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Valence band splittings and band offsets of AlN, GaN, and InN

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First-principles electronic structure calculations on wurtzite AlN, GaN, and InN reveal crystal-field splitting parameters Δ_{CF} of -217, 42, and 41 meV, respectively, and spin–orbit splitting parameters Δ_0 of 19, 13, and 1 meV, respectively. In the zinc blende structure $\Delta_{CF} \equiv 0$ and Δ_0 are 19, 15, and 6 meV, respectively. The unstrained AlN/GaN, GaN/InN, and AlN/InN valence band offsets for the wurtzite (zinc blende) materials are 0.81 (0.84), 0.48 (0.26), and 1.25 (1.04) eV, respectively. The trends in these spectroscopic quantities are discussed and recent experimental findings are analyzed in light of these predictions. © *1996 American Institute of Physics.* [S0003-6951(96)02044-X]

The valence band maximum of wurtzite semiconductors is split both by spin–orbit interaction Δ_0 and by the noncubic crystal-field Δ_{CF}, giving rise to three states at the Brillouin zone center: Γ_{9v}, $\Gamma_{7v}^{(1)}$, and $\Gamma_{7v}^{(2)}$. (In the absence of spin–orbit splitting, these levels become a doubly degenerate Γ_{6v} and a singly degenerate Γ_{1v}). This letter addresses theoretically the magnitude and trends of Δ_0 and Δ_{CF} in group III nitrides AlN, GaN, and InN, and a related quantity, the valence band offsets between these binary crystals. A number of interesting questions arise here. *First*, regarding the crystal-field splitting parameters, previous band structure calculations[1] using the linearized muffin-tin orbital method with atomic sphere approximation (LMTO-ASA) suggest that Δ_{CF} is negative in wurtzite AlN, GaN, and InN (Γ_{1v} is above Γ_{6v}), but more recent calculations[2–4] and interpretation of experimental measurements[4,5] clearly indicate that Δ_{CF} (GaN) should be positive. *Second*, regarding the spin–orbit parameter Δ_0, experience from other column III pnictides[6] shows that Δ_0 increases with the atomic number of the cation, i.e., Δ_0 (InX) $> \Delta_0$(GaX) $> \Delta_0$(AlX) for X=P, As, Sb, but in nitrides there is a substantial hybridization with the cation d orbitals[1,7] that could reverse the order of Δ_0 when the cation changes in a column of the Periodic Table. *Third*, regarding the band offset ΔE_v, previous core-level photoemission measurements[8,9] and calculations[10–13] suggest that the band offset for AlN/GaN is around 0.8 eV, but a recent core-level photoemission measurement[14] suggested a much higher value of 1.36 eV. Furthermore, for GaN/InN and AlN/InN, the recently measured values[9] of $\Delta E_v = 1.05$ and 1.81 eV, respectively, are considerably larger than the corresponding values in other III–V systems, ΔE_v(GaX/InX) ~ 0.1 eV and ΔE_v(AlX/InX) ~ 0.6 eV for X=P, As, Sb.[15] In this letter, we will use the first-principles general potential linearized augmented plane wave (LAPW) method to study the crystal-field and spin–orbit parameters as well as the unstrained valence band offsets of AlN, GaN, and InN in both the wurtzite (WZ) structure and the metastable[16] zinc blende (ZB) structure. Our results will be analyzed and compared with previously published data, clearing up the three issues raised above.

The band structure calculations in the present study are performed using the density functional theory[17] as implemented by the general potential, fully relativistic LAPW method.[18,19] We used the Ceperley–Alder exchange correlation potential[20] as parameterized by Perdew and Zunger.[21] In

the nitrides, the Ga 3d and In 4d states participate in chemical bonding,[1,7] thus, they are treated here dynamically in the same way as the s and p valence states are. The band structures are calculated at the experimental lattice constants[22] for all but zinc blende AlN, for which experimental data are unavailable, so the LAPW method is used to predict the lattice constant. The cell-internal structural parameter u of the wurtzite unit cell is obtained by minimizing the total energy and force.[19]

