Determination of the surface band bending in In$_x$Ga$_{1-x}$N films by hard x-ray photoemission spectroscopy

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Abstract
Core-level and valence band spectra of In$_x$Ga$_{1-x}$N films were measured using hard x-ray photoemission spectroscopy (HX-PES). Fine structure, caused by the coupling of the localized Ga 3d and In 4d with N 2s states, was experimentally observed in the films. Because of the large detection depth of HX-PES ($\sim$20 nm), the spectra contain both surface and bulk information due to the surface band bending. The In$_x$Ga$_{1-x}$N films ($x = 0$–0.21) exhibited upward surface band bending, and the valence band maximum was shifted to lower binding energy when the mole fraction of InN was increased. On the other hand, downward surface band bending was confirmed for an InN film with low carrier density despite its n-type conduction. Although the Fermi level ($E_F$) near the surface of the InN film was detected inside the conduction band as reported previously, it can be concluded that $E_F$ in the bulk of the film must be located in the band gap below the conduction band minimum.

Keywords: GaN, InGaN, InN, hard x-ray photoemission spectroscopy, HX-PES, band bending, core level, hybridization, valence band maximum

1. Introduction
Indium nitride (InN) materials are desirable for applications such as high-speed transistors, terahertz emission devices and solar cells because of their low band gap of $\sim$0.7 eV [1]. However, their intrinsic carrier density is higher than $1.0 \times 10^{18}$ cm$^{-3}$, which has made it difficult to realize these applications. Recently, the quality of InN films has been improved so that the residual carrier density can be reduced to the order of $10^{17}$ cm$^{-3}$ [2]. InN can be doped with Mg as an acceptor, and the formation of p-type InN has been confirmed by capacitance–voltage ($C$–$V$) measurements [3]. However, it is still very difficult to fabricate Schottky or p–n-junctions using InN films to obtain functional devices. It has been reported that the Fermi level ($E_F$) must be located in the conduction band for InN with carrier concentrations greater than $1.0 \times 10^{18}$ cm$^{-3}$ [4]. Also, it has been proposed that electrons are likely to accumulate on the InN surface [5, 6]. However, no clear evidence of downward band bending at the InN surface has been detected directly.
The band offset between GaN and its alloys such as Al$_{x}$Ga$_{1-x}$N and In$_{x}$Ga$_{1-x}$N affects the performance of electronic devices. Although the band offsets of the InN/GaN system have been studied, there are discrepancies between theoretical (from 0.3 [7] to 0.6 eV [8, 9]) and experimental values (0.58–1.1 eV [10–15]). Therefore, it is necessary to evaluate the variation of the valence band structure in In$_{x}$Ga$_{1-x}$N films as a function of InN mole fraction.

X-ray photoelectron spectroscopy (XPS) has been used as the surface-analysis method to detect core-level spectra with respect to chemical bonding and shift of materials. Conventional XPS is sensitive to surface contamination because its detection depth is only a few nanometers. The intensity of photoelectrons from the valence band is generally too weak to precisely determine surface band bending and offset. To overcome these disadvantages of conventional XPS, In$_{x}$Ga$_{1-x}$N films were investigated using hard x-rays from the synchrotron radiation at SPring-8 (hard x-ray photoemission spectroscopy (HX-PES) [16]). Because of the high kinetic energy of electrons excited by hard x-rays (5.95 keV), the detection depth of HX-PES is $\sim$20 nm. HX-PES detects photoelectrons sufficiently well to allow the valence band structure and band bending of In$_{x}$Ga$_{1-x}$N films to be evaluated in a similar manner to that previously reported for p-Al$_{x}$Ga$_{1-x}$N films [17].

In this paper, we have studied the valence band and core levels of In$_{x}$Ga$_{1-x}$N films using HX-PES. Ga 3d and In 4d core spectra and valence band structures are assessed to determine the effects of alloying GaN with InN. The influence of surface band bending on the determination of the valence band maximum (VBM) from the angular dependence of the N 1s core level and valence band spectra is discussed.

2. Experiment

Undoped In$_{x}$Ga$_{1-x}$N films ($x = 0–0.21$) were grown on GaN templates with Ga-face (+c) polarity that were deposited on a c-plane sapphire substrate by metal-organic chemical vapor deposition. Each In$_{x}$Ga$_{1-x}$N layer was 0.3–0.4 $\mu$m thick. The mole fraction of InN was controlled by the substrate temperature and was determined by x-ray diffraction measurement [18, 19]. From Hall measurement characterization the carrier concentration was in the range of $(1.8–5.0) \times 10^{17} \text{cm}^{-3}$. For comparison with high indium concentration films, InN films with carrier concentrations of $5.0 \times 10^{17}$, $1.5 \times 10^{18}$ and $5.0 \times 10^{18} \text{cm}^{-3}$ were also prepared by molecular beam epitaxy (MBE) as reported elsewhere [3].

