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Small valence-band offset of In0.17Al0.83N/GaN heterostructure grown by metal-organic vapor phase epitaxy

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Small valence-band offset of $\text{In}_{0.17}\text{Al}_{0.83}\text{N}/\text{GaN}$ heterostructure grown by metal-organic vapor phase epitaxy

M. Akazawa,¹,²,a T. Matsuyama,¹ T. Hashizume,¹,² M. Hiroki,³ S. Yamahata,³ and N. Shigekawa³
¹Research Center for Integrated Quantum Electronics, Hokkaido University, Sapporo 060-8628, Japan
²JST-CREST, Sanbancho, Chiyoda-ku, Tokyo 102-0075, Japan
³NTT Photonics Laboratories, NTT Corporation, Atsugi, Kanagawa 243-0198, Japan

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The valence-band offset of a lattice-matched $\text{In}_{0.17}\text{Al}_{0.83}\text{N}/\text{GaN}$ heterostructure grown by metal-organic vapor phase epitaxy (MOVPE) was investigated by x-ray photoelectron spectroscopy (XPS). Atomic force microscopy and angle-resolved XPS indicated that a thin $\text{In}_{0.17}\text{Al}_{0.83}\text{N}$ (2.5 nm) layer was successfully grown by MOVPE on GaN. The XPS result showed that the valence band offset was $0.2 \pm 0.3$ eV. This result indicates that the conduction-band offset at the $\text{In}_{0.17}\text{Al}_{0.83}\text{N}/\text{GaN}$ interface is large, i.e., 0.9 to 1.0 eV, and occupies a large part of the entire band discontinuity. © 2010 American Institute of Physics. [doi:10.1063/1.3368689]

Group III-nitrides, with their wide variation of band gap, are promising materials for achieving excellent high-power and high-frequency devices because their heterostructures can provide a high density two-dimensional electron gas (2DEG) with a high saturation velocity. Especially, lattice-matched $\text{In}_{x}\text{Al}_{1-x}\text{N}$ ($x=0.17–0.18$)/GaN heterostructures can provide a 2DEG with a high density exceeding $2 \times 10^{13}$ cm$^{-2}$.¹–⁶ Actually, InAlN/GaN high-electron mobility transistors with high performance have been reported.³,⁵ To generate a high density 2DEG, a large conduction-band offset, $\Delta E_C$, in addition to the strong polarization-induced effects,⁷ is required. In a previous report,⁸ it was predicted by calculation that a large part of the band discontinuity is occupied by $\Delta E_C$, resulting in a small valence band offset, $\Delta E_V$. However, as far as the authors know, no experimental evidence of small $\Delta E_V$ has been reported. One of the methods for evaluating $\Delta E_V$ directly is x-ray photoelectron spectroscopy (XPS). In the present study, we attempted to evaluate $\Delta E_V$ at a lattice-matched $\text{In}_{0.17}\text{Al}_{0.83}\text{N}$ on GaN interface by XPS.

The schematic structure of the sample used for investigating the $\text{In}_{0.17}\text{Al}_{0.83}\text{N}/\text{GaN}$ interface is shown in Fig. 1 where the photoelectron exit angle, $\theta$, is also indicated.

![FIG. 1. (Color online) Schematic diagram of the sample structure and the definition of exit angle, $\theta$.](image1)

The valence-band offset of $\text{In}_{0.17}\text{Al}_{0.83}\text{N}$ (14.5 nm)/GaN (2 μm) heterostructure and GaN (2 μm) single layer were also prepared. All the samples were grown by metal-organic vapor phase epitaxy (MOVPE). Trimethylgallium, trimethylaluminum, trimethylindium, and ammonia were used as precursors of gallium, aluminum, indium, and nitrogen, respectively. The GaN and $\text{In}_{0.17}\text{Al}_{0.83}\text{N}$ layers were grown at 1000 °C and 820 °C, respectively. The growth conditions are described in detail in Ref. 6. X-ray diffraction confirmed that molar fraction in the 14.5 nm thick $\text{In}_{0.17}\text{Al}_{0.83}\text{N}$ was successfully controlled by the MOVPE growth. XPS was done by using a monochromated Al-Kα x-ray source (1486.6 eV). The binding energy was corrected by adjusting the C 1s core-level peak position to 285.0 eV for each sample surface. Oxide layers at sample surfaces were removed by pretreatment with HF acid. Only when the exit angle was small (i.e., 15°), oxide components were detected.

