Valence band offset of InN/AlN heterojunctions measured by x-ray photoelectron spectroscopy

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The valence band offset of wurtzite-InN/AlN (0001) heterojunctions is determined by x-ray photoelectron spectroscopy to be 1.52±0.17 eV. Together with the resulting conduction band offset of 4.0±0.2 eV, a type-I heterojunction forms between InN and AlN in the straddling arrangement. © 2007 American Institute of Physics. [DOI: 10.1063/1.2716994]

The band gaps of group III-N semiconductors span an extremely wide range from a now generally accepted zerotemperature value of approximately 0.7 eV for InN (Refs. 1 and 2) to approximately 6.25 eV for AlN. This introduces the possibility for III-N alloys and heterostructures to be used in a wide variety of optoelectronic devices, where a large variation in the operating wavelength range of the device is required. Of crucial importance to the design of such devices is an accurate characterization of the band offsets. The band offset at InN/AlN heterojunctions has received interest both experimentally and theoretically. However, there has been a large variation both within and between the measured and theoretical values reported previously. In addition, a number of these studies were performed before the revision of the InN band gap from the previously accepted value of 1.89 eV, and so these results should be re-evaluated in light of this change. In this letter, we present a determination of the wurtzite-InN/AlN band offsets using x-ray photoelectron spectroscopy (XPS).

The InN and InN/AlN samples were grown on c-plane sapphire substrates by plasma assisted molecular-beam epitaxy at growth temperatures of 480 °C for the InN layers and 800 °C for the AlN layers. Details of the growth are reported elsewhere. The InN sample had a layer thickness of 310 nm and a carrier concentration and electron mobility measured by the single-field Hall effect of 2×10^18 cm^-3 and 1100 cm^2 V^{-1} s^{-1}, respectively. The InN/AlN sample consisted of a thin layer of InN grown on a 200 nm layer of AlN. The InN layer thickness was estimated at 4.5 nm from growth-rate calibrations and at 4.6 nm by considering the variation of intensity of the Al2O3 components but not significant N–O bonding. Adventitious hydrocarbons were also identified on the surface.

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The AlN film was grown to a thickness of 1 μm on a c-plane sapphire substrate at a temperature of 1150 °C by metalorganic chemical vapor deposition. The XPS measurements were performed at room temperature using a Scienta ESCA300 spectrometer at the National Centre for Electron Spectroscopy and Surface analysis, Daresbury Laboratory, UK. Details of the spectrometer and its arrangement are reported elsewhere.

The position of the valence band maximum (VBM) is calculated by extrapolating a linear fit to the leading edge of the valence band photoemission to the background level in order to take account of the finite resolution (0.45 eV) of the spectrometer. A low-energy electron flood gun was utilized for the measurements of the AlN sample to achieve charge compensation. Calibration to a universal energy reference was not required as it is the relative energy separation of spectral features that is of importance for the determination of a valence band offset (VBO).

Measurements are presented for as-loaded (oxidized) samples due to the difficulty in cleaning the samples without causing electronic damage. This is especially important for the InN/AlN sample, where cleaning could additionally cause significant reduction in the thickness of the already very thin InN layer. Investigation of the In3d, Al2p, N1s, C1s, and O1s core level peaks from XPS indicated III–O oxide components but not significant N–O bonding. Adventitious hydrocarbons were also identified on the surface.