The crystal-field splitting parameters Δ_{CF} are calculated in the absence of spin–orbit interaction. The spin–orbit splitting parameters Δ_0 are obtained by fitting the fully relativistic LAPW calculated top three energy levels at Γ (E_1, E_2, and E_3, in decreasing order) to the quasicubic model of Hopfield[23] [shifted by $(\Delta_0 + \Delta_{CF})/6$]

$$E(\Gamma_{9v}) = 1/2(\Delta_0 + \Delta_{CF}),$$
$$E(\Gamma_{7v}^{(1)}) = +1/2[(\Delta_0 + \Delta_{CF})^2 - 8/3\Delta_0\Delta_{CF}]^{1/2}, \quad (1)$$
$$E(\Gamma_{7v}^{(2)}) - 1/2[(\Delta_0 + \Delta_{CF})^2 - 8/3\Delta_0\Delta_{CF}]^{1/2}.$$

Note that the valence band splitting $\Delta E_{12} = E_1 - E_2$ and $\Delta E_{13} = E_1 - E_3$ are directly measurable quantities whereas the crystal-field splitting Δ_{CF} and the spin–orbit splitting Δ_0 are parameters of the theory, obtainable in experiment only indirectly via fitting to Eq. (1).

The unstrained valence band offset ΔE_v(AN/BN) between two nitrides AN and BN is calculated using the same procedure as in the photoemission core-level spectroscopy measurement.[8,9,14] The valence band offset is given in this procedure as

$$\Delta E_v(\text{AN/BN}) = (E_v - E_{CL})_{BN} - (E_v - E_{CL})_{AN} + \Delta E_{CL}. \quad (2)$$

Here, $(E_v - E_{CL})_{AN}$ and $(E_v - E_{CL})_{BN}$ are the core-level to valence-band-maximum (VBM) energy separations for pure AN and BN, respectively at their respective *equilibrium* lattice constants, hence, these quantities are characteristic of each *bulk* material. The last term in Eq. (2) is the difference in core-level binding energy between AN and BN at the AN/BN heterojunction, thus, this quantity depends on the interface orientation and on the strain at the heterojunction. However, the dependence is usually small.[24] In this study, we calculate ΔE_{CL} using (001) superlattices for the zinc blende nitrides, and (0001) superlattices for the wurtzite nitrides. The superlattice substrate lattice constant $\bar{a}$ is taken as

TABLE I. LAPW calculated cell-internal structural parameter u, the spin–orbit parameter Δ_0, the crystal-field parameter Δ_{CF}, and the valence band splittings ΔE_{12} and ΔE_{13} of *wurtzite* AlN, GaN, and InN. For GaN and InN E_1 is a $\Gamma_{9v}^{(1)}$ state and E_2 is $\Gamma_{7v}^{(1)}$, while for AlN E_1 is a $\Gamma_{7v}^{(1)}$ state and E_2 is Γ_{9v}. In all cases, E_3 is $\Gamma_{7v}^{(2)}$. The bottom part of the table gives results for the *zinc blende* forms (where $\Delta_{CF} \equiv 0$). All results are calculated at the experimental lattice constants reviewed in Ref. 22 and given in the table, except for zinc blende AlN for which our calculated value is used.

Properties	AlN	GaN	InN
Wurtzite:			
a_{exp}(Å)	3.112	3.189	3.544
c_{exp}(Å)	4.982	5.185	5.718
u	0.3819	0.3768	0.3790
Δ_{CF}(meV)	−217	42	41
Δ_0(meV)	19	13	1
ΔE_{12}(meV)	211	7	2
ΔE_{13}(meV)	224	48	43
Zinc blende:			
a(Å)	4.36[a]	4.50	4.98
Δ_0(meV)	19	15	6

[a]Present calculation.

the average lattice constants of the constituents. The other structural parameters of the superlattices are fully relaxed by minimizing the quantum mechanical force,[19] thus, interfacial effects on the band offsets are taken into account. Our method has been demonstrated to be successful in predicting valence band offsets of numerous semiconductor systems.[25–28] The uncertainty in our present calculation is estimated to be about 0.1 eV.

Table I shows the calculated spectroscopic valence band parameters in wurtzite and zinc blende AlN, GaN, and InN, while Table II gives the calculated valence band offsets between AlN, GaN, and InN in the zinc blende structures [with (001) orientation] or wurtzite structures [with (0001) orientation]. We next discuss the salient features of these results.

