X-ray photoemission spectroscopy determination of the InN/yttria stabilized cubic-zirconia valence band offset

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The valence band offset of wurtzite InN(0001)/yttria stabilized cubic-zirconia (YSZ)(111) heterojunctions is determined by x-ray photoemission spectroscopy to be 1.19±0.17 eV giving a conduction band offset of 3.06±0.20 eV. Consequently, a type-I heterojunction forms between InN and YSZ in the straddling arrangement. The low lattice mismatch and high band offsets suggest potential for use of YSZ as a gate dielectric in high-frequency InN-based electronic devices. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2783214]

The low effective mass,[1] high mobility,[2] and excellent predicted transport characteristics[3,4] of InN make this material a promising candidate for high-frequency electronic devices. The band offsets of InN with other materials are crucial to the design of such devices, and the valence band offset (VBO) of InN with other III-N semiconductors has been investigated previously.[5–7]

The realization of practical devices requires the growth of high quality InN layers. InN is commonly grown on (0001) sapphire substrates, incorporating an AlN and/or GaN buffer layer.[8] The lattice mismatch between these buffer layers and the InN layer is, however, large (14% and 11%, respectively). This mismatch relaxes largely through the introduction of threading dislocations,[9,10] and these have been shown[10,11] to be one source of the high unintentional *n*-type conductivity observed in InN films grown to date. Recently, (111) oriented yttria stabilized cubic-zirconia (YSZ) has been investigated as an alternative substrate for growth due to its much smaller lattice mismatch with InN of only 2.5%. Consequently, InN films grown on YSZ substrates have been shown to have lower measured carrier concentrations than comparable thickness films grown directly on sapphire substrates,[12] with further reductions likely following improvement in growth optimization, suggesting their potential for use in high quality growth for device applications.

Another current limitation in the design of InN-based high-frequency electronic devices is the lack of a suitable material for use as a gate dielectric, with the oxide In_2O_3 being one of the few materials suggested as a potential candidate.[13] However, from theoretical calculations of the charge neutrality level positions and band gaps in InN and In_2O_3[14,15] the conduction band offset (CBO) between InN and In_2O_3 is estimated to be only 0.71 eV, which may limit its potential for use as a gate dielectric material. Due to its high dielectric constant (it is a so-called high-*K* material) and good predicted band offsets, YSZ has previously been shown to be a potential material to replace the SiO_2 gate dielectric commonly utilized in Si-based devices,[16] indicating its potential application in electronic devices based on alternative material systems.

In this letter, we present a determination of the VBO at wurtzite InN(0001)/YSZ(111) heterojunctions using x-ray photoemission spectroscopy (XPS). The consequences of this on the potential for use of YSZ as a gate dielectric in InN-based devices are discussed.

Measurements were performed on two InN samples grown on YSZ(111) substrates by plasma assisted molecular beam epitaxy at a growth temperature of approximately 400 °C. Details of the growth are reported elsewhere.[12] The thicker film (referred to hereafter as InN) had an InN layer thickness of 520 nm and an average carrier concentration and electron mobility measured by the single-field Hall effect of 2.6×10^{18} cm^{-3} and 176 cm^2 V^{-1} s^{-1}, respectively. The thickness of the thinner film (referred to hereafter as InN/YSZ) was estimated as 4.9 nm from growth rate calibrations and as 5.9 nm by considering the variation of intensity of the Zr 3*d* XPS core-level peak with take-off angle due to the exponential attenuation of photoelectrons by the InN overlayer described by the Beer-Lambert law. The inelastic mean free path of the photoelectrons in the InN layer was calculated using the TPP-2M predictive formula of Tanuma *et al.*[17] The YSZ substrates consisted of zirconia (ZrO_2) stabilized in the cubic phase at room temperature by the addition of approximately 33 mol % (determined by Rutherford backscattering measurements) of yttria (Y_2O_3).

