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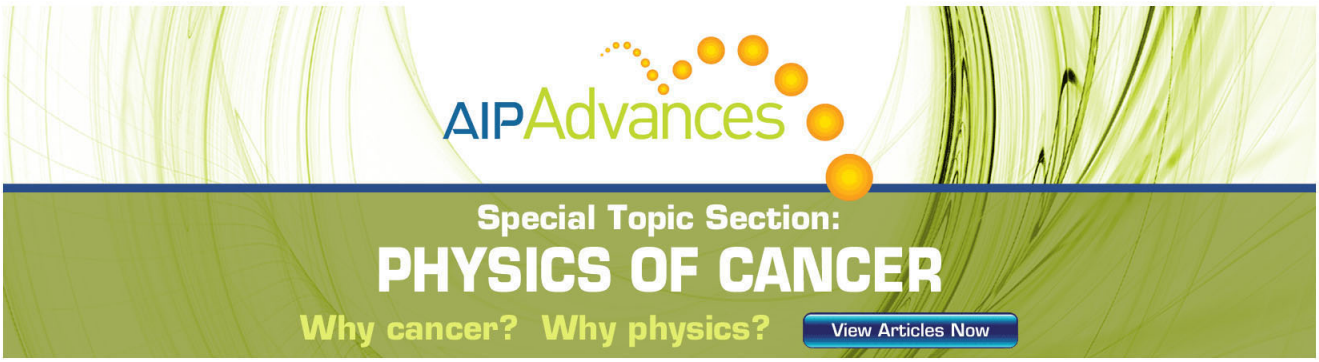

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Small valence-band offset of $In_{0.17}Al_{0.83}N/GaN$ heterostructure grown by metal-organic vapor phase epitaxy

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The valence-band offset of a lattice-matched $In_{0.17}Al_{0.83}N/GaN$ 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 $In_{0.17}Al_{0.83}N$ (2.5 nm) layer was successfully grown by MOVPE on GaN. The XPS result showed that the valence band offset was 0.2 ± 0.3 eV. This result indicates that the conduction-band offset at the $In_{0.17}Al_{0.83}N/GaN$ 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 $In_xAl_{1-x}N$ $(x=0.17-0.18)/GaN$ heterostructures can provide a 2DEG with a high density exceeding 2×10^{13} cm^{-2}.[1–6] Actually, InAlN/GaN high-electron mobility transistors with high performance have been reported.[2,3,5] To generate a high density 2DEG, a large conduction-band offset, ΔE_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 ΔE_C, resulting in a small valence band offset, ΔE_V. However, as far as the authors know, no experimental evidence of small ΔE_V has been reported. One of the methods for evaluating ΔE_V directly is x-ray photoelectron spectroscopy (XPS). In the present study, we attempted to evaluate ΔE_V at a lattice-matched $In_{0.17}Al_{0.83}N/GaN$ interface by XPS.

The schematic structure of the sample used for investigating the $In_{0.17}Al_{0.83}N/GaN$ interface is shown in Fig. 1 where the photoelectron exit angle, θ, is also indicated. To measure bulk material constants, $In_{0.17}Al_{0.83}N$ (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 $In_{0.17}Al_{0.83}N$ 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 $In_{0.17}Al_{0.83}N$ was successfully controlled by the MOVPE growth. XPS was done by using a monochromated Al-$K\alpha$ 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.

The surface morphology of the $In_{0.17}Al_{0.83}N$ (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 $In_{0.17}Al_{0.83}N$ layer had uniform thickness as a result of layer-by-layer growth. Angle-resolved

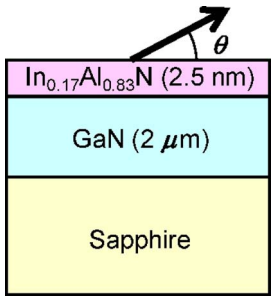

FIG. 1. (Color online) Schematic diagram of the sample structure and the definition of exit angle, θ.

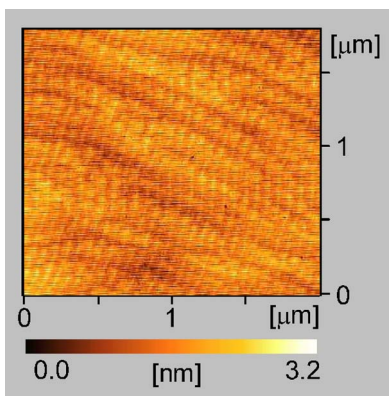

FIG. 2. (Color online) AFM image of the surface morphology of the $In_{0.17}Al_{0.83}N$ (2.5 nm) /GaN heterostructure.

