First-principles calculations for AlN, GaN and InN: bulk and alloy properties

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ABSTRACT

First-principles density-functional calculations utilizing *ab initio* pseudopotentials and plane-wave expansions are used to determine lattice parameters, bulk moduli, and band structures for AlN, GaN and InN. It is found that large numbers of plane waves are necessary to resolve the nitrogen $2p$ wave functions and that explicit treatment of the gallium $3d$ and indium $4d$ electrons is important for an accurate description of GaN and InN. Several properties of ternary zinc-blende alloys are determined including their bond-length and bond-angle relaxation and their energy-gap bowing parameters. The similarity of the calculated zinc-blende and wurtzite direct gaps also allows estimates to be made of the energy gap versus composition for wurtzite alloys.

keywords: AlN, GaN, InN, wide-gap semiconductors, semiconductor alloys

1. INTRODUCTION

Interest in AlN, GaN, InN and their alloys stems primarily from the possibilities these materials offer for fabricating optical devices operating within the visible-to-ultraviolet region of the spectrum. Recently, this potential was demonstrated in dramatic fashion with the development of a bright blue light-emitting diode based on GaN and its alloys with AlN and InN.¹ Furthermore, several components needed for a vertical-cavity surface-emitting laser have been demonstrated within the past few years including quantum wells² and quarter-wave mirror stacks.^{3,4} While these developments are encouraging, much more basic research will be needed before the nitride semiconductors can be routinely used in fabricating optical devices. A large part of this research will necessarily be experimental in nature addressing long-standing problems associated with the growth of these materials via vapor-phase and molecular-beam epitaxy.^{5,6}

Theoretical techniques will likely also play an important role in the development of nitride semiconductors and progress has recently been made towards overcoming a long-standing problem in this area, namely the adequate treatment of compact electronic states associated with the gallium $3d$, indium $4d$, and nitrogen $2p$ electrons. This progress has been due to two factors: the development of efficient algorithms for solving self-consistent electronic structure problems and the computational power provided by modern massively parallel computers. As a result, it is now feasible to perform accurate calculations not only bulk AlN, GaN and InN, but also for their alloys. In Section 2, we briefly describe the theoretical technique used in these studies and discuss the difficulties caused by the cation d and nitrogen $2p$ electrons. In Section 3, we describe results for the bulk compounds including their structural parameters, bulk moduli, and electronic band structures. We then describe results obtained for zinc-blende ternary alloys in Section 4 including their bond-length and bond-angle distributions and their energy-gap bowing parameters. Finally, we summarize our results in Section 5.

2. THEORETICAL TECHNIQUE

The theoretical technique used in this research is based on density-functional theory^{7,8} (DFT) within the local-density approximation^{9,10} (LDA) for exchange and correlation. In addition, we utilize *ab initio*

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pseudopotentials¹¹⁻¹³ to describe the interactions between the ion cores (nuclei and electrons that do not participate in bonding) and valence electrons and we expand the wave functions in a plane-wave basis.¹⁴ This technique - known as the plane-wave pseudopotential (PWPP) method - has proven useful for modeling a wide variety of materials and is the premier DFT-LDA technique for studying semiconductors.

The use of a plane wave basis is particularly helpful for the studies described herein because it allows for simple calculation of atomic forces used to relax the wurtzite and alloy structures. However, applying the PWPP method to elements without *p* core electrons such as nitrogen has been difficult because their *p* pseudopotentials are narrow and deep requiring large numbers of plane waves. In addition, accurate calculations for GaN and InN require explicit treatment of the gallium *3d*¹⁵⁻¹⁷ and indium *4d*¹⁸ electrons which further necessitates the use of large numbers of plane waves. One approach which has been used by several researchers is to "soften" the troublesome pseudopotentials (make them shallower and wider) so that fewer plane waves are needed.¹⁹⁻²¹ While this approach can lessen computational demands, extreme care must be taken in order to maintain accuracy. We have taken a different approach in that we use standard nitrogen pseudopotentials and only slightly soften the gallium and indium *d* pseudopotentials.^{17, 18} We then perform the calculations on modern massively parallel computers which have the capacity and speed to treat large numbers of plane waves.

