InN/GaN valence band offset: High-resolution x-ray photoemission spectroscopy measurements

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High-resolution x-ray photoemission spectroscopy measurements are used to determine the valence band offset of wurtzite-InN/GaN(0001) heterojunctions to be 0.58 ± 0.08 eV. This is discussed within the context of previous measurements and calculations and is in agreement with the value of 0.52 ± 0.14 eV determined from the alignment of the experimentally determined charge neutrality levels in InN and GaN. The heterojunction forms in the type-I straddling configuration with a conduction band offset of 2.22 ± 0.10 eV.

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The InGaN material system presents enormous promise for a variety of optoelectronic device applications. The fundamental band gaps span from ~0.7 (Ref. 1) to ~3.5 eV (Ref. 2), suggesting potential applications in full-solar-spectrum photovoltaics,[3] high-performance light-emitting and laser diodes,[4] and solid-state lighting.[5] Detailed knowledge of the conduction and valence band offsets between InN and GaN are crucial to both obtaining a fundamental understanding of the electronic properties of InGaN alloys and to the design of heterostructure-based InGaN optoelectronic devices. Consequently these quantities have received considerable interest in recent years both experimentally[6–12] and theoretically,[13–17] although there is a large variety within the results obtained. In particular, the most widely cited value for the InN/GaN valence band offset (VBO) from Martin *et al.*,[6] which lies right at the top end of the range of previously determined values and substantially above those from theoretical predictions, was determined over a decade ago. Following significant recent improvements in epitaxial growth of InN and understanding of its band structure, an updated study of the InN/GaN VBO is required. This is presented here and the results discussed within the context of other studies. The determined VBO shows good agreement with the natural band alignment calculated from the relative positions of the charge neutrality level (CNL) in InN and GaN.

Wurtzite InN, GaN, and InN/GaN (thin InN grown on a GaN template) (0001) samples were grown on *c*-plane sapphire substrates by plasma-assisted molecular beam epitaxy (MBE), incorporating a GaN buffer layer for the InN sample. The InN (GaN) was grown at a temperature of ~450 °C (~620 °C). The InN layer in the InN/GaN sample was estimated to have a thickness of ~5 nm from growth rate calibrations and 5 ± 1 nm by considering the variation in intensity of the Ga x-ray photoemission spectroscopy (XPS) core-level peaks with emission angle due to the exponential attenuation of photoelectrons in the InN overlayer. Sample preparation was achieved by etching in HCl (10 M/l) for 60 s (InN and GaN) or 10 s (InN/GaN) followed by annealing *in vacuo* at ~275 °C (InN and InN/GaN) or ~325 °C (GaN) for 2 h. High-resolution XPS measurements were performed at room temperature using a Scienta ESCA300 spectrometer at the National Centre for Electron Spectroscopy and Surface Analysis, Daresbury Laboratory, U.K. Details of the spectrometer and its arrangement are reported elsewhere.[18] The binding-energy values reported here are referenced to the valence band maximum (VBM) of each sample, determined by extrapolating a linear fit of the leading edge of the valence band photoemission to the baseline in order to account for broadening of the photoemission spectra.[19]

The VBO of two semiconductor materials is "most reliably determined"[20] from XPS measurements of the valence band and core-level photoemission from bulklike samples of the two constituent materials and a heterojunction sample forming the interface of interest. The overlayer of this heterojunction sample must be sufficiently thin to allow XPS core levels from the underlying material to be probed due to the finite escape depth of the photoelectrons. The VBO is calculated from

$$\Delta E_V = \Delta E_{\mathrm{CL}} + [E(n\ell) - E_V]^{\mathrm{InN}} - [E(n'\ell') - E_V]^{\mathrm{GaN}}, \quad (1)$$

where the core-level difference ΔE_{CL} between the $n'\ell'$ core level of GaN and the $n\ell$ core level of InN is determined from the heterojunction sample and the $n\ell$ core level to VBM separation is determined for each material from the bulklike samples.

