Consistent structural properties for AlN, GaN, and InN

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The plane-wave pseudopotential method is used to calculate structural properties for wurtzite and zinc-blende AlN and InN using large plane-wave basis sets and treating the indium $4d$ electrons as valence. These calculations, together with corresponding ones for GaN [A. F. Wright and J. S. Nelson, Phys. Rev. B **50**, 2159 (1994)], yield a consistent set of well-converged structural properties for AlN, GaN, and InN. In particular, the measured lattice mismatch among these compounds—essential for an accurate description of alloy properties—is well reproduced.

Studies of AlN, GaN, and InN are motivated primarily by the possibilities these materials offer for fabricating optical devices such as detectors, solid-state lasers, and light-emitting diodes. In their ground-state structure (wurtzite), these compounds have direct energy gaps of 1.89 eV (InN),[1] 3.50 eV (GaN),[2] and 6.28 eV (AlN) (Ref. 3) ranging from the visible to the ultraviolet regions of the spectrum. By alloying it should, therefore, be possible to produce materials with direct gaps anywhere within this range including the blue-green region. A number of experimental studies have already been performed for the ternary alloys $In_xAl_{1-x}N$, $In_xGa_{1-x}N$, and $Al_xGa_{1-x}N$. However, many of their fundamental properties are still not well established. (See Ref. 4 for a review of these studies.) Self-consistent calculations, such as those recently performed by Albanesi, Lambrecht, and Segall for zinc-blende $Al_xGa_{1-x}N$,[5] could therefore play an important role in determining the properties of nitride alloys.

The plane-wave-pseudopotential (PWPP) method has been used extensively to study other III-V alloys and would appear to be well suited for studying nitride alloys. However, in order to accurately describe properties such as optical bowing, any theoretical technique must be capable of reproducing the lattice mismatch of the constituents. (See Ref. 6 for a discussion of optical bowing in III-V semiconductors.) In this regard AlN, GaN, and InN seem to present difficulties for pseudopotential methods in general and the PWPP method in particular. In Table I, for example, we list measured values of the wurtzite AlN and GaN lattice constants and their mismatch together with corresponding results from three recent pseudopotential studies. The measurements indicate that the GaN lattice constants are larger by 2.50% for a and 4.03% for c. However, the pseudopotential results imply nearly identical a lattice constants and a GaN c lattice constant at most 2.6% larger. We find that these discrepancies are not due to fundamental limitations in the pseudopotential formalism, but rather to technical approximations regarding the size of the basis set and the choice of which electrons to include as valence. In fact, it is both possible and practical to limit the effect of these approximations to the point that the lattice mismatch

among all three compounds is well reproduced. Our present results for wurtzite AlN and previous results for GaN,[7] for example, yield lattice mismatch in excellent agreement with measured values: GaN a and c lattice constants are 2.50% and 3.85% larger. In the remainder of this paper, we describe how the technical approximations mentioned above affect lattice mismatch and we present structural properties for AlN and InN including fully independent determinations of their wurtzite structural parameters. These results along with the previous ones for GaN (Ref. 7) provide a consistent set of well-converged structural properties that should serve both as a foundation upon which to calculate the properties of nitride alloys and as reliable theoretical values for future reference.

The PWPP method is based on density-functional theory (DFT) within the local-density approximation (LDA) for exchange and correlation.[8] In this formalism, the self-consistent electronic structure of the valence electrons is determined explicitly while effects due to the core electrons are approximated using *ab initio* pseudopotential.[9] In contrast with previous pseudopotential calculations for InN, we treat the indium $4d$ electrons as valence similar to our previous treatment of the gallium $3d$ electrons in GaN.[7] In addition, we use large plane-wave

TABLE I. Measured and calculated lattice constants (Å) for wurtzite AlN and GaN together with their lattice mismatch $\Delta\%$ [see Eq. (3)]. PWPP refers to plane-wave pseudopotential results and MBPP refers to pseudopotential calculations using a mixed basis of plane waves and Gaussian functions.

	AlN		GaN		$\Delta\%$	
	a	c	a	c	a	c
Expt.[a]	3.110	4.980	3.190	5.189	+2.50	+4.03
PWPP[b]	3.099	4.997	3.095	5.000	−0.13	+0.06
PWPP[c]	3.129	4.988	3.126	5.119	−0.10	+2.59
MBPP[d]	3.144	5.046	3.146	5.125	+0.06	+1.55

[a]Reference 21.
[b]Reference 15.
[c]References 14 and 17.
[d]Reference 22.