An additional problem related to the large plane-wave basis sets is that the procedure used to determine the self-consistent electronic structure can become unstable. In order to deal with this problem, we use the preconditioned conjugate gradients algorithm developed by Teter, Payne and Allan.²² This algorithm updates the wave functions and electron-electron potential simultaneously and preconditions the wave-function updates so that the plane waves with large kinetic energies (short wave lengths) do not dominate the iterative process. Further information about self-consistency algorithms can be found in the review by Payne *et al.*²³ and an overview of the PWPP method has been written by Pickett.²⁴ Further details on the application of the PWPP method to AlN, GaN, InN and their zinc-blende alloys can be found in Refs. 17, 18, 25 and 26.

3. BULK PROPERTIES

3.1 Wurtzite

Observations indicate that wurtzite is the preferred structure for all three compounds although there have been a few reports of zinc-blende AlN and InN and many of zinc-blende GaN. The wurtzite structure consists of a hexagonal lattice with a four-atom basis. Lattice constants *a* and *c* define the hexagonal lattice and an internal parameter *u* denotes the fractional separation of the cation and anion sublattices along the *c*-axis. Equilibrium values were determined by calculating the energies corresponding to a set of values of the volume and the *c/a* ratio using calculated atomic forces to optimize *u*. These energies were then fit to the general cubic equation

$$z = C_{00} + C_{10}x + C_{01}y + C_{20}x^2 + C_{11}xy + C_{02}y^2 + C_{30}x^3 + C_{21}x^2y + C_{12}xy^2 + C_{03}y^3, \quad (1)$$

where *z* is the energy, *x* is the volume, *y* is the *c/a* ratio, and *C_{ij}* are coefficients determined from the fit. The bulk modulus, *B*, was determined by fitting the energies for each volume to the equation

$$z = C_0 + C_1y + C_2y^2, \quad (2)$$

where *C_i* are coefficients determined from the fit. The minimum energies and their associated volumes were then fit to the Murnaghan equation²⁷ yielding the bulk modulus.

Table I lists the predicted lattice constants, c/a ratios, internal parameters, and bulk moduli along with measured values. In general, the predicted lattice constants are about 1% smaller than measured values which is a typical level of agreement for well converged DFT-LDA calculations. Furthermore, the lattice mismatch among the different compounds is well reproduced by these calculations.¹⁸ This will be important in determining alloy bowing parameters which are very sensitive to lattice mismatch. The predicted bulk moduli are generally larger than the measured values (also typical of DFT-LDA), although there are significant differences among the measured values for GaN. At this point, it is worth noting that such differences among measured values are rather common for all three compounds, but especially for AlN and InN which have received less attention than GaN. The InN lattice constants, for example, are still not very well known and no value has yet been reported for the internal parameter. This is likely due to the difficulty in producing high-quality samples of InN.

Table I. Predicted and measured wurtzite lattice constants (Bohr radii), c/a ratios, internal parameters, and bulk moduli (Mbar).

	a	c	c/a	u	B
AlN: measured ^{28, 29}	5.877	9.411	1.601	0.3821	2.02
calculated	5.829	9.350	1.604	0.3814	2.05
GaN: measured ^{28, 30, 31}	6.028	9.806	1.627	0.377	1.95, 2.37
calculated	5.975	9.718	1.626	0.3770	2.02
InN: measured ³⁰⁻³²	6.697	10.805	1.613	--	1.26, 1.39
calculated	6.616	10.712	1.619	0.3784	1.39