The In $3d_{5/2}$ and Ga $2p_{3/2}$ XPS core-level peaks from each sample and the valence band photoemission from the bulklike samples are shown in Fig. 1. All core-level peaks have been fitted using a Shirley background and Voigt (mixed Lorentzian-Gaussian) line shapes. Two components were required to fit the In $3d$ peaks; the higher binding-energy peak is attributed to the photoelectrons undergoing inelastic losses to conduction-band plasmons due to the high carrier densities present in the surface electron accumulation layer in InN (Ref. 21). The peak positions are listed in Table I, from which the VBO was calculated to be 0.59 ± 0.17 eV. To improve the accuracy of this value, the binding energies of a number of other In and Ga core-level and Auger peaks were also determined (listed in Table I). As above, the core-level peaks were fitted using a Shirley background and Voigt line shapes. The binding energy for the Auger peaks was taken as the energy corresponding to their maximum intensity. The In $4d$ and Ga $3d$ semicore-level peaks have not been included in the analysis as these levels are located at very low binding energies and hybridize with the N-like s levels at the bottom of the valence band.[22,23] Separating the cation d-like contribution from the anion s-like contribution is nontrivial as they cannot be curve fitted using the symmetric Voigt

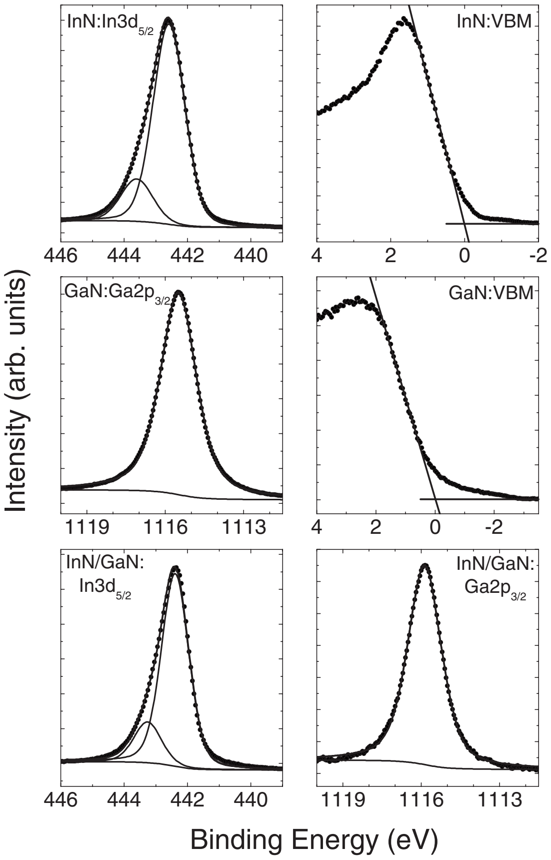

FIG. 1. In $3d_{5/2}$ and Ga $2p_{3/2}$ XPS core-level peaks for the InN, GaN, and InN/GaN samples and valence band photoemission spectra for the InN and GaN samples. The binding-energy scale is given with respect to the VBM in each sample. All peaks have been fitted using a Shirley background and Voigt (mixed Lorentzian-Gaussian) line shapes.

functions normally employed for core levels, leading to erroneous results and making these shallow semicore levels inappropriate to use in the band offset determination. Additionally, the In 4*d* and Ga 3*d* peaks lie very close in energy and so are not fully resolvable in photoemission spectra of the InN/GaN sample,[7,9] which will further limit the accuracy of the results attained using these semicore levels.

The VBO values derived from each combination of XPS core-level and Auger peaks used here are given in Table II. The room-temperature InN/GaN VBO is determined from the average of these values to be 0.58 ± 0.08 eV. Taking the room-temperature band gaps of InN (Ref. 24) and GaN (Ref. 2) to be 0.64 and 3.44 eV, respectively, this gives a conduction band offset (CBO) between InN and GaN of 2.22 ± 0.10 eV. At the interface, the bands align in a type-I straddling configuration, shown in Fig. 2, with a VBO:CBO ratio of approximately 20:80.

TABLE I. Binding energy (eV) of the XPS core-level and Auger peaks in the InN/GaN, InN, and GaN samples relative to the valence band maximum of each sample.

	InN/GaN	InN	GaN
In $3d_{5/2}$	442.39	442.60	
In $3p_{3/2}$	663.76	664.04	
In 3*s*	824.51	824.82	
In MNN Auger	1084.29	1084.53	
Ga $3p_{3/2}$	103.26		102.97
Ga 3*s*	158.54		158.22
Ga $2p_{3/2}$	1115.87		1115.49
Ga LMM Auger	420.74		420.44

TABLE II. InN/GaN VBO calculated using each set of XPS core-level and Auger peaks.