![FIG. 2. (Color online) AFM image of the surface morphology of the $\text{In}_{0.17}\text{Al}_{0.83}\text{N}$ (2.5 nm)/GaN heterostructure.](image2)

The surface morphology of the $\text{In}_{0.17}\text{Al}_{0.83}\text{N}$ (2.5 nm)/GaN sample was investigated by atomic force microscopy (AFM). A typical AFM image is shown in Fig. 2. The surface of the sample was smooth, showing monolayer steps, which indicated that the thin $\text{In}_{0.17}\text{Al}_{0.83}\text{N}$ layer had uniform thickness as a result of layer-by-layer growth. Angle-resolved
shown in Fig. 5. Large, shifts of VBM depending on
In0.17Al0.83N was grown as a layer. It should be noted that the
energy band diagram for the In0.17Al0.83N
samples for three different exit angles, whereas N 1s, Al 2p,
and valence band, EV, spectra are shown in Figs. 4(a)–4(c).
These spectra show that successful chemical bonding with-
out any metallic or segregated components was achieved.
Moreover, the Ga 3d and Ga Auger spectra from the GaN
layer become more intense as θ increases, indicating that
In0.17Al0.83N was grown as a layer. It should be noted that the
location of the valence-band maximum (VBM) is independ-
ent of θ, as shown in Fig. 4(c), where the fine solid lines
show the results of straight-line extrapolation. If ΔEV is
large, shifts of VBM depending on θ should be observed.
Since there is no remarkable VBM shift in Fig. 4(c), it is
highly likely that ΔEV is small.

To estimate ΔEV more precisely, energy separations be-
tween observed spectra were investigated. A schematic en-
ergy band diagram for the In0.17Al0.83N/GaN interface is
shown in Fig. 5. ΔEV can be estimated from the following
equation:9

\[ ΔEV = -ΔECL + (E_{Ga\;3d}^{GaN} - E_{V}^{GaN}) − (E_{InAlN\;4d} − E_{V}^{InAlN}), \] (1)

where ΔECL = (E_{Ga\;3d}^{GaN} − E_{In\;4d}^{GaN}) is the core-level separation
between the measured In 4d and Ga 3d spectra of the
In0.17Al0.83N(2.5 nm)/GaN sample. The two (E_{CL}^{material} − E_{V}^{material}) terms are separations between a core level and a
VBM of the thick GaN and In0.17Al0.83N samples. Here, the
band gap of In0.17Al0.83N is larger than that of GaN. The
band alignment is therefore type I when ΔEV > 0 but type II
when ΔEV < 0.

Although piezoelectric polarization in the thin lattice-
matched In0.17Al0.83N layer on GaN can be ignored, sponta-
neous polarization existed. According to a previous report,7 it
is theoretically expected that the maximum polarization
charge density can be 4 \times 10^{−6} C/cm² at the interface. As a
result of this effect and surface Fermi level pinning, a strong
internal electric field is generated in the thin In0.17Al0.83N
layer. The internal electric field therefore leads to a potential
drop large enough to affect the kinetic energy of photoelec-
tron from the thin In0.17Al0.83N layer, which results in broad-
ing and energy-shift of XPS spectra.

