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Valence band offset of the ZnO/AlN heterojunction determined by x-ray photoemission spectroscopy

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The valence band offset of ZnO/AlN heterojunctions is determined by high resolution x-ray photoemission spectroscopy. The valence band of ZnO is found to be 0.43 ± 0.17 eV below that of AlN. Together with the resulting conduction band offset of 3.29 ± 0.20 eV, this indicates that a type-II (staggered) band line up exists at the ZnO/AlN heterojunction. Using the III-nitride band offsets and the transitivity rule, the valence band offsets for ZnO/GaN and ZnO/InN heterojunctions are derived as 1.37 and 1.95 eV, respectively, significantly higher than the previously determined values. © 2008 American Institute of Physics. [DOI: 10.1063/1.3032911]

ZnO is of interest in a range of current research areas as a result of its wide band gap (~ 3.3 eV at 300 K) and particularly high exciton binding energy (60 meV).¹ Since excitons are stable at room temperature, ZnO is very attractive for the realization of optoelectronic devices based on cavity-coupled polariton lasers operated at room temperature.²⁻⁴ Other promising optoelectronic device applications include blue and green light emitting diodes,⁵⁻⁷ where ZnO can be used either as the active region or as a transparent contact.

Combinations of ZnO and III-N materials have considerable potential for heterostructure devices as a result of their high epitaxial compatibility (wurtzite structures with lattice mismatches between -4% and 9%) and the range of band gaps available using III-N binary and ternary materials (from ~ 0.7 to ~ 6.2 eV).⁸ Most work on hybrid oxide/nitride systems to date has focused on ZnO/GaN,^{9,10} but in order to fully exploit these materials other combinations must be explored.

For heterostructure devices, knowledge of the valence and conduction band offsets of the different material combinations is of particular importance. The III-N/III-N heterojunction band offsets have been determined by x-ray photoemission spectroscopy (XPS),^{11,12} with type-I (straddling) band line-ups being found in all cases, as predicted from *ab initio* calculations^{13,14} and charge neutrality level arguments.^{12,15,16}

Of the ZnO/III-N heterojunctions, ZnO/InN (Ref. 17) and ZnO/GaN (Ref. 18) band offsets have been measured and show type-I and type-II junctions, respectively. While these junction types are in agreement with theoretical studies, as discussed later, the actual values of the valence band offsets seem to be too low when compared with the predictions of both previous theory and the transitivity rule.^{14,19-21} The band offsets of the ZnO/AlN combination have not previously been investigated experimentally. In this letter, high resolution XPS has been used to directly determine the valence band offset between ZnO and AlN.

Three samples were used for the XPS experiments: a 550-nm-thick ZnO layer grown on a 25-nm-thick low tem-

perature (LT)-grown ZnO buffer layer on *c*-plane sapphire, a 250 nm layer of AlN grown on Si(111), and 5 nm of ZnO on 250 nm of AlN grown on Si(111). The ZnO was grown by radio frequency plasma-assisted molecular-beam epitaxy (MBE), as described elsewhere,²² at ~ 500 °C for the "thick" ZnO layer and ~ 370 °C for the LT-buffer and 5 nm layer. The AlN was grown at ~ 910 °C by MBE using ammonia as the nitrogen source.²³

XPS was performed at the National Centre for Electron Spectroscopy and Surface Analysis, Daresbury Laboratory, U.K., using a Scienta ESCA300 spectrometer with a monochromated rotating anode Al $K\alpha$ x-ray source, providing a high intensity 1486.7 eV line. Photoelectrons are detected by a 300 mm radius concentric hemispherical analyzer with a multichannel detector. XPS data were recorded at room temperature with a resolution of 0.45 eV. Binding energies are calibrated using the Fermi edge of an Ar⁺-ion bombarded silver sample.

The thickness of the ZnO film in the ZnO/AlN sample was determined by the ratio of the epilayer and substrate photoemission peak areas, taking into account appropriate atomic sensitivity factors and inelastic mean free paths.²⁴ The calculated epilayer thickness was 5 ± 1 nm, in agreement with the value obtained from the estimated growth rate.