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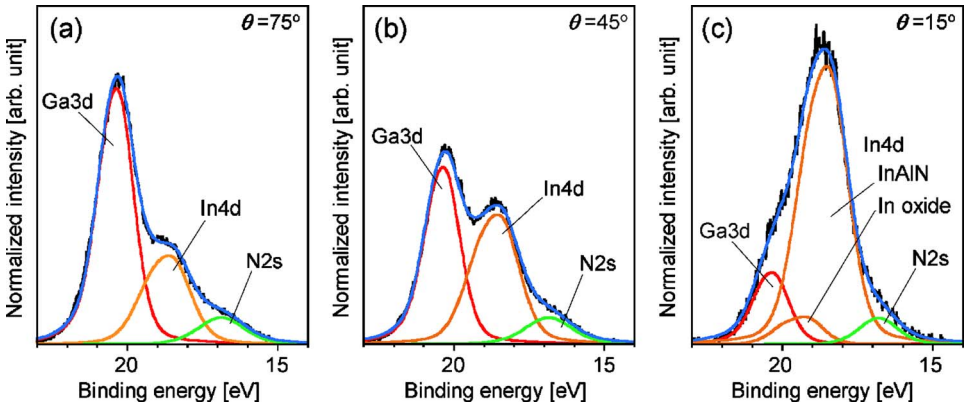

FIG. 3. (Color online) XPS Ga 3d, In 4d, and N 2s core-level spectra obtained for the $In_{0.17}Al_{0.83}N$ (2.5 nm) /GaN heterostructure. (a) θ=75°, (b) θ=45°, and (c) θ=15°.

XPS data also indicated this state, as described in the following.

Figures 3(a)–3(c) illustrate the observed Ga 3d, In 4d, and N 2s core-level spectra of the $In_{0.17}Al_{0.83}N$ (2.5 nm)/GaN samples for three different exit angles, whereas N 1s, Al 2p, and valence band, E_V, spectra are shown in Figs. 4(a)–4(c). These spectra show that successful chemical bonding without 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 $In_{0.17}Al_{0.83}N$ was grown as a layer. It should be noted that the location of the valence-band maximum (VBM) is independent of θ, as shown in Fig. 4(c), where the fine solid lines show the results of straight-line extrapolation. If ΔE_V 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 ΔE_V is small.

To estimate ΔE_V more precisely, energy separations between observed spectra were investigated. A schematic energy band diagram for the $In_{0.17}Al_{0.83}N/GaN$ interface is shown in Fig. 5. ΔE_V can be estimated from the following equation:[9]

$$\Delta E_V = -\Delta E_{CL} + (E^{GaN}_{Ga\ 3d} - E^{GaN}_{V}) - (E^{InAlN}_{In\ 4d} - E^{InAlN}_{V}), \quad (1)$$

where $\Delta E_{CL}=(E^{GaN}_{Ga\ 3d}-E^{InAlN}_{In\ 4d})$ is the core-level separation between the measured In 4d and Ga 3d spectra of the $In_{0.17}Al_{0.83}N(2.5\ nm)/GaN$ sample. The two $(E^{material}_{CL} - E^{material}_{V})$ terms are separations between a core level and a VBM of the thick GaN and $In_{0.17}Al_{0.83}N$ samples. Here, the band gap of $In_{0.17}Al_{0.83}N$ is larger than that of GaN. The band alignment is therefore type I when $\Delta E_V > 0$ but type II when $\Delta E_V < 0$.

Although piezoelectric polarization in the thin lattice-matched $In_{0.17}Al_{0.83}N$ layer on GaN can be ignored, spontaneous polarization existed. According to a previous report,[7] it is theoretically expected that the maximum polarization charge density can be 4×10^{-6} C/cm^2 at the interface. As a result of this effect and surface Fermi level pinning, a strong internal electric field is generated in the thin $In_{0.17}Al_{0.83}N$ layer. The internal electric field therefore leads to a potential drop large enough to affect the kinetic energy of photoelectron from the thin $In_{0.17}Al_{0.83}N$ layer, which results in broadening and energy-shift of XPS spectra.

