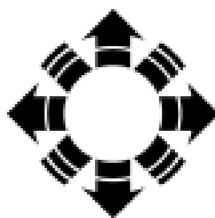
May 2003 • NREL/CP-590-33560

Conference Paper

III-Nitride Semiconductors for Photovoltaic Applications

S.-H. Wei

Presented at the National Center for Photovoltaics and Solar Program Review Meeting
Denver, Colorado
March 24-26, 2003



NREL

National Renewable Energy Laboratory

1617 Cole Boulevard
Golden, Colorado 80401-3393

NREL is a U.S. Department of Energy Laboratory
Operated by Midwest Research Institute • Battelle • Bechtel

Contract No. DE-AC36-99-GO10337

NOTICE

The submitted manuscript has been offered by an employee of the Midwest Research Institute (MRI), a contractor of the US Government under Contract No. DE-AC36-99GO10337. Accordingly, the US Government and MRI retain a nonexclusive royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for US Government purposes.

This report was prepared as an account of work sponsored by an agency of the United States government. Neither the United States government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States government or any agency thereof.

Available electronically at http://www.osti.gov/bridge

Available for a processing fee to U.S. Department of Energy
and its contractors, in paper, from:
U.S. Department of Energy
Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831-0062
phone: 865.576.8401
fax: 865.576.5728
email: reports@adonis.osti.gov

Available for sale to the public, in paper, from:
U.S. Department of Commerce
National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
phone: 800.553.6847
fax: 703.605.6900
email: orders@ntis.fedworld.gov
online ordering: http://www.ntis.gov/ordering.htm

Printed on paper containing at least 50% wastepaper, including 20% postconsumer waste

III-Nitride Semiconductors for Photovoltaic Applications

Su-Huai Wei
National Renewable Energy Laboratory
Golden, Colorado 80401

ABSTRACT

Using a band-structure method that includes bandgap correction, we study the chemical trends of the bandgap variation in III-V semiconductors and predict that the bandgap for InN is 0.85 ± 0.1 eV. This result suggests that InN and its III-nitride alloys are suitable for photovoltaic applications. The unusually small bandgap for InN is explained in terms of the atomic energies and the bandgap deformation potentials. The electronic and structural properties of the nitrides and their alloys are also provided.

1. Introduction

III-nitrides are usually considered as wide-band gap materials that have applications in devices such as ultraviolet/blue/green light-emitting diodes and lasers [1]. However, recent measurements suggest that the bandgap of wurtzite (WZ) InN is below 1.0 eV [2], much smaller than the 1.89 eV bandgap [3] widely accepted in the past to interpret experimental data [1] and to fit empirical pseudopotentials for modeling InN and related alloy properties [4]. If InN indeed has a less than 1.0 eV bandgap, which is even smaller than that for InP (1.4 eV), then InN and its III-nitride alloys could cover most of the solar spectrum range, and thus, are suitable for future-generation photovoltaic applications. On the other hand, the low bandgap of InN also provides a challenge because it suggests that the In*X* (*X*=N, P, As, Sb) system does not obey the bandgap common-cation rule, which states that for common-cation semiconductors, the bandgap increases as the cation atomic number decrease.

To predict the InN bandgap and understand the origin of the InN bandgap anomaly, we have performed band-structure calculations using a semiempirical method based on local density approximation (LDA) [5]. We find that the bandgap of WZ InN is 0.85 ± 0.1 eV, in good agreement with recent experimental measurements, but much smaller than the previously reported value of 1.89 eV. We show that the reason that InN has a smaller bandgap than InP is due to the much more electronegative N 2*s* orbital and the much smaller bandgap deformation potential for the ionic InN. To complete the study, we also calculated the electronic and structural properties of the III-nitrides and their alloys.

