \text{In}_{0.25}\text{Al}_{0.75}\text{N} \)\(/\text{GaN} \), as listed in Table IV with the corrected values of \( E_{\text{CL}} \). The measured band alignments for the quasiflat-band situation using the reported \( E_{\text{g}} \) values11 are summarized in Figs. 12a and 12b for the \( \text{In}_{0.17}\text{Al}_{0.83}\text{N} \)\(/\text{GaN} \) and \( \text{In}_{0.25}\text{Al}_{0.75}\text{N} \)\(/\text{GaN} \) interfaces. Note that the resulting \( E_{\text{surf}} \) position for the \( \text{In}_{0.17}\text{Al}_{0.84}\text{N} \) layer in Fig. 12a is close to the experimental result previously reported for \( \text{In}_{0.16}\text{Al}_{0.84}\text{N} \).23

For the \( \text{In}_{0.30}\text{Al}_{0.70}\text{N} \)\(/\text{GaN} \) sample, however, no large increases depending on \( \theta \) were observed in either the \( E_{\text{Al2p}} \) or FWHM as summarized in Table III. Nevertheless, piezoelectric polarization did not completely compensate for spontaneous polarization in the pseudomorphic \( \text{In}_{0.30}\text{Al}_{0.70}\text{N} \) layer.

### Table II. Summary of measured results without correction for InAlN/GaN interfaces.

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<tr>
<th>( x )</th>
<th>( \theta )</th>
<th>( \Delta E_{\text{CL}} ) (eV)</th>
<th>( \Delta E_{\text{V}} ) (eV)</th>
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<tr>
<td>0.17</td>
<td>15°</td>
<td>53.61</td>
<td>-0.4</td>
</tr>
<tr>
<td></td>
<td>45°</td>
<td>53.75</td>
<td>-0.3</td>
</tr>
<tr>
<td></td>
<td>75°</td>
<td>53.73</td>
<td>-0.3</td>
</tr>
<tr>
<td>0.25</td>
<td>15°</td>
<td>53.70</td>
<td>-0.3</td>
</tr>
<tr>
<td></td>
<td>45°</td>
<td>53.75</td>
<td>-0.3</td>
</tr>
<tr>
<td></td>
<td>75°</td>
<td>53.78</td>
<td>-0.2</td>
</tr>
<tr>
<td>0.30</td>
<td>15°</td>
<td>53.85</td>
<td>-0.2</td>
</tr>
<tr>
<td></td>
<td>45°</td>
<td>53.85</td>
<td>-0.2</td>
</tr>
<tr>
<td></td>
<td>75°</td>
<td>53.85</td>
<td>-0.2</td>
</tr>
</tbody>
</table>
according to the theoretical estimate in Ref. 9. Therefore, it is likely there was an internal electric field in the 
In0.30Al0.70N layer. The numerical calculations indicated that the increases in apparent $E_A\ \text{Al}\ 2p$ and FWHM were negligible 
within experimental error with internal electric fields up to 1.2 MV/cm in the In0.30Al0.70N layer. This maximum value 
for the electric field is in good agreement with the theoretical 
estimates in Ref. 9 and leads to the correction of 
the vacuum level in all semiconductors. The Fermi-level stabilization energy, 
$E_F\ stab$, has been re-
seen in the corrected data for the In0.17Al0.83N/GaN and 
In0.25Al0.75N/GaN interfaces. The difference in uncorrected 
values of $(E_{F\ surf}\ -\ E_{F\ stab})$ for the In0.30Al0.70N/GaN interface 
must have been caused by the internal electric field. After 
correction assuming 1.2 MV/cm in In0.30Al0.70N, the 
difference disappeared, as seen in Table V. Moreover, the 
dispersion of $E_{F\ surf}$ for the same pretreatment for InAlN/ 
GaN heterostructures should be discussed. Even though the 
$E_{F\ surf}$ positions of the HF-treated samples may disperse 
statistically depending on the sample, the dispersion for the 
same treatment is likely to be within a few 0.1 eV. As can be 
seen from Table V, the $(E_{F\ surf}\ -\ E_{F\ stab})$ was evaluated to be 
0.0 eV for the In0.17Al0.83N/GaN interface and $-0.2$ eV for the 
In0.25Al0.75N/GaN interface. For the In0.3Al0.7N/GaN sample, however, the value was estimated to be 0.3 eV for 
the GaN surface without correction resulting in a wide dis-
persion of 0.5 eV. This discrepancy dependent on the sample 
is not acceptable. After correction assuming 1.2 MV/cm in 
In0.30Al0.70N, the dispersion width reduced to an accept-
able value of 0.2 eV. Therefore, correction resulting in a $\Delta E_V$ 
value of 0.0 eV for In0.30Al0.70N was appropriate.

