JU`YbWY`VUbX`gd`]hh]b[`g`UbX`VUbX`cZZgYhg`cZ`5`Bž;`UBž`UbX`±bB

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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 D_{CF} of $\gtrsim$217, 42, and 41 meV, respectively, and spin–orbit splitting parameters D_0 of 19, 13, and 1 meV, respectively. In the zinc blende structure $D_{CF}[0$ and D_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 D_0 and by the noncubic crystal-field D_{CF}, giving rise to three states at the Brillouin zone center: G_{9v}, $G_{7v}^{(1)}$, and $G_{7v}^{(2)}$. ~In the absence of spin–orbit splitting, these levels become a doubly degenerate G_{6v} and a singly degenerate G_{1v}!. This letter addresses theoretically the magnitude and trends of D_0 and D_{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 D_{CF} is negative in wurtzite AlN, GaN, and InN ~G_{1v} is above G_{6v}!, but more recent calculations[2–4] and interpretation of experimental measurements[4,5] clearly indicate that D_{CF} ~GaN! should be positive. *Second*, regarding the spin–orbit parameter D_0, experience from other column III pnictides[6] shows that D_0 increases with the atomic number of the cation, i.e., D_0 (InX). D_0(GaX). D_0(AlX) for X5P, As, Sb, but in nitrides there is a substantial hybridization with the cation d orbitals[1,7] that could reverse the order of D_0 when the cation changes in a column of the Periodic Table. *Third*, regarding the band offset DE_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 DE_v5 1.05 and 1.81 eV, respectively, are considerably larger than the corresponding values in other III–V systems, DE_v(GaX/InX); 0.1 eV and DE_v(AlX/InX); 0.6 eV for X5P, 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 D_{CF} are calculated in the absence of spin–orbit interaction. The spin–orbit splitting parameters

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.

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 $e_p \gtrsim e$