	In $3d_{5/2}$	In $3p_{3/2}$	In 3*s*	In MNN Auger
Ga $3p_{3/2}$	0.50	0.57	0.60	0.53
Ga 3*s*	0.53	0.60	0.63	0.56
Ga $2p_{3/2}$	0.59	0.66	0.69	0.62
Ga LMM Auger	0.51	0.58	0.61	0.54

The VBO determined here is approximately half that of the widely cited value of 1.05 ± 0.25 eV suggested by Martin *et al.*[6] over a decade ago. At that time, the growth of InN had not been optimized with impurity and/or defect concentrations generally so high that the fundamental band gap of the material was thought to be around 1.9 eV (Ref. 25). Consequently, the structural quality of the material may not have been as high as that of optimized MBE grown material today. Also, extremely thin overlayers (5–20 Å) were used for the heterojunction samples. The wurtzite nitride materials are pyroelectric,[26] and so Martin *et al.* employ calculations to account for a possible influence of strain-induced piezoelectric fields on the interface band offsets measured for InN/GaN and GaN/InN. They assumed that a strain-induced piezoelectric field always acts to decrease the measured value of the VBO. However, the piezoelectric coefficient changes sign for InN coherently strained on GaN compared to GaN coherently strained on InN (Ref. 27). Furthermore, they note that the critical thickness for strain to be relieved by the introduction of dislocations in this material system is very small, and so the assumption of pseudomorphic strained layers is not valid. Consequently, they apply an estimated correction for potential effects of an unknown degree of strain,

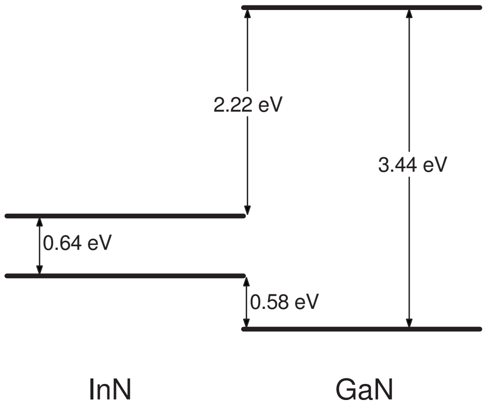

FIG. 2. Schematic of the room-temperature interface band alignment at an InN/GaN heterojunction.

which introduces substantial errors into the final result. Neglecting the correction they applied, the VBO value determined here actually agrees rather well with their experimental value of the GaN/InN VBO of 0.59 ± 0.24 eV, although it is still somewhat lower than the value of 0.93 ± 0.25 eV determined for InN/GaN. Due to the extremely large lattice mismatch between GaN and InN (~11%), the majority of the strain relaxes within the first few monolayers of growth[28,29] and any residual strain-induced piezoelectric field would be screened by the high carrier densities in InN (Ref. 13). Consequently, there will be no contribution from strain-induced piezoelectric fields to our measured VBO.

Shih *et al.*[7] also employed XPS to determine the InN/GaN VBO, obtaining a value of 0.5 ± 0.1 eV, which is in good agreement with our results. However, we find this agreement rather coincidental as Shih *et al.* employ the In 4*d* and Ga 3*d* peaks to determine the band offset. As discussed above, these peaks essentially form part of the valence band structure, hybridizing with the N 2*s*-like level, making them inappropriate to use in the band offset measurement. Additionally, Shih *et al.* perform deconvolution of the overlapping In 4*d* and Ga 3*d* peaks in the InN/GaN sample using a single Gaussian function for each component, neglecting not only the effects of the hybridization but also the spin-orbit split *d*-level character of these peaks, lifetime broadening effects, and inelastic losses to conduction-band plasmons.[21]

Wu *et al.* used 120 and 130 eV photoemission spectroscopies[9] and 380 eV microscopic-area photoemission spectroscopy[12] to investigate the InN/GaN VBO as a function of polarity of the film, determining values of 1.04 and 0.54 eV for In/Ga- and N-polarity cases, respectively, and 0.78 eV for the N-polarity VBO measured at the cleaved *a*-plane surface. These investigations again used the In 4*d* and Ga 3*d* peaks for the VBO determination, which would be expected to lead to large errors in the results as discussed above. Inelastic losses,[21] which complicate the shape of these peaks yet further are again not considered in the fitting of these semicore levels. Further, the intensity ratio of the various components used in the peak fitting changed markedly between the In/Ga- and N-polar samples, and indeed the number of components changed between the fittings performed for the polar and cleaved *a*-plane surfaces, making determination of any shift in binding energy of the components (leading to the change in measured VBO as a function of polarity) ambiguous. The effect of polarity on the VBO was attributed to the effect of spontaneous polarization (SP) dipoles at the interface. However, a large effect of SP seems unlikely due to an efficient screening of the SP as for the piezoelectric contribution.