TABLE II. Measured and calculated wurtzite lattice constants (Å), c/a ratios, internal parameters, bulk moduli (Mbar), and energy gaps (eV) at the Γ point.

	a	c	c/a	u	B	E_Γ
AlN: expt.	3.110[a]	4.980[a]	1.601	0.3821[a]	2.02[b]	6.28[c]
This work	3.084	4.948	1.604	0.3814	2.05	4.41
GaN: expt.	3.190[a]	5.189[a]	1.627	0.377[a]	1.95,[d] 2.37[e]	3.50[f]
Previous work[g]	3.162	5.142	1.626	0.3770	2.02	2.04
InN: expt.	3.544[h]	5.718[h]	1.613		1.26,[e]1.39[d]	1.89[i]
This work	3.501	5.669	1.619	0.3784	1.39	−0.04

[a]Reference 21.
[b]Reference 23.
[c]Reference 3.
[d]Reference 24.
[e]Reference 25.

[f]Reference 2.
[g]Reference 7.
[h]Reference 26.
[i]Reference 1.

basis sets (kinetic-energy cutoffs of 140 and 120 Ry for the AlN and InN plane-wave expansions) in order to converge both the nitrogen $2p$ states and the indium $4d$ states. As further technical notes, we used the iterative scheme of Teter, Payne, and Allan[10] to determine the self-consistent solutions and we performed Brillouin-zone integration using six special $\mathbf{k}$ points[11] for wurtzite and ten for zinc blende.

The wurtzite structure is specified by two lattice parameters a and c and an internal parameter u. Equilibrium values were found by calculating total energies for a set of values of the c/a ratio and the volume per unit cell using calculated forces to determine the optimum value of u. These energies were 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 unit cell volume, y is c/a, and C_{ij} are coefficients determined by the fit. To determine the bulk modulus the computed energies for each volume were fit to the equation

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

where C_i are coefficients determined by the fit. The minimum energies and their associated volumes were then fit to the Murnaghan equation[12] yielding the bulk modulus.

In Table II, we list the calculated AlN and InN wurtzite lattice constants and bulk moduli together with measured values and our previous results for GaN. Overall, the lattice constants are about 1% smaller than the measured values, which is typical of well-converged LDA-DFT results. Furthermore, calculated values of the lattice mismatch (defined below for common anion compounds AC and BC),

$$\Delta\% = 200(a_{AC} - a_{BC})/(a_{AC} + a_{BC}) , \quad (3)$$

are in excellent agreement with the measurements: For AlN-GaN, we find a mismatch of 2.50% for a and 3.85% for c whereas the measured values are 2.50% and 4.03%. For AlN-InN, we find 12.7% mismatch for a and 13.6%

for c (measured values are 13.0% and 14.5%) while for GaN-InN we find 10.2% mismatch for a and 9.8% for c (measured values are 10.5% and 9.7%). The bulk moduli of all three compounds are also in good agreement with measured values, although there is some disagreement among the measured values for GaN. In addition to the structural properties, we also compare (Table II) the calculated energy gaps at Γ with measured values (room temperature for InN and low temperature for AlN and GaN). The calculated values are lower; however, this is a well-known failure of DFT for which corrections exist yielding gaps in good agreement with the measurements.[13]

The zinc-blende structure is characterized by the cubic lattice constant a. The equilibrium value and bulk modulus were determined by calculating total energies for a set of volumes and fitting these to the Murnaghan equation.[12] In Table III, we list the results for AlN and InN, our previous results for GaN, measured values for the lattice constants, and estimates of the bulk moduli. As for wurtzite, the calculated lattice constants are smaller than the measured values, but within about 1%. The lattice mismatch is also well described: Measured and calculated values are 2.70% and 2.68% for AlN-GaN,

TABLE III. Measured and calculated zinc-blende lattice constants (Å), bulk moduli (Mbar), and energy gaps (eV) at the Γ point.

	a	B	E_Γ
AlN: expt.	4.38[a]	2.02[b]	
This work	4.342	2.07	4.35
GaN: expt.	4.5[c]	1.90[b]	3.45[c]
Previous work[d]	4.460	1.87	1.89
InN: expt.	4.98[e]	1.37[b]	
This work	4.932	1.40	−0.35

[a]Reference 27.
[b]Reference 28.
[c]Reference 29.
[d]Reference 7.
[e]Reference 30.