Zn $2p_{3/2}$ and Al $2p$ XPS spectra are shown in Figs. 1(a)–1(d) fitted using Shirley backgrounds and Voigt (mixed Lorentzian-Gaussian) functions, the parameters for which are shown in Table I. The Zn $2p_{3/2}$ spectrum of both the ZnO and the ZnO/AlN samples and the Al $2p$ spectrum of the AlN sample were fitted by a single contribution, attributed to the bonding configurations Zn–O and Al–N, respectively. However, for the Al $2p$ spectrum of the ZnO/AlN sample [Fig. 1(d)], an additional low intensity higher binding energy component was also required. This extra component is attributed to Al–O bonding at the ZnO/AlN interface and/or inelastic losses to free carriers in the ZnO layer, as recently observed in photoemission of InN.²⁵

The valence band XPS spectra for the thick layer ZnO and AlN samples are shown in Figs. 1(e) and 1(f). The position of the valence band maximum (VBM) with respect to the surface Fermi level was determined by the intersection of

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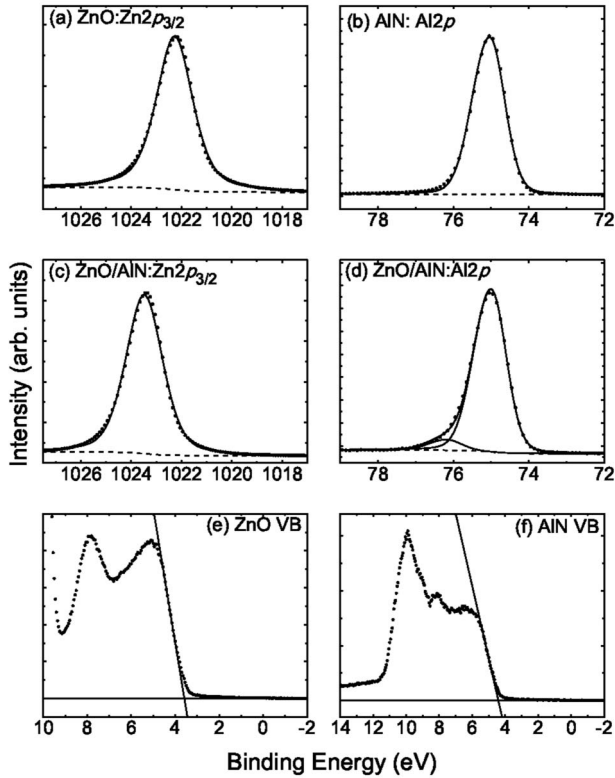


FIG. 1. Zn $2p_{3/2}$ XPS spectra for (a) ZnO and (c) ZnO/AlN samples, and Al $2p$ XPS spectra for (b) AlN and (d) ZnO/AlN samples. Experimental data points are fitted by Voigt (mixed Lorentzian-Gaussian) lineshapes (solid lines) after the application of a Shirley background (dashed line). Also shown are valence band spectra for (e) ZnO and (f) AlN. The peak and VBM positions are summarized in Table I.

linear fits to the leading edge of the valence band photoemission and the background.²⁶ The VBM positions are shown in Table I.

The valence band offset of the ZnO/AlN heterojunction was determined from the energy separation between the core levels in the ZnO/AlN sample and the VBM to core level separations in the thick layer ZnO and AlN samples, as described by

$$E_{\text{VBO}} = E_{\text{Zn } 2p_{3/2}}^{\text{ZnO/AlN}} - E_{\text{Al } 2p}^{\text{ZnO/AlN}} - (E_{\text{Zn } 2p_{3/2}}^{\text{ZnO}} - E_{\text{VBM}}^{\text{ZnO}}) + (E_{\text{Al } 2p}^{\text{AlN}} - E_{\text{VBM}}^{\text{AlN}}), \quad (1)$$

where E_i^s denotes the energy of feature i in sample s . The Zn $2p_{3/2}$ and Al $2p$ core levels have been used in Eq. (1), but equally the O $1s$ and N $1s$ peaks can be used. Indeed, from the results given in Table II, it can be seen that valence band offsets calculated for all four combinations of core levels are

TABLE I. Binding energies (in eV) of the XPS peaks and VBM for the ZnO, AlN, and ZnO/AlN samples. Energies are referenced to the Fermi level (0 eV). The errors in the peak positions and VBM are ± 0.05 and ± 0.10 eV, respectively.

	ZnO	AlN	ZnO/AlN
Zn $2p_{3/2}$	1022.27	...	1023.48
O $1s$	531.03	...	532.22
Al $2p$...	74.94	74.90
N $1s$...	398.25	398.23
VBM	3.58	4.38	4.80

TABLE II. Valence band offset values (in eV) determined for a ZnO/AlN heterojunction using various combinations of XPS core levels. All values correspond to the VBM of ZnO being below that of AlN. The error in each value is ± 0.17 eV.

	Al $2p$	N $1s$
Zn $2p$	0.45	0.43
O $1s$	0.43	0.41

well within experimental error of one another, and place the ZnO VBM 0.43 ± 0.17 eV below that of AlN. Using the room temperature band gaps for ZnO and AlN [3.30 (Ref. 1) and 6.16 eV (Ref. 27), respectively], the ZnO/AlN heterojunction is found to have a type-II (staggered) band line-up, as shown in Fig. 2, with a corresponding conduction band offset of 3.29 ± 0.20 eV.