Figures 1-3 display the valence bands and the four lowest conduction bands (adjusted so that the valence-band maxima occur at 0 eV) along several directions in the Brillouin zone. Table II lists energy gaps between the valence-band maximum at Γ and conduction-band minima at several points in the Brillouin zone. One feature of DFT-LDA worth noting is that it always underestimates the valence-conduction energy gaps. The measured minimum energy gaps of AlN, GaN and InN, for example, are 6.28 eV³³, 3.50 eV³⁴ and 1.89 eV³⁵ whereas the predicted values are 4.41 eV, 2.04 eV and -0.04 eV. While these are significant discrepancies, results for other III-V compounds indicate that the conduction and valence dispersions themselves are rather well described by DFT-LDA. Thus, it is generally accepted that DFT-LDA yields reasonable approximations to quantities such as effective masses in addition to predicting the ratios of the various energy gaps fairly well. Furthermore, the source of the DFT-LDA discrepancies is well understood and theoretical formulations have been developed which correct the DFT-LDA energy bands resulting in good quantitative agreement with measured band structures (see Ref. 36 and references therein). We also note that the DFT-LDA energy-gap errors tend to cancel in determining an alloy bowing parameter since it is the difference between the alloy gap and the average of the constituent gaps (see below) that determines this quantity.

Several features are worth noting with regard to the band structures. The lowest valence bands shown for AlN are due to the nitrogen 2s electrons and a gap of almost 7 eV exists between these bands and the upper valence bands which are dominated by nitrogen 2p electrons. This "ionicity gap" does not occur among group IV semiconductors, but is a typical feature of III-V semiconductors reflecting their partly ionic character. We also note that the ionicity gap is largest in AlN suggesting that it is the most ionic and smallest in GaN suggesting that it is the least ionic. One feature absent in the AlN band structure is valence bands derived from d electrons. In GaN and InN, the d bands occur near -12 eV, about the same energy as the nitrogen 2s bands. This results in a large s - d hybridization which is one of the reasons the gallium 3d and indium 4d electrons must be treated explicitly.¹⁶

Figure 1. Predicted energy bands for wurtzite AlN.

Figure 2. Predicted energy bands for wurtzite GaN.

Figure 3. Predicted energy bands for wurtzite InN.

The conduction bands of AlN, GaN and InN are similar in that the minimum values occur at the Γ -point resulting in direct energy gaps. In addition, the minimum gaps decrease from 4.41 eV for AlN to 2.04 eV for GaN to -0.04 eV for InN, consistent with the generally observed trend among semiconductors that energy gaps decrease with increasing atomic mass. Another feature of AlN worth noting is that its conduction-band minimum at Γ is only slightly lower than the minima at other points in the Brillouin zone. This feature results in zinc-blende AlN having an indirect minimum energy gap in contrast to the direct gaps found for zinc-blende GaN and InN.³⁷ Related to this, the dispersion near the conduction-band Γ -point in AlN are noticeably flatter than in InN or GaN. This means that the conduction-band effective mass will be larger in AlN than in InN or GaN.

Table II. Predicted valence-band maxima and conduction-band minima (eV) at Γ , A, L, M, H and K.

	Γ	A	L	M	H	K
AlN: valence	0.00	-0.55	-1.41	-0.70	-0.82	-2.46
conduction	4.41	6.60	5.25	5.72	7.37	4.90
GaN: valence	0.00	-0.56	-1.97	-1.05	-1.54	-2.86
conduction	2.04	4.29	4.33	4.92	6.40	4.99
InN: valence	0.00	-0.48	-1.67	-0.94	-1.35	-2.28
conduction	-0.04	2.36	3.35	3.84	5.17	4.78

3.2 Zinc blende

The zinc-blende structure is characterized by the cubic lattice constant a_0 . The equilibrium value and bulk modulus, B , for each compound were determined by calculating energies for a set of volumes and fitting these to the Murnaghan equation.²⁷ In Table III we list our results for the three compounds together

with measured values of the lattice constants and estimates of the bulk moduli derived from measured wurtzite elastic constants. The predicted lattice constants are roughly 1% smaller than the measured values and the predicted bulk moduli are generally larger than the estimated values. As noted above, this is a typical level of agreement for DFT-LDA calculations. We should also note that there are still rather large differences among measured values for zinc-blende GaN owing to its scarcity compared with wurtzite GaN. Only a few samples of zinc-blende AlN and InN have been produced and their properties are even less well known.