TABLE IV. Calculated wurtzite AlN lattice constants (Å), c/a ratios, internal parameters, bulk moduli (Mbar), and energy gaps (eV) at the Γ point. The FP-LMTO energy gap was calculated at the experimental volume/atom (10.428 Å^3) instead of the theoretical value.

	a	c	c/a	u	B	E_Γ
FP-LMTO[a]	3.072	4.904	1.596	0.3820	2.05	4.52
This work	3.084	4.948	1.604	0.3814	2.05	4.41

[a]Reference 18.

12.8% and 12.7% for AlN-InN, and 10.1% and 10.1% for GaN-InN.

Our success in reproducing the lattice mismatch among the nitrides can be attributed to two factors: (1) the use of large energy cutoffs for the plane-wave expansions and (2) treatment of the gallium $3d$ and indium $4d$ electrons as valence. In general, lattice constants tend to converge toward smaller values as the number of plane waves (or the energy cutoff) is increased. This is illustrated in Tables I and II for AlN. Our 140-Ry energy cutoff is larger than those used by either Van Camp, Van Doren, and Devreese (30 Ry) (Ref. 14) or Yet et al. (50 Ry) (Ref. 15) and our lattice constants are noticeably smaller. Treating the gallium $3d$ and indium $4d$ electrons as valence rather than core, on the other hand, yields larger lattice constants for GaN (Refs. 7 and 16) and InN. For GaN, the combination of this effect with that due to our 240-Ry cutoff results in larger lattice constants (Table II) than were found by either Van Camp, Van Doren, and Devreese (34-Ry cutoff) (Ref. 17) or Yeh et al. (50-Ry cutoff) (Ref. 15) (Table I) treating the gallium $3d$ electrons as core.

Another possible source of error in pseudopotential calculations is the pseudopotentials themselves. To assess their effect, we compare our AlN and InN results with those from full-potential linear-muffin-tin orbitals (FP-LMTO) and full-potential linear-augmented plane-wave (LAPW) calculations in Tables IV and V. These techniques are considered to be the most reliable in the sense that they make the fewest approximations, and, in particular, they treat all of the electrons explicitly. For AlN, Christensen and Gorczyca[18] performed FP-LMTO calculations for both the wurtzite and zinc-blende structures. For wurtzite (Table IV), our lattice constants are larger by 0.4% for a and 0.9% for c, our bulk moduli are identical, and our energy gap at Γ is 0.11 eV smaller. For zinc blende (Table V), our lattice constant is 0.2% larger and our bulk modulus is 4% smaller. The different levels of

TABLE V. Calculated zinc-blende lattice constants (Å), bulk moduli (Mbar), and energy gaps (eV) at the Γ point.

	a	B	E_Γ
AlN: FP-LMTO[a]	4.334	2.16	
This work	4.342	2.07	4.35
InN: FP-LMTO[b]	4.929	1.38	
LAPW[c]	4.953	1.44	−0.20
This work	4.932	1.40	−0.35

[a]Reference 18.
[b]Reference 19.
[c]Reference 20.

agreement for the wurtzite and zinc-blende lattice constants are somewhat inconsistent; however, the overall agreement is good. For InN, both FP-LMTO (Ref. 19) and LAPW (Ref. 20) results are available for zinc blende and are in excellent agreement with each other—the lattice constants agree to within 0.5% and the bulk moduli to within 4%. Our results show a similar level of agreement—within 0.4% for the lattice constants, 3% for the bulk moduli, and the energy gaps at Γ differ by no more than 0.15 eV. The overall good agreement between ours and the full-potential, all-electron results indicates that effects due to the pseudopotential approximation are small—at least as small as effects due to differences between the LAPW and FP-LMTO techniques. For completeness, we note that this level of agreement is consistent with that found previously for our GaN results.[7]

In conclusion, we find that the PWPP method is capable of reproducing the lattice mismatch among AlN, GaN, and InN as long as consistent technical approximations are used. These include the use of large energy cutoffs for the plane-wave expansions and explicit treatment of the gallium $3d$ and indium $4d$ electrons. Furthermore, effects due to the pseudopotential approximation appear to be small indicating that these results should serve both as reliable values for future reference and as a foundation for studying nitride alloys.

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