Mahmood *et al.*[10] have used internal photoemission measurements to investigate the InN/GaN VBO, determining a value of ~0.85 eV, slightly higher than the value determined here. However, there seem to be large experimental errors associated with this measurement particularly in extracting the relevant transition energies from the photocurrent data. Additionally, an estimate of the Fermi level in the material is required in order to determine the CBO, which is very low in comparison to the optical-absorption data presented with the resulting combination of VBO, CBO, internal photoemission transitions, and InN Fermi-level position being inconsistent. Wang *et al.*[11] used capacitance-voltage and photocurrent spectroscopy to determine the InN/GaN CBO to be 1.68 ± 0.1 eV, giving a VBO of ~1.07 eV, which is significantly higher than determined here. However, their determination of the band offsets requires calculation of band bending at the interface, introducing many assumptions which, as Wang *et al.*[11] themselves point out, limits the accuracy. Ohashi *et al.*[8] have estimated the InN/GaN VBO to be 0.9 eV from modeling of photoluminescence peak wavelengths from InN/$In_{0.75}Ga_{0.25}N$ quantum wells. However, the use of InN/$In_{0.75}Ga_{0.25}N$ rather than InN/GaN quantum wells, combined with the many parameters needed for the modeling, which the authors themselves point out are not all well known, introduces substantial error into this result.

Wei and Zunger[13] directly determined the InN/GaN VBO from density-functional theory (DFT) calculations, obtaining a value of 0.48 ± 0.1 eV for the wurtzite structure in agreement with the VBO determined here. Van de Walle and Neugebauer[14] calculated the InN/GaN VBO to be 0.3 ± 0.1 eV for zinc-blende material. Wei and Zunger[13] obtained 0.26 ± 0.1 eV for zinc-blende material, suggesting a smaller value of the VBO for zinc blende rather than wurtzite material. Consequently, the calculations of Van de Walle and Neugebauer[14] are also consistent with the band offset determined here for wurtzite material.

The natural band lineup of two semiconductors can also be determined from the locations of the CNL relative to the VBM in each material.[30,31] The influence of charge transfer at the interface[32] can be neglected here due to the extremely similar electronegativities of InN and GaN. Mönch[20] has shown the alignment of CNLs to hold for metamorphic heterostructures, making it an excellent way to predict the VBO in this case. From the preferred CNL values of Robertson and Falabretti,[17] the *ab initio* calculations of Van de Walle *et al.*,[15,33] and the empirical tight-binding calculations of Mönch,[16] the InN/GaN VBO can be estimated as 0.43, 0.37, and 0.86 eV, respectively. The value of the VBO determined here lies within this range of theoretical values.

The CNL has recently been experimentally located 1.83 ± 0.10 eV above the VBM in InN (Ref. 34). A number of studies[35,36] have determined the Schottky barrier height (SBH) for Pd/GaN to be in the range of 0.94–1.24 eV. As there is only a small electronegativity difference between Pd and GaN, this approximates to the zero-charge-transfer barrier height, from which the CNL can be estimated to lie 2.20–2.50 eV above the VBM in GaN. Kampen and Mönch[37] and Lüth[38] considered SBHs of a range of metals of varying electronegativity deposited on GaN analyzed within the metal-induced gap states model,[39] showing the CNL to be located 2.35 eV above the VBM. We therefore take the experimental location of the CNL in GaN to be 2.35 ± 0.10 eV above the VBM. The difference of the CNL positions in InN and GaN therefore gives the InN/GaN VBO as 0.52 ± 0.14 eV, in agreement with the value determined directly from XPS measurements here.

Although reasonable scatter exists within the previous experimental and theoretical results, the InN/AlN and GaN/AlN VBO are approximately 1.5 (Refs. 16 and 40) and 0.9 eV (Ref. 2), respectively. Consequently, the transitivity rule is obeyed to within experimental error. The predominant factor in determining the relative energy of the valence band edges in the common-anion III-N material system is a hybridization (*p*-*d* repulsion) between the cation *d* orbitals and N 2*p* orbital (Refs. 13, 14, and 34), which pushes the VBM to higher energies.[41] Al has no occupied *d* orbitals, whereas Ga and In both have occupied *d* orbitals, explaining the relatively smaller VBO between InN and GaN than between AlN and (In/Ga)N.

In conclusion, we have determined the InN/GaN valence band offset to be 0.58 ± 0.08 eV, in agreement with the value determined from the positions of the charge neutrality level in InN and GaN. A type-I heterojunction forms between InN and GaN in the straddling configuration with a conduction-band offset of 2.22 ± 0.10 eV. The valence band offset determined here is smaller than from most previous experimental investigations, although it is consistent with theoretical calculations. Its relatively small value can be understood as it derives largely from the difference in *p*-*d* repulsion strength between the In/Ga *d* orbitals and N 2*p* orbital.

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