Table III. Predicted and measured zinc-blende lattice constants (Bohr radii) and bulk moduli (Mbar).

	a_0	B
AlN: measured ^{38, 39}	8.28	2.02
calculated	8.206	2.07
GaN: measured ^{39, 40}	8.50	1.90
calculated	8.428	1.87
InN: measured ^{39, 41}	9.41	1.39
calculated	9.319	1.40

In Figs. 4-6 we display the predicted valence bands and the four lowest conduction bands (adjusted so that the valence-band maxima are at 0 eV) along several directions in the Brillouin zone. Table IV lists energy gaps between the valence-band maximum at Γ and conduction-band minima at several points in the Brillouin zone. Most of the remarks about the wurtzite energy bands also apply here. One exception is that the minimum energy gap in zinc-blende AlN is indirect (at the X-point) instead of direct as in wurtzite AlN. Another feature worth noting in AlN is that valence bands at -4 eV and just to the right of the

Figure 4. Predicted energy bands for zinc-blende AlN.

Figure 5. Predicted energy bands for zinc-blende GaN.

Figure 6. Predicted energy bands for zinc-blende InN.

K-point appear to cross in AlN whereas they do not in GaN and InN. This crossing is reminiscent of the band structures of ionic compounds that crystallize in the rocksalt structure⁴² suggesting that the bonding in AlN is more ionic than in either GaN or InN. A similar feature also appears in the DFT-LDA band structure of zinc-blende BN as does the indirect minimum energy gap at the X-point.⁴³

Table IV. Predicted zinc-blende valence-band maxima and conduction-band minima (eV) at Γ , L, X and K.

	Γ	L	X	K
AlN: valence	0.00	-0.49	-1.83	-1.42
conduction	4.35	7.36	3.22	5.09
GaN: valence	0.00	-1.03	-2.87	-2.31
conduction	1.89	4.67	3.23	4.91
InN: valence	0.00	-0.92	-2.47	-1.98
conduction	-0.35	3.09	2.81	4.25

4. ZINC-BLENDE ALLOYS

Alloys will be an important component of optical-device designs because they allow the minimum energy gap to be tuned to a specific desired value. GaN, for example, has an energy gap of 3.50 eV³⁴ corresponding to the near ultra-violet region of the spectrum. This gap can be raised further into the ultra-violet by forming a ternary alloy with AlN (6.28 eV³³ energy gap) or lowered into the visible by alloying with InN (1.89 eV³⁵ energy gap). (The ternary alloys studied herein are also referred to as quasi-binary alloys since the alloying occurs solely among the cations.) As a first approximation, the energy gap of an alloy such as Ga_{1-x}In_xN is given by the composition-weighted average of the GaN and InN gaps,

$$\epsilon_{\text{GaInN}}(x) = (1 - x)\epsilon_{\text{GaN}} + x\epsilon_{\text{InN}}. \quad (3)$$

A more realistic description includes a non-linear term,

$$\epsilon_{\text{GaInN}}(x) = (1 - x)\epsilon_{\text{GaN}} + x\epsilon_{\text{InN}} - bx(1 - x), \quad (4)$$

where b is known as the bowing parameter. In the discussion below, we provide details of calculations for the energy gaps of zinc-blende AlN, GaN, InN and their 50% alloys. Using Eqn. 4, these values are then used to determine bowing parameters for transitions from the valence-band Γ -point to the conduction-band Γ -point (direct, optical transition) and to the conduction-band X-point (indirect transition). While these results apply strictly to zinc blende, the similarity of the calculated Γ -point transitions for bulk wurtzite and zinc blende (see Tables II and IV) suggests that the direct-gap bowing parameters also provide reasonable estimates for wurtzite alloys. With this in mind, we compare our results directly with experimental measurements of the optical bowing parameters for wurtzite alloys.