Actually, binding energy and full-width-at-half maximum (FWHM) of the In 4d, In 3d, and Al 2p spectra both slightly 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 observed XPS spectra in the following sequence. First, a magnitude of the potential drop in the $In_{0.17}Al_{0.83}N$ layer is assumed. 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 $In_{0.17}Al_{0.83}N$ thickness of 2.5 nm could reproduce the observed energy shift and FWHM of the XPS spectra. Here, the

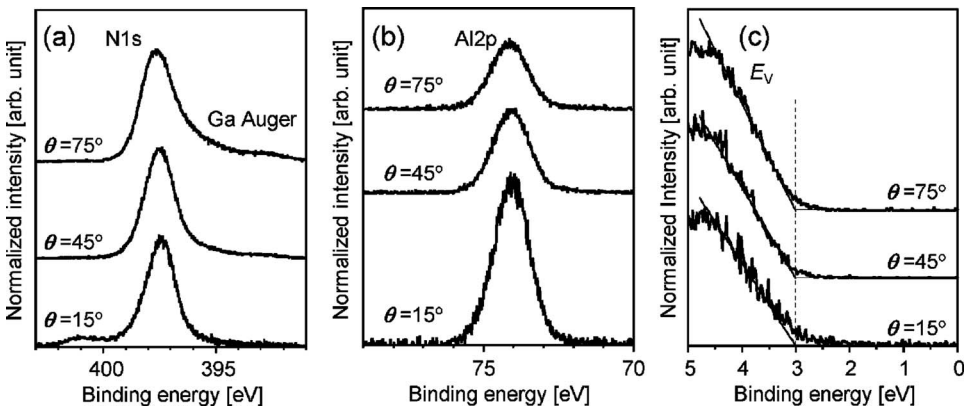

FIG. 4. XPS spectra for the $In_{0.17}Al_{0.83}N$ (2.5 nm) /GaN heterostructure with θ=15°, 45°, and 75°. (a) N 1s and Ga Auger spectra. (b) Al 2p spectra. (c) E_V spectra.

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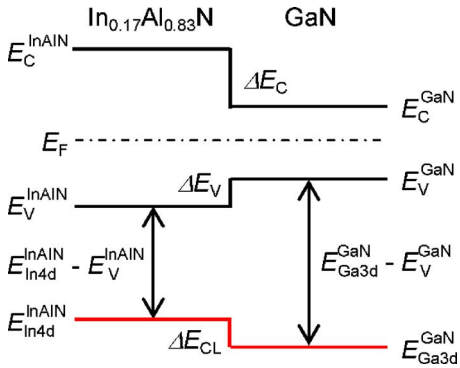

FIG. 5. (Color online) Schematic energy-band diagram of $In_{0.17}Al_{0.83}N/GaN$ interface.

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 4×10^{-6} C/cm^2 at the $In_{0.17}Al_{0.83}N/GaN$ interface. The derived electric field was therefore taken into account in determining ΔE_{CL} to be 1.2 eV. (The apparent separation in Fig. 3 is larger than this ΔE_{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, $E_{Ga\ 3d}^{GaN}-E_V^{GaN}$ and $E_{In\ 4d}^{InAlN}-E_V^{InAlN}$ were 17.1 eV and 15.7 eV, respectively. Consequently, Eq. (1) gives ΔE_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 ΔE_V value.

Figure 6 shows the schematic band alignment based on reported band gap energy values[10,11] and the present result of ΔE_V. Applying an amphoteric native-defect model,

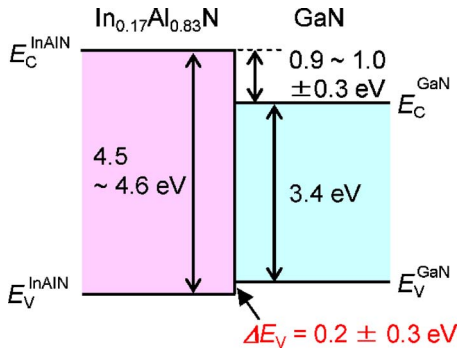

FIG. 6. (Color online) Schematic band alignment based on the measured ΔE_V.

Walukiewicz proposed the Fermi-level stabilization energy (E_{FS}) as a reference energy level for Schottky-barrier formation in GaAs[12] and heterointerface band line-up in III-V semiconductors.[13] He also calculated band edges of III-N ternary alloys (AlGaN, InGaN, and InAlN) in reference to E_{FS}, and estimated a small ΔE_V of around 0.3 eV at the $In_{0.2}Al_{0.8}N/GaN$ interface.[8] The present value of measured ΔE_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, ΔE_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 ΔE_C was large, namely, 0.9 to 1.0 eV.

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