The XPS measurements were performed using a Scienta ESCA300 spectrometer at the National Centre for Electron Spectroscopy and Surface Analysis, Daresbury Laboratory, UK. X rays of energy $h\nu=1486.6$ eV were produced using a monochromated rotating anode Al $K\alpha$ x-ray source. The ejected photoelectrons were analyzed by a 300 mm mean radius spherical-sector electron energy analyzer with 0.8 mm slits at a pass energy of 150 eV. The effective instrumental resolution is 0.45 eV derived from the Gaussian convolution of the analyzer broadening and the natural linewidth of the x-ray source (0.27 eV). The position of the valence band maximum (VBM) is determined 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 of the spectrometer.[18] A low-energy electron flood gun was utilized for the measurements of the YSZ sample to achieve charge compensation. Measurements are presented

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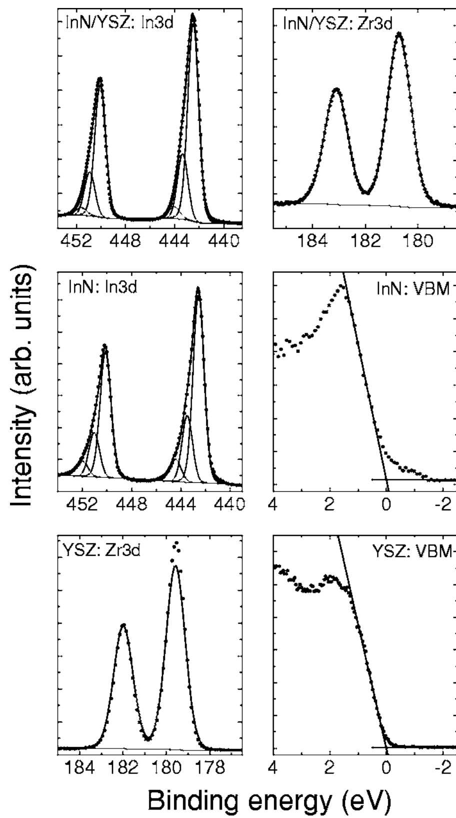

FIG. 1. In 3*d* core level peaks for the InN/YSZ and InN samples, Zr 3*d* core level peaks for the InN/YSZ and YSZ samples, and valence band photoemission for the InN and YSZ samples. All peaks have been fitted using a Shirley background and Voigt (mixed Lorentzian-Gaussian) line shapes, as detailed in Table I, and have been shifted in energy to align the VBM for all samples at 0 eV.

for as-loaded (oxidized) samples due to the difficulty in cleaning InN without causing electronic damage.[19,20]

The core-level and valence band photoemission spectra for the InN/YSZ, InN, and YSZ samples are shown in Fig. 1. All peaks have been fitted using a Shirley background and Voigt (mixed Lorentzian-Gaussian) line shapes and have been shifted in energy to align the VBM for all samples at 0 eV. The relevant peak parameters are listed in Table I. Each of the spin-orbit split In 3*d* peaks in both the InN and InN/YSZ samples consist of three components. The lowest binding energy component is associated with In bonded to N. The higher binding energy components are associated with surface oxide contamination and inelastic scattering losses (plasmons) in the InN layer.[21] For all other core level peaks, a single (spin-orbit split) component was sufficient to fit the XPS data.

The VBO was calculated from

$$\Delta E_V = \Delta E_{CL} + (E_{\mathrm{In}\ 3d}^{\mathrm{InN}} - E_V^{\mathrm{InN}}) - (E_{\mathrm{Zr}\ 3d}^{\mathrm{YSZ}} - E_V^{\mathrm{YSZ}}), \quad (1)$$

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 ΔE_{CL} is the energy separation of the Zr 3*d* and In 3*d* core level peaks in the InN/YSZ sample. This gives an InN/YSZ VBO of 1.19 ± 0.17 eV. The above analysis does not include any effects of strain. As III-nitrides are piezoelectric materials, strain induced piezoelectric fields in the InN overlayer could influence the measured valence band discontinuity.[7] However, the required layer thickness for InN grown on YSZ to be fully relaxed has been estimated as 5 nm;[22] any strain in the samples measured here should therefore be minimal, and consequently the measured VBO is expected to represent the natural band lineup.