The samples were introduced into the HX-PES apparatus at the undulator beamline BL15XU [20] of SPring-8. The energy and diameter of the x-ray beam were 5.95 keV and $\sim 60 \mu$m, respectively. The detection depth was approximately $\sim 20 \text{nm}$, three times the inelastic free path of the photoelectrons, with respect to the sample surface in the normal emission geometry where the E-vector of the x-ray and the detection direction of photoelectrons are parallel [21]. This experimental configuration enabled us to detect bulk-sensitive information with minimizing the influence from surface contamination. Another advantage of HX-PES in this configuration is the photoionization cross-section of the s-orbital is larger than that of conventional XPS (Al Kα x-ray source: 1486.6 eV) [22]. The total energy resolution was as good as 240 meV, which is significantly higher than that of conventional XPS of $\sim 600 \text{meV}$, comparable to the band gap value of InN. The system was referenced to the $E_F$ of bulk gold. A gold layer was also deposited over half of the sample surface, and the C 1s core level was measured on both areas. Thus the binding energy of the sample was calibrated by monitoring the shift in position of the C 1s core-level peak detected on the gold layer. The spectra were corrected with a Shirley-type background subtraction [23].

3. Results and discussion

3.1. Core-level spectra of Ga 3d and In 4d for In$_{x}$Ga$_{1-x}$N

Figure 1 presents Ga 3d, N 2s and N 2p-Al$_{x}$Ga$_{1-x}$N films with $x = 0–0.21$ and InN films with a carrier concentration of $5.0 \times 10^{17} \text{cm}^{-3}$ measured in the take-off angle (TOA) of 88° (bulk-sensitive, detection depth $\sim 20 \text{nm}$) conditions. The small Ga 3d–N 2s energy separation gives rise to hybridization between Ga 3d and N 2s in GaN. The hybridization causes a splitting of the $t_{2g}$ state into bonding ($t_{2g}$) and antibonding ($t_{2u}$) states, while the nonbonding state $e_g$ remains nearly atomic, showing spin–orbit splitting [24]. The peak at $\sim 19.8 \text{eV}$ is mainly bonding $t_{2g}$ state of Ga 3d-like, whereas the broad peak at $\sim 16 \text{eV}$ is dominantly antibonding $t_{2u}$ state of N 2s.

From the angular-momentum decomposition of the atom projected densities of states, done by Litimein et al [25], the orbital of N 2s in InN is attributed to three peaks, which are detected at 14, 16 and 17.3 eV in figure 1. In the calculation, three densities of states in the range 16–18 eV contribute...
predominantly to the In 4d orbital, as indicated by arrows in figure 1. The highest peak at 17 eV originates from In 4d as reported previously [26]. Although the peak of In 4d–N 2s at 17.3 eV should be theoretically smaller [25], the intensity gets higher experimentally due to the larger cross-section of the s-orbitals in the HX-PES.

Alloying GaN with InN, the localized Ga 3d and In 4d states were dispersed through hybridization with N 2s, as calculated in the model of In0.5Ga0.5N [27]. This is supported by two peaks emerging predominately around 17.5 and 18.3 eV.

### 3.2. Surface band bending and valence band maximum (VBM) of GaN films

The valence band structures also change when the mole fraction of InN is increased, as shown in figure 2. The intensity of the Ga 4s–N 2p peak at around 8.5 eV [28] is enhanced because the cross-section of the s-orbital in HX-PES is larger than that in conventional XPS. The VBM shifts to a lower binding energy (toward \( E_F \)) when GaN is alloyed with InN.

There are two possible extrapolations, lines a and b in figure 2 (expanded plot in figure 4), which are used to determine the VBM for the intrinsic GaN film at a TOA of 88°. The VBM calculated using line a is 2.9–3.0 eV. By taking the band gap of GaN (\( E_{GaN} \): 3.4 eV) into account, the energy difference between \( E_F \) and the conduction band minimum near the surface implies a value of 0.5 eV. This value is too small to explain the Schottky barrier height (SBH) on GaN films being larger than ~1.0 eV [29, 30]. On the other hand, the VBM determined using line b is 2.1 eV, which is consistent with both the SBH and the built-in potential evaluated at 1.2 eV from C–V measurements [31]. It can be concluded that the VBM determined from line a originates from the bulk of the film, whereas that calculated from line b is related to the surface region, as shown in the inset of figure 2.

### 3.3. N 1s core-level spectra of InN films grown by MBE

At a TOA of 88°, the peak position of N 1s core-level spectra was chemically shifted from 397.3 eV for GaN to 395.8 eV for InN when increasing the indium composition. Figure 3 presents the N 1s core-level spectra of InN films measured under bulk (TOA of 88°) and surface-sensitive (a TOA of 30° and a detection depth ~10 nm) conditions. For the sample with a carrier concentration of 5.0 × 10^{17} cm^{-3}, the spectrum with a TOA of 88° exhibits an asymmetrical shape with a tail.
at higher binding energy (figure 3(a)). A clear shift to higher binding energy is observed at a TOA of 30° and the spectrum becomes more symmetric with a smaller tail at higher binding energy compared to the spectrum at a TOA of 88°. This implies the presence of a downward band bending near the film surface, as shown in the inset of figure 3(a).