The crystal-field parameter Δ_{CF} is proportional to the deviation of the structural parameters u and c/a from their unrelaxed value 3/8 and $\sqrt{8/3}$, respectively (when $u = 3/8$ and $c/a = \sqrt{8/3}$, the two anion–cation bond lengths are equal):[16]

$$\Delta_{CF} \equiv E(\Gamma_{6v}) - E(\Gamma_{1v})$$
$$= \Delta_{CF}^0 + \alpha(u - 0.375) + \beta(c/a - 1.633). \quad (3)$$

We find $\alpha = -17$ eV and $\beta = 2$ eV for GaN, suggesting that accurate determination of Δ_{CF} requires careful calculation of

TABLE II. Calculated and measured valence band offsets between AlN, GaN, and InN in *zinc blende* [with (001) orientation] or *wurtzite* [with (0001) orientation] structures. We use the convention that a positive value indicates that the compounds on the right-hand side have a higher valence band.

	AlN/GaN	GaN/InN	AlN/InN
LMTO (ZB)[a]	0.85	0.51	1.09
LAPW (ZB)	0.84	0.26	1.04
LAPW (WZ)	0.81	0.48	1.25
Exptl (WZ)[b]	1.36±0.07	⋯	⋯
Exptl (WZ)[c]	0.70±0.24	1.05±0.25	1.81±0.20

[a]Reference 11, for (110) interface.
[b]Reference 14.
[c]Reference 9.

u. Unfortunately, most[1–3,29] previous calculations of Δ_{CF} used an ideal value of $u = 0.375$, thus overestimating Δ_{CF}. Our u values are in good agreement with previous pseudopotential calculations[16,30,31] and with the LMTO calculations of Christensen and Gorczyca,[32] but the calculated values of Kim *et al.*[33] using a full-potential LMTO method ($u = 0.383$, 0.379, and 0.388, for AlN, GaN, and InN, respectively) are somewhat larger than the present results, especially for InN. We find that Δ_{CF} is large and negative for AlN but positive for both GaN and InN. The large and negative Δ_{CF} value for AlN is partly due to its large u value [Eq. (3)]. Our calculated $\Delta_{CF}(\text{GaN}) = 42$ meV is consistent with the interpretation of recent experimental measurements.[4,5] Correcting via Eq. (3) the calculated Δ_{CF} value of Palummo *et al.*[3] of $\Delta_{CF}(\text{GaN}) = 80$ meV and that of Suzuki and Uenoyama[2] of $\Delta_{CF}(\text{GaN}) = 73$ meV for their use of $u = 0.375$ rather than the relaxed u values (Table I), we find that their Δ_{CF} values are consistent with ours. However, applying an analogous correction to the unrelaxed LMTO-ASA calculation of Lambrecht and Segall[1] (which gave $\Delta_{CF} = -250$, −20, and −10 meV for AlN, GaN, and InN) produces even more negative values of Δ_{CF}, in disagreement with our calculated values and with experimental observations.[4,5] Most likely, the error in the LMTO-ASA calculation is due to the neglect of non-spherical potential terms.

The magnitude of the spin–orbit splitting increases with atomic number. In general, p states have a positive contribution to Δ_0, while d states have a negative contribution. In phosphides, arsenides, and antimonides there is but a weak coupling of cation d character at the VBM, so Δ_0 reflects mostly p bonding and increases as the cation is heavier.[6] $\Delta_0(\text{Al}X) < \Delta_0(\text{Ga}X) < \Delta_0(\text{In}X)$. In nitrides, on the other hand, the N $2p$ orbital is so deep in energy as to effectively hybridize with the semicore cation d state, leading to a significant mixture of d character at the VBM. This reverses the order to $\Delta_0(\text{AlN}) > \Delta_0(\text{GaN}) > \Delta_0(\text{InN})$. This d-hybridization-induced reduction of Δ_0 is more effective in the heavier InN than in the lighter AlN. We, thus, find that the former has almost zero spin–orbit splitting. Table I compares Δ_0 for wurtzite and zinc blende structures, showing the latter to be larger. This is because in the wurtzite structure the s orbital is mixed into the top of the valence band, thus, displacing p character and reducing Δ_0 (in the zinc blende structure this mixing is symmetry forbidden). This $s–p$ mixing is larger in InN than in AlN since the former has a smaller band gap.