Using the previously determined valence band offsets of the wurtzite III-nitrides [0.58 eV for InN/GaN (Ref. 12) and 1.52 eV for InN/AlN (Ref. 11)] and applying the transitivity rule²⁸ allows the valence band offsets of ZnO with GaN and InN to be derived. Values of 1.37 eV for ZnO/GaN and 1.95 eV for ZnO/InN are thus obtained, as depicted in Fig. 2. These are significantly higher than the values previously determined of 0.8 eV for ZnO/GaN (Ref. 18) and 0.82 eV for InN/ZnO.¹⁷ One or both of these values must be incorrect because the InN/GaN valence band offset¹² is known to be much greater than 0.02 eV.

The value of 0.8 eV for ZnO/GaN of Hong *et al.*¹⁸ is unreliable due to the use of a combination of ultraviolet photoemission spectroscopy to determine the VBM positions and XPS to determine the core-level positions, while different references were used to calibrate the binding energy scale for the two techniques. Moreover, the Ga $3d$ and Zn $3d$ shallow core levels were used, which are inappropriate for determining a valence band offset¹² because they hybridize with the valence band, forming part of the band structure. Along with the uncertainty introduced by spectral broadening due to the use of nonmonochromated x-rays, this means that the result of Hong *et al.*¹⁸ must be treated with caution. The XPS-determined value of 0.82 eV for InN/ZnO of Zhang *et al.*¹⁷ is also questionable due to a combination of neither the ZnO nor the InN valence band photoemission spectra exhibiting the expected shape for an anion $2p$ -dominated valence

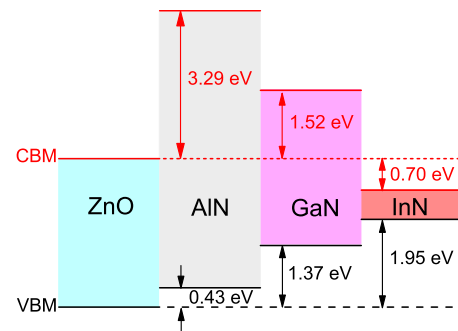


FIG. 2. (Color online) The room temperature VBM and conduction band minimum line-up of the ZnO/AlN heterojunction, showing a type-II band alignment. The band line-ups with GaN and InN are also shown. These are derived from the previously determined valence band offsets of the III-Ns (Refs. 11 and 12) and the transitivity rule (Ref. 28). The room temperature band gaps of 3.45 eV for GaN (Ref. 27) and 0.65 eV for InN (Ref. 31) were used to derive the depicted conduction band offsets with ZnO.

band^{29,30} and the poor In 3*d* peak fitting, where components of very different widths have been used to fit the In 3*d*_{5/2} and In 3*d*_{3/2} lines.

In conclusion, the valence band offset between ZnO and AlN has been determined by XPS to be 0.43 ± 0.17 eV, with a type II band line-up. The corresponding conduction band offset is 3.29 eV. Additionally, III-nitride offsets and the transitivity rule have been used to derive valence band offsets of 1.37 eV for ZnO/GaN and 1.95 eV for ZnO/InN, indicating that previously determined values are too low. These are important quantities for the design of hybrid II-O/III-N devices. For example, the large conduction band *and* valence band offsets reported here are sufficient to provide significant electron and hole confinement potentials for hybrid ZnO/III-N heterostructures. Importantly, the confining potentials can also be tuned by varying the III-N alloy composition.

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- ¹Ü. Özgür, Y. I. Alivov, C. Liu, A. Teke, M. A. Reshchikov, S. Doğan, V. Avrutin, S. J. Cho, and H. Morkoç, *J. Appl. Phys.* **98**, 041301 (2005).
²M. Zamfirescu, A. Kavokin, B. Gil, G. Malpuech, and M. Kaliteevski, *Phys. Rev. B* **65**, 161205 (2002).
³M. Mihailovic, A.-L. Henneghien, S. Faure, P. Disseix, J. Leymarie, A. Vasson, D. A. Buell, F. Semon, C. Morhain, and J. Zuniga-Pérez, "Optical and excitonic properties of ZnO films," *Opt. Mater.* (Amsterdam, Neth.) (to be published), doi:10.1016/j.optmat.2007.10.023.
⁴J. Kasprzak, M. Richard, S. Kundermann, A. Baas, P. Jeambrun, J. M. J. Keeling, F. M. Marchetti, M. H. Szymańska, R. André, J. L. Staehli, V. Savona, P. B. Littlewood, B. Deveaud, and L. S. Dang, *Nature (London)* **443**, 409 (2006).
⁵A. Tsukazaki, A. Ohtomo, T. Onuma, M. Ohtani, T. Makino, M. Sumiya, K. Ohtani, S. F. Chichibu, S. Fuke, Y. Segawa, H. Ohno, H. Koinuma, and M. Kawasaki, *Nature Mater.* **4**, 42 (2005).
⁶Z. P. Wei, Y. M. Lu, D. Z. Shen, Z. Z. Zhang, B. Yao, B. H. Li, J. Zhang,