The disordered zinc-blende alloys were modeled using special quasirandom structures⁴⁴ (SQSs) which are simply ordered structures designed to reproduce the most important pair-correlation functions of a random zinc-blende (disordered) alloy. (SQSs have not yet been developed for wurtzite alloys.) For these studies, we considered two SQSs: SQS-4, a [110] (GaN)₂(InN)₂ superlattice (using GaInN₂ as an example) and one variant of SQS-8, a [113] (InN)₂(GaN)₃(InN)₂(GaN)₁ superlattice. All of the calculations included full relaxation of the internal structure (bond-lengths and bond-angles). The SQS-4 GaInN₂ unit cell, for example, was first constructed using the average of the calculated GaN and InN lattice constants and placing the atoms in ideal positions. The internal structure and volume were then relaxed to minimize the total energy. For all three alloy systems, the SQS-4 equilibrium volumes were found to be within 0.5% of the average values. Thus, we simply used the average volumes for the SQS-8

calculations, but fully relaxed the internal structures. We should note that relaxation of the bond-lengths and bond-angles is crucial in determining bowing parameters. The direct-gap bowing parameter of SQS-4 GaInN₂, for example, decreased from +1.21 eV to +1.05 eV upon relaxation while the indirect-gap bowing parameter increased from +0.24 eV to +0.42 eV.

In Figs. 5-7, we display the cation-anion bond-lengths and the anion-cation-anion bond-angles for the relaxed SQS-4 structures. The solid vertical lines in the bond-length plots indicate the calculated bulk

Figure 5. Bond-lengths and bond-angles for SQS-4 AlGaInN₂.

Figure 6. Bond-lengths and bond-angles for SQS-4 GaInN₂.

Figure 7. Bond-lengths and bond-angles for SQS-4 AlInN₂.

values for the two constituents and the vertical double-line denotes the average of these two values. The solid vertical line in the bond-angle plots indicates the ideal tetrahedral angle, 109.5° . For all three alloys, the bond-lengths cluster around the respective constituent values similar to results found previously for the Ga_2PAs alloy.⁴⁴ For the AlN-GaN system, the lattice mismatch is smallest (2.7%) and the distribution of bond lengths within the two clusters is small. The lattice mismatch is larger for the GaN-InN and AlN-InN systems (10.1% and 12.7%, respectively) and the distributions are correspondingly larger. In addition, we note that the bond lengths for the constituent with smaller bulk lattice constant are somewhat larger than the bulk value while the opposite holds for the constituent with the larger bulk lattice constant. The bond-angles for all three alloys cluster around the ideal tetrahedral angle. The widths of the distributions, however, increase with lattice mismatch as was the case for the bond-lengths. We add that corresponding plots for SQS-8 display the same features as the SQS-4 plots. The SQS-8 distributions, however, are smoother reflecting the increased number of structural degrees of freedom.

Table V lists the predicted bowing parameters for the three alloys. As a technical note, we point out the similarity of the parameters for SQS-4 and SQS-8. To the extent that these structures approximate a disordered alloy, this implies that the results provide reasonable estimates of the bowing in random zinc-blende alloys. (SQS-8 should provide a better approximation than SQS-4. We therefore use its results in the analysis below.) As a further technical note, we have verified the convergence of these results with respect to the number of plane waves and the Brillouin-zone sampling.^{25, 26} The bowing parameters themselves display several noticeable trends. The direct-gap parameters, for example, are positive and larger in magnitude than the (X-point) indirect-gap parameters consistent with results found for other III-V alloys.⁴⁴ In addition, the direct-gap parameter increases significantly with lattice mismatch (from AlGaIn_2 to GaInN_2 to AlInN_2) also consistent with results for other III-V alloys. On the other hand, the direct-gap bowing parameters for the nitride alloys are generally larger than for other III-V alloys. This is reasonable given the larger energy gaps of the nitride semiconductors.