Theoretical calculations of the VBO between InN and YSZ have not been performed. However, using the charge neutrality level positions determined from Green's functions, calculations by Robertson and Falabretti[14,23] for InN, zirconia, and yttria, the predicted VBOs for InN/ZrO_2 and InN/Y_2O_3 are 1.73 and 0.53 eV, respectively. Our measured value for InN/YSZ lies between these two values, consistent with these theoretical values considering the composite nature of the YSZ. Indeed, if a linear variation of the valence band edge with yttria content is assumed, which is an approximation given the differing crystal phases of YSZ, these theoretical values imply an InN/YSZ VBO of 1.33 eV, in agreement with the measured value.

From room temperature optical absorption measurements (not shown), the band gap of the YSZ substrate is determined to be 4.89 ± 0.10 eV, consistent with previous results.[24,25] From this and a room temperature InN band gap of 0.64 eV,[26] the band lineup can be determined, as shown in

TABLE I. Parameters [binding energy, full width at half maximum (FWHM), Lorentzian percentage of the Voigt line shape (L), and spin-orbit splitting (Δ_{so})] of the peaks used in the core-level fitting and VBO determination, and the valence band photoemission extrapolations used to fit the XPS data shown in Fig. 1. All spectra have been shifted so that the VBM for each sample lies at 0 eV.

Sample	Region	Binding energy (eV)	FWHM (eV)	*L* (%)	Δ_{so} (eV)
InN/YSZ	In 3*d*[a,b]	442.49±0.05	1.09	8	7.57
	Zr 3*d*[a]	180.71±0.05	1.05	8	2.40
	VBM	0.00±0.10	⋯	⋯	⋯
InN	In 3*d*[a]	442.55±0.05	1.09	8	7.57
	VBM	0.00±0.10	⋯	⋯	⋯
YSZ	Zr 3*d*[b]	179.58±0.05	1.05	8	2.40
	VBM	0.00±0.10	⋯	⋯	⋯

[a]Listed values are for the $3d_{5/2}$ peak. The $3d_{3/2}$ peak width and Lorentzian-Gaussian parameters are the same, with the binding energy shifted by the spin-orbit splitting Δ_{so}.
[b]Only the lowest binding energy (In–N) component is tabulated. The higher binding energy components associated with oxide bonding and inelastic scattering losses in the InN layer are not shown.

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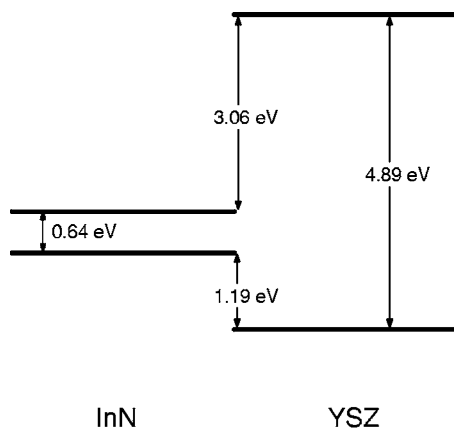

FIG. 2. Schematic representation of the band lineup at an InN/YSZ heterojunction at room temperature.

Fig. 2. A type-I heterojunction forms in the straddling configuration with a CBO of 3.06±0.2 eV.

As discussed, in order to utilize InN in high-frequency electronic devices such as high electron mobility transistors, a suitable gate dielectric must be used. This must form high quality interfaces with InN with few interfacial defects and must have both valence and conduction band offsets of at least 1 eV to prevent electron and hole leakage via Schottky emission.[23] The band offsets between InN and YSZ have been shown above to be large enough to ensure sufficiently low leakage currents, and the low lattice mismatch makes this a suitable candidate for forming high quality interfaces under optimized growth conditions; YSZ may therefore be suitable for use as a gate dielectric in high-frequency InN electronic device applications.

In conclusion, the valence band offset of an InN/YSZ heterojunction has been measured as 1.19±0.17 eV. This is within the range expected from previous theoretical calculations. This offset gives a type-I heterojunction between InN and YSZ in the straddling arrangement with a conduction band offset of 3.06±0.20 eV. The large band offsets and small lattice mismatch between InN and YSZ suggest potential for the use of YSZ as a gate dielectric in InN-based high-frequency electronic devices.

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