- D. X. Zhao, X. W. Fan, and Z. K. Tang, *Appl. Phys. Lett.* **90**, 042113 (2007).
⁷C. Bayram, F. Hosseini Teherani, D. J. Rogers, and M. Razeghi, *Appl. Phys. Lett.* **93**, 081111 (2008).
⁸J. Wu, W. Walukiewicz, K. M. Yu, W. Shan, J. W. Ager III, E. E. Haller, H. Lu, W. J. Schaff, W. K. Metzger, and S. Kurtz, *J. Appl. Phys.* **94**, 6477 (2003a).
⁹Y. A. Alivov, J. E. Van Nostrand, D. C. Look, M. V. Chukichev, and B. M. Ataev, *Appl. Phys. Lett.* **83**, 2943 (2003).
¹⁰D. J. Rogers, F. Hosseini Teherani, A. Yasan, K. Minder, P. Kung, and M. Razeghi, *Appl. Phys. Lett.* **88**, 141918 (2006).
¹¹P. D. C. King, T. D. Veal, P. H. Jefferson, C. F. McConville, T. Wang, P. J. Parbrook, H. Lu, and W. J. Schaff, *Appl. Phys. Lett.* **90**, 132105 (2007).
¹²P. D. C. King, T. D. Veal, C. E. Kendrick, L. R. Bailey, S. M. Durbin, and C. F. McConville, *Phys. Rev. B* **78**, 033308 (2008).
¹³S.-H. Wei and A. Zunger, *Appl. Phys. Lett.* **69**, 2719 (1996).
¹⁴C. G. Van de Walle and J. Neugebauer, *Appl. Phys. Lett.* **70**, 2577 (1997).
¹⁵J. Robertson and B. Falabretti, *J. Appl. Phys.* **100**, 014111 (2006).
¹⁶W. Mönch, *J. Appl. Phys.* **80**, 5076 (1996).
¹⁷R. Zhang, P. Zhang, T. Kang, H. Fan, X. Liu, S. Yang, H. Wei, Q. Zhu, and Z. Wang, *Appl. Phys. Lett.* **91**, 162104 (2007).
¹⁸S.-K. Hong, T. Hanada, H. Makino, H.-J. Ko, Y. Chen, A. Tanaka, H. Sasaki, S. Sato, D. Imai, K. Araki, and M. Shinohara, *J. Vac. Sci. Technol. B* **19**, 1429 (2001).
¹⁹W. Mönch, *Appl. Phys. Lett.* **86**, 162101 (2005).
²⁰J. von Pezold and P. D. Bristowe, *J. Mater. Sci.* **40**, 3051 (2005).
²¹M. W. Wang, J. O. McCaldin, J. F. Swenberg, T. C. McGill, and R. J. Hauenstein, *Appl. Phys. Lett.* **66**, 1974 (1995).
²²F. Vigué, P. Vennéguès, C. Deparis, S. Vézian, M. Laügt, and J.-P. Faurie, *J. Appl. Phys.* **90**, 5115 (2001).
²³F. Semon, Y. Cordier, N. Grandjean, F. Natali, B. Damilano, S. Vézian, and J. Massies, *Phys. Status Solidi A* **188**, 501 (2001).
²⁴S. Tanuma, J. Powell, and D. R. Penn, *Surf. Interface Anal.* **21**, 165 (1993).
²⁵P. D. C. King, T. D. Veal, H. Lu, S. A. Hatfield, W. J. Schaff, and C. F. McConville, *Surf. Sci.* **602**, 871 (2008).
²⁶S. A. Chambers, T. Droubay, T. C. Kaspar, and M. Gutowski, *J. Vac. Sci. Technol. B* **22**, 2205 (2004).
²⁷I. Vurgaftman and J. R. Meyer, *J. Appl. Phys.* **94**, 3675 (2003).
²⁸S.-H. Wei and A. Zunger, *Appl. Phys. Lett.* **72**, 2011 (1998).
²⁹L. Ley, R. A. Pollak, F. R. McFreely, S. P. Kowalczyk, and D. A. Shirley, *Phys. Rev. B* **9**, 600 (1974).
³⁰P. D. C. King, T. D. Veal, C. F. McConville, F. Fuchs, J. Furthmüller, F. Bechstedt, J. Schörmann, D. J. As, K. Lischka, H. Lu, and W. J. Schaff, *Phys. Rev. B* **77**, 115213 (2008).
³¹J. Wu, W. Walukiewicz, W. Shan, K. M. Yu, J. W. Ager III, S. X. Li, E. E. Haller, H. Lu, and W. J. Schaff, *J. Appl. Phys.* **94**, 4457 (2003).