The In3d core level peaks for the InN and InN/AlN samples, the Al2p core level peaks for the AlN and InN/AlN samples, and the valence band photoemission for the InN and AlN samples are shown in Fig. 1. All peaks have been fitted using a Shirley background (incorporating a linear component) and Voigt (mixed Lorentzian-Gaussian) line shapes. The peak parameters and valence band maximum positions are listed in Table I. The spin-orbit split In3d peaks in both the InN and InN/AlN samples are seen to consist of three components. The lowest binding energy component is associated with In bonded to N. The higher ratio of the In–N peak intensity to the (higher binding energy) contaminant related peaks for the InN sample compared to the InN/AlN sample is consistent with the relative thicknesses of the InN layer in the two samples. The higher binding energy peaks...
are identified as being due to surface contamination. Comparison of their binding energy separation with previous results suggests assignments of In–O bonding (from the oxidized surface, In$_2$O$_3$) and In–(OH)$_3$ bonding for the mid and highest-binding energy components, respectively. The Al$_{2p}$ peak is composed of a single component (Al–N bonding) in the InN/AlN sample as the AlN layer is below the surface and so does not have an oxide component. The spin-orbit splitting of the Al$_{2p}$ peak is not resolvable in Fig. 1, but is included in the fitting. In the AlN sample, an additional small peak was required to fit the spectrum at high binding energy, consistent with Al–O bonding due to the oxide contamination when AlN is present at the surface. The valence band photoemission for the InN and AlN samples. All peaks have been fitted using a Shirley background with a linear component and Voigt (mixed Lorentzian-Gaussian) line shapes as shown.

Table I. Parameters (binding energy, full width at half maximum (FWHM), Lorentzian to percentage of the Voigt line shape (L), and spin-orbit splitting ($\Delta_{\text{so}}$) of the peaks used in the core level fitting and the valence band photoemission extrapolations used to fit the XPS data shown in Fig. 1. No correction for the shift in binding energies due to the operation of the flood gun has been applied for the AIN sample as this does not affect the relative separation of the spectral features.

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\Delta E_v = \Delta E_{\text{CL}} + (E_{\text{InN}}^{3d} - E_v^{\text{InN}}) - (E_{\text{AlN}}^{3d} - E_{\text{AlN}}^{\text{VBM}}),
\]

where $E_v^A$ denotes the VBM in material $A$, $E_B^A$ denotes the energy of the core level $B$ in material $A$, and $\Delta E_{\text{CL}}$ is the energy separation of the Al$_{2p}$ and In$_{3d}$ core level peaks in the InN/AlN sample. Using the In–N bonding component of the In$_{3d_{3/2}}$ and the Al–N bonding component of the Al$_{2p_{3/2}}$ core level peaks, the InN/AlN VBO is calculated as 1.52±0.17 eV. This value is comparable to, although slightly lower than, the experimental value of 1.81±0.20 eV determined from XPS by Martin et al. and significantly lower than the value of 3.10±0.04 eV recently determined from photoelectron spectroscopy utilizing 110 eV incident photons by Wu et al.

The theoretically determined values of the VBO are close to or somewhat lower than the experimental value reported here. 1.46 eV calculated from charge neutrality levels determined from empirical tight-binding calculations, 1.25 eV using a first-principles general potential linearized augmented plane wave method and 0.97 eV calculated from charge neutrality levels determined from Green’s functions) with better agreement seen here than with previous experimental studies.

The room temperature band gaps of InN [0.64 eV (Ref. 2)] and of AlN [6.16 eV (Ref. 3)], calculated from the zero-temperature values and Varshni parameters, allow the band lineup to be determined, as shown in Fig. 2. The resulting conduction band offset is therefore calculated as 4.0±0.2 eV. A type-I heterojunction is seen to be formed in the straddling configuration.

In conclusion, we have measured the valence band offset of an InN/AlN heterojunction as 1.52±0.17 eV. This is

![FIG. 1. In$_{3d}$ core level peaks for the InN and InN/AlN samples, Al$_{2p}$ core level peaks for the AlN and InN/AlN samples, and valence band photoemission for the InN and AlN samples. All peaks have been fitted using a Shirley background with a linear component and Voigt (mixed Lorentzian-Gaussian) line shapes as shown.](image-url)
similar, although somewhat higher, than previous theoretical calculations, and somewhat lower than previous experimental results. This offset causes a type-I heterojunction to form between InN and AlN in the straddling arrangement.

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