The N 1s core-level spectra at a TOA of 30° are symmetrical and the peak positions are constant at ~396.2 eV in spite of the carrier concentration, which is the same as the value determined by conventional XPS [32]. The asymmetric spectrum shape originates from two dominant components at a lower binding energy of 395.8 eV in the bulk of the film and at 396.2 eV near its surface due to the downward surface band bending. We attempted to determine the value of surface band bending according to the previous work analyzing surface band bending of Si [33]. However, the N 1s core spectra were found not to be simulated by a simple surface band bending profile. The profiles were not simulated even by introducing flat potential near the surface. The surface state of InN is not yet well understood.

As the carrier concentration increases, the shift of the N 1s core-level spectra is reduced and a more symmetric shape is observed in figure 3(c). For the InN film with a carrier concentration of $5.0 \times 10^{18}$ cm$^{-3}$, the surface band should be almost flat, implying that the depletion layer should be too shallow to detect the difference between detection depths of ~10 nm (TOA of 30°) and ~20 nm (TOA of 88°) (inset of figure 3(c)). The TOA dependence of the N 1s core-level spectra shape and its position shift is consistent with the expected thickness variation of the accumulation layer depending on the carrier concentration.

### 3.4. VBM of InN films

Figure 4 shows an expanded plot near the VBM of In$_x$Ga$_{1-x}$N films. The valence band spectra for the InN films with various carrier concentrations are represented as colored lines. At lower carrier concentration, the VBM of the InN films shift to lower binding energy. Two possible lines, c and d, were used to determine the VBM of InN. It can be considered that the VBM determined from line d originates from the bulk of the film, whereas that calculated from line c is related to the surface region, as shown in the inset of figure 3. By extrapolating line c, the VBM of InN with a carrier concentration of $5.0 \times 10^{17}$ cm$^{-3}$ is around 1.0 eV below $E_F$, which means that $E_F$ is located inside the conduction band. As far as normal carrier conduction occurs, the $E_F$ should not be located inside the conduction band as per the common understanding of semiconductor materials. It was therefore assumed that surface band bending influences the estimation of VBM as mentioned in section 3.2.

A slight difference of the VBM was observed between the spectra detected at TOAs of 88° and 30° for the InN film with a carrier concentration of $5.0 \times 10^{18}$ cm$^{-3}$. The VBM evaluated from both spectra was 1.3 eV (figure 5(a)), which is the same as the $E_F$ on the surface lying above the VBM previously determined using conventional XPS [4]. On the other hand, for InN with a carrier concentration of $5.0 \times 10^{17}$ cm$^{-3}$, the valence band spectrum near the surface of the film (TOA of 30°) is clearly shifted toward higher binding

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**Figure 4.** Enlarged valence band near $E_F$ of figure 2 at a TOA of 88°. The lines are extrapolated to determine the VBM.

**Figure 5.** Valence band structures detected at TOAs of 88° and 30° for InN films with carrier concentrations of (a) $5 \times 10^{19}$ cm$^{-3}$ and (b) $5 \times 10^{17}$ cm$^{-3}$. 

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energy, as shown in figure 5(b). When the conventional method is used (i.e. extrapolation of line c), the VBM values from both spectra are the same at 1.0 eV. The valence band spectrum at a TOA of 30° is apparently shifted toward a higher binding energy. The conventional approach is likely to overestimate the VBM because of the downward band bending at the surface of InN films.

The energy shift between TOAs of 88° and 30° is 0.5 eV (figure 5(b)). Hence, the VBM determined from the spectrum detected at a TOA of 88° must be located at the binding energy of 0.5 eV, which corresponds to the value determined from line d in figure 4. By taking both this estimated VBM and the band gap of 0.7 eV for InN into account, the E_F in the bulk must be located inside its band gap under the condition of a carrier concentration of less than 5.0 × 10^{17} cm^{-3}.

4. Conclusions

The electronic structures of In_{x}Ga_{1−x}N films were investigated by HX-PES. Because of the larger observation depth (~20 nm) of HX-PES than conventional XPS, the spectra contain both surface and bulk information reflecting the band bending on the surface. At higher mole fractions of InN, the VBM of In_{x}Ga_{1−x}N was shifted toward lower binding energy. Downward band bending near the surface was confirmed for InN films with a carrier concentration lower than ~1.0 × 10^{18} cm^{-3} for the first time. The HX-PES measurement revealed that E_F must be located inside the band gap of InN at higher detection depth.

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