Table V. Bowing parameters for the direct (Γ) and indirect (X) transitions in eV.

	b_Γ	b_X
AlGaIn_2 : SQS-4	+0.56	-0.03
SQS-8	+0.53	-0.10
GaInN_2 : SQS-4	+1.05	+0.42
SQS-8	+1.02	+0.38
AlInN_2 : SQS-4	+2.40	-0.09
SQS-8	+2.53	-0.29

Before discussing measured values of the optical bowing parameters, we reiterate that these measurements have so far only been performed for wurtzite alloys whereas our calculations are for zinc blende. Nevertheless, the similarity of the calculated Γ -point transitions for bulk zinc-blende and wurtzite suggests that our direct-gap parameters should provide reasonable estimates for wurtzite alloys. Furthermore, we have recently determined direct-gap bowing parameters for both a [0001]-oriented wurtzite $(\text{AlN})_1(\text{InN})_1$ superlattice and the similar [111]-oriented zinc-blende $(\text{AlN})_1(\text{InN})_1$ superlattice. The values differ by only 3% suggesting that our assumption is reasonable.

There have been several measurements on $\text{Al}_{1-x}\text{Ga}_x\text{N}$ alloys. The earliest study yielded an upward bowing (estimated bowing parameter -0.8 eV) and a non-linear relationship between the lattice constant and composition.⁴⁵ In contrast, later studies found a linear relationship between the lattice constant and composition in addition to non-negative bowing parameters: either ≈ 0 eV^{46, 47} or $\approx +1.0$ eV.^{48, 49} Our

direct-gap parameter is consistent with these later studies, and in fact, falls roughly in the middle of the measured values. For $\text{Ga}_{1-x}\text{In}_x\text{N}$, the only measurement to date indicated a bowing parameter of +1.05 eV,⁵⁰ almost identical to our value. For $\text{Al}_{1-x}\text{In}_x\text{N}$, there has also been only one measurement of bowing parameter on samples grown by magnetron sputtering.⁵¹ These measurements indicated a large amount of bowing to the extent that the alloy lattice matched to GaN was estimated to have an energy gap of 3.34 eV, slightly smaller than the GaN gap. In contrast, an estimate based on our direct-gap bowing parameter indicates a value of 5.0 eV for the lattice matched alloy (see Eqn. 7 below²⁵), significantly larger than the GaN value.

Given the overall reasonable agreement between the calculated and measured bowing parameters, we derive expressions relating the direct energy gap to composition for wurtzite alloys. Specifically, we use our SQS-8 bowing parameters together with the measured bulk wurtzite energy gaps to generate the equations^{25, 26}

$$\varepsilon_{\text{AlGaIn}}(x) = 0.53x^2 - 3.31x + 6.28 \text{ eV}, \quad (5)$$

$$\varepsilon_{\text{GaInN}}(x) = 1.02x^2 - 2.63x + 3.50 \text{ eV}, \quad (6)$$

and

$$\varepsilon_{\text{AlInN}}(x) = 2.53x^2 - 6.92x + 6.28 \text{ eV}. \quad (7)$$

Plots corresponding to these equations are shown in Fig. 8. Using Eqn. 6, for example, a $\text{Ga}_{0.54}\text{In}_{0.46}\text{N}$ alloy is predicted to have an energy gap of about 2.5 eV, in the blue region of the visible spectrum. A $\text{Ga}_{0.82}\text{In}_{0.18}\text{N}$ alloy lattice matched to hexagonal ZnO, on the other hand, is predicted to have a direct energy gap of about 3.1 eV corresponding to the near ultra-violet region.

Figure 8. Direct-gap versus composition estimated for wurtzite alloys.

5. SUMMARY AND CONCLUSIONS

We have performed PWPP calculations for AlN, GaN and InN utilizing large plane-wave basis sets and treating the gallium 3d and indium 4d electrons as valence. The bulk structural properties are in good agreement with available measurements including the independently determined wurtzite structural parameters and the lattice mismatch. We have also determined bowing parameters for the disordered zinc-blende alloys AlGaInN₂, GaInN₂ and AlInN₂. The values display similarities with results found for other III-V alloys and are in reasonable agreement with measurements. Overall, the advances made recently in the PWPP method and the good agreement found here for bulk and alloy properties indicate that this technique will play an important role in guiding the development of nitride-based devices as it already has for phosphide- and arsenide-based devices.

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