2. Method of Calculations

The LDA band-structure calculations in this study are performed using the fully relativistic, self-consistent, linearized augmented plane wave (LAPW) method [6]. The band structures are calculated at experimental lattice constants [7]. To correct the well-known LDA bandgap error, we added to the LDA potential a δ-like external potential inside the muffin-tin (MT) spheres centered at each atomic site α [8]:

$$V_{ext}^{\alpha}(r) = \bar{V}^{\alpha} + V_0^{\alpha}(\frac{r_0^{\alpha}}{r})e^{-(\frac{r}{r_0^{\alpha}})^2}, \qquad (1)$$

and performed the calculation self-consistently. This functional form of the correction potential is based on the observation that the LDA bandgap error is orbital dependent. To correct the bandgap error, one needs to have a potential that is more repulsive to the *s* orbital than to the *p* orbital. Because the *p* orbital has zero charge density at the nuclear site, whereas the *s* orbital has finite density at the nuclear site, a δ-like function centered at the nuclear site can increase the band gap. The parameters in Eq. (1) are fitted first to the available experimental energy levels and to the quasiparticle energies [9] at high-symmetry k-points for AlP, GaP, and InP [8]. To improve the fit, empty spheres centered at tetrahedral sites are also used. The MT radii for the empty sphere are 2.05 *a.u.* The fitting parameters are given in Table I. The same parameters given in Table I are then used to predict the bandgaps of arsenides, antimonides, and nitrides. For the nitrides, however, we have to use smaller muffin-tin radii to avoid having overlapping MT spheres. In this case, we use R_{MT}=1.68 *a.u.* for the empty spheres. This value is chosen to obtain the correct bandgap of GaN. The same parameters given in Table I are used to predict the bandgaps of AlN and InN. To find the bandgap for the wurtzite structure, we add the LDA-calculated bandgap differences between the WZ and zincblende (ZB) compounds to the calculated bandgap for the ZB compound. The overall bandgap uncertainty associated with this fitting procedure is estimated to be 0.1 eV.

3. Bandgap of InN

The predicted direct bandgaps at the Γ-point for the ZB and WZ III-V semiconductors are shown in Table II. These values are compared with available experimental data [7] and quasiparticle calculations [9]. We find that for nearly all the III-V semiconductors, the differences between the predicted and the experimental bandgaps are less than 0.1 eV. For InN, however, our predicted value of 0.85 eV is much smaller than the previous experimental value of 1.89 eV, but it is in very good agreement with recent experimental measurements.

Table I. Fitted parameters in Eq. (1) for group III and group V atoms. ES denotes empty sphere.

Atom	$\bar{V}$ (Ry)	V_0 (Ry)	r_0 (a.u)
N, P, As, Sb	0.00	80	0.025
Al	0.00	360	0.025
Ga	0.00	280	0.025
In	0.00	200	0.025
ES	0.36	100	0.025

Table II. Calculated bandgaps and deformation potentials at Γ for ZB and WZ compounds at experimental (exp) lattice constants using the LDA and LDA-plus-correction (LDA+C) methods. The E_g^{LDA+C} values with an (*) are fitted values, whereas all the others are predicted values.

	a_{exp} (Å)	E_g^{LDA} (eV)	E_g^{LDA+C} (eV)	E_g^{QP} (eV)	E_g^{exp} (eV)	$-a_g^{LDA+C}$ (eV)
AlSb	6.133	1.24	2.28	2.23	2.32	8.9
GaSb	6.096	-0.38	0.81	0.62	0.81	8.0
InSb	6.479	-0.70	0.15	0.08	0.24	6.4
AlAs	5.660	1.75	3.05	2.88	3.13	8.9
GaAs	5.653	0.09	1.43	1.22	1.52	8.2
InAs	6.058	-0.64	0.36	0.31	0.42	5.7
AlP	5.467	3.06	4.42*	4.38	—	9.5
GaP	5.451	1.50	2.86*	2.85	2.86	8.8
InP	5.869	0.37	1.40*	1.44	1.46	5.9
AlN	4.360	4.28	6.00	6.0	—	10.2
GaN	4.500	1.72	3.34*	3.1	3.3	7.4
InN	4.980	-0.48	0.70	—	—	3.7
AlN(WZ)	a=3.112 c=4.982 u=0.3819	4.23	5.95	5.8	6.1	10.4
GaN(WZ)	a=3.189 c=5.185 u=0.3768	1.87	3.49	3.5	3.5	7.8
InN(WZ)	a=3.544 c=5.718 u=0.3790	-0.34	0.85	—	—	4.2