Actually, binding energy and full-width-at-half maxi-
mum (FWHM) of the In 4d, In 3d, and Al 2p spectra both
increased with the increase of θ. Especially, FWHM
increased up to 80 meV with increasing θ from 15° to 75°.
We carried out a computer simulation to reproduce the ob-
served XPS spectra in the following sequence. First, a mag-
nitude of the potential drop in the In0.17Al0.83N layer is as-
sumed. Then, an integrand spectrum is integrated versus
depth, considering the assumed potential drop and in-depth
signal decay, to predict apparent XPS spectra. It was found
that a linear potential drop of 0.8 eV over the entire
In0.17Al0.83N thickness of 2.5 nm could reproduce the ob-
served energy shift and FWHM of the XPS spectra. Here, the

FIG. 3. (Color online) XPS Ga 3d, In 4d, and N 2s core-level spectra obtained for the In0.17Al0.83N (2.5 nm) /GaN heterostructure. (a) θ=75°, (b) θ=45°, and (c) θ=15°.

FIG. 4. XPS spectra for the In0.17Al0.83N (2.5 nm) /GaN heterostructure with θ=15°, 45°, and 75°. (a) N 1s and Ga Auger spectra. (b) Al 2p spectra. (c) EV spectra.
escape depth at θ of 45° was assumed to be 2.3 nm for In 4d and Al 2p and 1.5 nm for In 3d. The potential drop of 0.8 eV in 2.5 nm of In\(_{0.17}\)Al\(_{0.83}\)N layer was in good agreement with the theoretical estimation assuming a polarization charge of \(\Delta E_{\text{CL}}\) to be 1.2 eV. (The apparent separation in Fig. 3 is larger than this \(\Delta E_{\text{CL}}\) value because of the internal electric field that makes a larger energy shift in the Ga 3d spectra.) Separate experiments on thick layers showed that, \(E_{\text{GaN}}^{\text{3d}} - E_{\text{AlN}}^{\text{3d}}\) and \(E_{\text{InAlN}}^{\text{3d}} - E_{\text{AlN}}^{\text{3d}}\) were 17.1 eV and 15.7 eV, respectively. Consequently, Eq. (1) gives \(\Delta E_{\text{V}}\) of 0.2 ± 0.3 eV. Evaluation using In 3d and Al 2p spectra in place of the In 4d spectrum resulted in the same \(\Delta E_{\text{V}}\) value.

Figure 6 shows the schematic band alignment based on reported band gap energy values\(^{0,11}\) and the present result of \(\Delta E_{\text{V}}\). Applying an amphoteric native-defect model, Walukiewicz proposed the Fermi-level stabilization energy (\(E_{\text{FS}}\)) as a reference energy level for Schottky-barrier formation in GaAs\(^2\) and heterointerface band line-up in III-V semiconductors.\(^3\) He also calculated band edges of III-N ternary alloys (AlGaN, InGaN, and InAlN) in reference to \(E_{\text{FS}}\), and estimated a small \(\Delta E_{\text{V}}\) of around 0.3 eV at the In\(_{0.17}\)Al\(_{0.83}\)N/GaN interface.\(^8\) The present value of measured \(\Delta E_{\text{V}}\) is in good agreement with the theoretically estimated value within the experimental error. On the other hand, XPS data in a previous report on the surface-Fermi-level pinning positions for thick InAlN alloys, concerning charge-neutrality level, support our results.\(^14\) It should be noted that the conduction-band offset is large, namely, 0.9–1.0 eV. It can therefore be concluded that a high electron barrier due to the large conduction-band offset is one of the reasons that high-density 2DEG is generated at the In\(_{0.17}\)Al\(_{0.83}\)N/GaN heterointerface.

In summary, \(\Delta E_{\text{V}}\) of a lattice-matched In\(_{0.17}\)Al\(_{0.83}\)N/GaN heterostructure grown by MOVPE was investigated by using XPS. AFM and angle-resolved XPS indicated a successful formation of a thin In\(_{0.17}\)Al\(_{0.83}\)N (2.5 nm thick) layer on GaN by MOVPE. The XPS result showed that the valence-band offset was 0.2 ± 0.3 eV, which indicated that \(\Delta E_{\text{C}}\) was large, namely, 0.9 to 1.0 eV.