As can be seen in Fig. 11, the corrected $\Delta E_V$ values are 
good in agreement with the calculated values for all the 
interfaces. The experimental error was evaluated by consider-
ing the fitting errors and the discrepancy between repeated 
measurements to be $\pm 40$ meV for $\Delta E_{\text{CL}}$ and $\pm 70$ meV for 
the two $(E_{\text{CL}}-E_V)$ components in Eq. (1). Without correction 
by using numerical calculations, the total error for $\Delta E_V$ is 
$\pm 180$ meV. Fitting by numerical calculations introduces an 
additional error of $\pm 60$ meV resulting in a total error of 
$\pm 240$ meV. Since the final results were approximated values 
in units of 0.1 eV, the errors in both cases should be $\pm 0.2$ eV.
FIG. 12. Schematic band alignments using measured $\Delta E_v$ values and reported $E_F$ values (Ref. 11), for (a) ln$_{0.17}$Al$_{0.83}$N/GaN, (b) ln$_{0.25}$Al$_{0.75}$N/GaN, and (c) ln$_{0.30}$Al$_{0.70}$N/GaN interfaces in quasiflat-band situation.

which is a typical value for the XPS measurements of $\Delta E_v$. Even though the evaluated $\Delta E_v$ values were small, the $E_g$ of semiconductors on both sides was much larger than the total error. Therefore, the present results provide important information that the $\Delta E_v$ values are small despite the large band gaps of all samples. The measurement of small $\Delta E_v$ values with similar error values can also be found in other reports on TiO$_2$/GaN (0.09 ± 0.25 eV) (Ref. 27) and HfO$_2$/GaN (~0.1 ± 0.1 eV) (Ref. 29) interfaces. As can be seen in Fig. 12, the decrease in $\Delta E_v$ according to the increase in the In molar fraction should have been much smaller than that in $\Delta E_C$. In other words, the change in $E_g$ discontinuity was mostly distributed to that in $\Delta E_C$ at the InAlN/GaN interfaces.

V. CONCLUSION

The $\Delta E_v$ of ln$_{0.17}$Al$_{0.83}$N/GaN, ln$_{0.25}$Al$_{0.75}$N/GaN, and ln$_{0.30}$Al$_{0.70}$N/GaN heterostructures grown by MOVPE were evaluated by using XPS. The $E_{CL}$ and FWHM of the Al 2p increased according to the exit angle, which was explained by band bending or due to the polarization-induced electric field in ultrathin InAlN layers combined with surface Fermi-level pinning. The $\Delta E_v$ values evaluated by the conventional method were in disagreement with the theoretical estimates for all samples. The evaluations were therefore corrected by numerical calculations taking into account band bending, which led to the $\Delta E_v$ values being in good agreement with the theoretical estimates for all the interfaces. The evaluated $\Delta E_v$ values were $0.2 \pm 0.2$ eV for ln$_{0.17}$Al$_{0.83}$N/GaN, $0.1 \pm 0.2$ eV for ln$_{0.25}$Al$_{0.75}$N/GaN, and $0.0 \pm 0.2$ eV for ln$_{0.30}$Al$_{0.70}$N/GaN, which indicated that the large change in band-gap discontinuity was mostly distributed to that in $\Delta E_C$.

TABLE V. ($E_{F_{surf}}$−$E_{F_{flat}}$) values for the InAlN(2.5 nm)/GaN heterostructures in quasiflat-band situation.

<table>
<thead>
<tr>
<th>InAlN/GaN</th>
<th>ln$<em>{0.17}$Al$</em>{0.83}$N/GaN (corrected)</th>
<th>ln$<em>{0.25}$Al$</em>{0.75}$N/GaN (corrected)</th>
<th>ln$<em>{0.30}$Al$</em>{0.70}$N/GaN (corrected)</th>
<th>ln$<em>{0.30}$Al$</em>{0.70}$N/GaN (uncorrected)</th>
</tr>
</thead>
<tbody>
<tr>
<td>InAlN surface</td>
<td>0.0</td>
<td>−0.2</td>
<td>0.1</td>
<td>0.0</td>
</tr>
<tr>
<td>GaN surface</td>
<td>0.0</td>
<td>−0.2</td>
<td>0.3</td>
<td>0.0</td>
</tr>
</tbody>
</table>

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