4. Trends of the Bandgap of III-V Semiconductors

Our calculations above show convincingly that the bandgap of InN is around 0.85 eV. However, this value is about 0.6 eV smaller than that of InP, thus contradicting the conventional wisdom that the bandgaps of common-cation (or anion) compounds increase as the anion atomic number decreases. Table II shows that the common-anion rule indeed holds for the entire common-anion system. For the common-cation system, this rule holds for the Al and the Ga compounds, but fails for the In compounds. To understand the general trends of the bandgap variation in the common-cation system, we study the chemical and size contributions to the bandgap. For the chemical contribution, we calculate the bandgaps of Al, Ga, and In compounds at the fixed lattice constants of AlP, GaP, and InP, respectively. The results are shown in Table III. LDA corrections are included. We find that at the phosphide volume, the bandgaps of the common-cation system decrease from *M*Sb to *M*P to *M*As to *M*N (*M*=Al, Ga, and In), following the same trend of the anion atomic valence *s* orbital energies shown in Table IV. This is because the conduction band minimum at the Γ-point is an anion *s* plus cation *s* state. The anion contribution increases as the compound becomes more ionic. Thus, the bandgaps of the common-cation compounds at fixed volume generally follow the same trend of the valence *s* orbital energies of the anion. Because the N 2*s* orbital energy is 5.3 eV, 3.8 eV, and 4.4 eV lower in energy than the Sb 5*s*, As 4*s* and P 3*s* orbital energies, respectively, the bandgap of the nitrides are also lower than the corresponding antimonies, asenides, and phosphides at fixed lattice constant.

Table III. Calculated (LDA+C) direct bandgaps (in eV) at Γ for zincblende Al, Ga, and In compounds at their equilibrium (eq) lattice constants and at their respective phosphide lattice constants.

	$a = a_{\rm AlP}$	a_{eq}		$a = a_{\rm GaP}$	a_{eq}		$a = a_{\rm InP}$	a_{eq}
AlN	0.45	6.00	GaN	-0.61	3.34	InN	-1.27	0.70
AlP	4.42	4.42	GaP	2.86	2.86	InP	1.40	1.40
AlAs	4.04	3.05	GaAs	2.36	1.43	InAs	0.92	0.36
AlSb	5.69	2.28	GaSb	3.67	0.81	InSb	2.15	0.15

Because the order of the bandgaps calculated at the fixed volume is generally opposite to what is observed at the equilibrium lattice constants, the chemical contribution alone cannot explain the experimentally observed trend in the bandgaps at equilibrium lattice constants. Next, we investigate the size or volume deformation contribution to the bandgap. The calculated volume deformation potentials [10] with the LDA correction for III-V semiconductors are also listed in Table II. We see that all the compounds have negative volume deformation potentials at Γ, i.e., when the volume decreases, the bandgap increases. Therefore, it is clear that the common-cation rule and the common-anion rule for the bandgap is mainly due to the large deformation potential of the III-V compounds. For example, at GaP lattice constant, the bandgap of GaSb is 0.81 eV larger than that of GaP. However, GaSb is about 34% larger in volume than GaP. So, with an average deformation potential of -8.4 eV, the bandgap of GaSb at its equilibrium lattice constant is about 2.05 eV smaller than the bandgap of GaP at its equilibrium lattice constant. The same situation applies to AlN and GaN: Even though AlN and GaN have much smaller bandgap than AlP and GaP at the lattice constants of AlP and GaP, respectively, their bandgaps are larger than the phosphides at their own equilibrium lattice constants (Table III). This is because AlN is 68% smaller than AlP and GaN is 58% smaller than GaP, and AlN and GaN have large bandgap deformation potentials [a_g(AlN)=-10.4 eV and a_g(GaN)=-7.8 eV]. However, for InN, although its volume is about 49% smaller than InP, its bandgap deformation potential is small, a_g(InN)=-4.2 eV. Because of this small $|a_g|$, the contribution due to the size or deformation potential is not sufficient to reverse the order of the bandgap due to the contribution of the chemical effect. This explains why InN has a smaller bandgap than InP.