The trends in the valence band offsets in common–anion II–VI and III–V semiconductors[28] reflect mainly the difference in their cation d to anion coupling: in Al compounds, the unoccupied cation d orbital is *above* the anion p, so $p–d$ repulsion pushes the anion p VBM *down* in energy. On the other hand, the energies of the occupied Ga $3d$ and the In $4d$ orbitals are *below* the anion p energy, so $p–d$ repulsion pushes the anion p VBM *up* in energy. The degree of VBM shift $\sim V_{pd}^2/(\epsilon_p - \epsilon_d)$ reflects the energy separation $\epsilon_p - \epsilon_d$ of anion p and cation d orbitals and the matrix element V_{pd}, which increases as the nearest-neighbor bond length decreases. We find that the calculated valence band offsets for the zinc blende nitrides (Table II) are larger than the corresponding values in other III–V systems.[15] This is because the

p–d repulsion is stronger in nitrides than in other III–V systems, both due to the shorter anion–cation bond lengths and the smaller energy differences $\epsilon_p - \epsilon_d$ between the cation d and the N $2p$ orbitals.

The calculated valence band offsets for the lattice mismatched GaN/InN and AlN/InN interfaces in the wurtzite structure are larger than in the zinc blende structure. To understand the difference between the WZ and ZB interfaces we have recalculated the core level difference ΔE_{CL} of Eq. (2) for zinc blende GaN/InN using (111) oriented interfaces [corresponding to the wurtzite (0001) superlattice] rather than (001) interfaces. We find that the calculated ΔE_{CL} is nearly the same as in the wurtzite superlattice calculation, leading to a ΔE_v(GaN/InN)=0.50 eV close to the wurtzite value of Table II. This suggests that the difference in zinc blende versus wurtzite valence band offsets of lattice-mismatched GaN/InN, and AlN/InN is mainly due to the difference in the strain relaxation at the interface. For the nearly lattice-matched AlN/GaN system, the wurtzite and zinc blende structures have similar offsets (the slightly smaller ΔE_v in the WZ structure is due to the large crystal-field splitting in wurtzite AlN that raises its VBM energy).

Using the LMTO method, Albanesi *et al.*[11] calculated the valence band offsets of the zinc blende nitrides with (110) interfaces. Their calculated band offsets (Table II) are consistent with our values. We further find that our calculated value of ΔE_v(AlN/GaN)=0.81 eV is in good agreement with the core-level photoemission measurement of Martin *et al.*[8,9] and is consistent with other band structure calculations.[10–13] Our results, however, do not support the recent core-level photoemission measurement of Waldrop and Grant[14] who find a much larger value ΔE_v(AlN/GaN)=1.36 eV. The reason for this anomalously large value is presently not understood. Furthermore, our calculated values of ΔE_v(GaN/InN) and ΔE_v(AlN/InN) are considerably smaller than the recent measured value of Martin *et al.*[9] (Table II). Martin *et al.* have observed a strong dependence of the core-level energy difference ΔE_{CL} on the substrate lattice constant a_s used. To test this effect, we have recalculated the core level differences ΔE_{CL} of GaN/InN using coherently strained superlattices with three values of $a_s = a_{\mathrm{GaN}}$, $\bar{a}$ and a_{InN}. We find that the variation of the calculated core level difference is only ± 0.1 eV, thus, this calculation does not support the larger variation observed by Martin *et al.*[9] Martin *et al.*[9] suggested that the strong substrate dependence of ΔE_{CL} could be due to strain induced electric field in the sample. We find that this explanation is unlikely, since any macroscopic electric field in the sample should be effectively screened by an external field of surface charges.

In summary, using first-principles density functional theory and the LAPW band structure method, we have calculated the valence band splittings and the valence band offsets of AlN, GaN, and InN in both the wurtzite and zinc blende structures. We have pointed out some interesting trends associated with the nitrides and compared our results with previously published data. Agreements and discrepancies between the present calculation and previous published data are discussed. Future experiments are called for to test our predictions.

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