Table IV. Calculated atomic s and p orbital energies (in eV) for group III and group V elements.

Atom	ϵ_s	ϵ_p
Al	-7.91	-2.86
Ga	-9.25	-2.81
In	-8.56	-2.78
N	-18.49	-7.32
P	-14.09	-5.68
As	-14.70	-5.34
Sb	-13.16	-5.08

5. Material Properties of III-Nitride Alloys

The small bandgap of InN suggests that InN and its III-nitride alloys could be suitable materials for photovoltaic applications. To see how the material properties of the alloys vary as a function of the alloy concentration, we have calculated the ground-state structural properties, band-structure parameters, mixing energies, optical bowing parameters and band offsets of the III-nitrides and their alloys. For the random alloy at x=0.5, we use the special quasirandom structure (SQS) approach, where ordered alloy with atomic correlation functions close to that of the random alloy are used to represent the random alloys.

Table V shows our calculated structural parameters and valence-band splittings of the binary nitrides. Table VI gives the calculated mixing energy and optical bowing parameters at x=0.5 and the valence-band offsets between AlN, GaN, and InN. We find that (i) the LDA calculated structural parameters are in very good agreement with experiment [7]. AlN and InN show significant deviation from the ideal wurtzite WZ structure parameters [11]. (ii) The crystal-field splitting Δ_{CF} is very sensitive to the internal structural parameter u and the c/a ratio. Because u and c/a for WZ AlN differ significantly from the ideal value (u=0.375 and c/a=1.632), it has a very large and *negative* Δ_{CF}, i.e., for AlN, the Γ_{1v} state is higher in energy than the Γ_{6v} state. This reversal of the band-edge states in AlN is responsible for the unusual optical polarization observed in this compound [12]. (iii) Spin-orbit splittings Δ_0 are small for all the three binary nitrides mostly due to the small atomic number of nitrogen. (iv) The binary compound is more stable in the WZ structure, in agreement with experiment. The calculated alloy mixing energy ΔH_{mix} increases as the lattice mismatch increases. The large mixing energies between AlN/InN and between GaN/InN suggest that these two systems are difficult to mix. (v) The optical bowing parameter b [8] is also proportional to the size and chemical mismatch of the constituents. It is relatively small for $Al_{0.5}Ga_{0.5}N$, but is large for $Al_{0.5}In_{0.5}N$. (vi) The absolute energy of the natural-valence band edge increases from AlN, GaN, to InN. The relatively large band offset compared to other common-anion III-V system is mostly due to the stronger p-d repulsion and ionicity in the nitride system [11].

Table V. Calculated structural and band parameters for the binary nitrides. The structural parameters are compared with experimental data (in parentheses). ΔE_{12} and ΔE_{13} are the valence-band splittings at the Γ point.

properties	AlN	GaN	InN
a (Å)	3.098 (3.112)	3.170 (3.189)	3.546 (3.544)
c/a (Å)	1.601 (1.601)	1.625 (1.626)	1.612 (1.613)
u	0.3819	0.3768	0.3790
a_{ZB} (Å)	4.355 (4.36)	4.476 (4.50)	4.964 (4.98)
ΔE_{ZB-WZ} (meV)	45	11	21
Δ_{CF} (meV)	-219	36	26
Δ_0 (meV)	19	14	3
ΔE_{12} (meV)	213	7	1
ΔE_{13} (meV)	226	43	29

Table VI. Calculated alloy mixing energy and the optical bowing coefficient at x=0.5 and the valence-band offsets, between AlN, GaN, and InN.

	AlN/GaN	GaN/InN	AlN/InN
$\Delta H_{mix}(x=0.5)$ (meV/2-atom)	3	94	108
b (eV)	0.35	2.44	1.14
ΔE_V(ZB)	0.84	0.26	1.04
ΔE_V(WZ)	0.81	0.48	1.25

6. Summary

In conclusion, using an LDA band-structure method with bandgap correction, we have shown that InN has a bandgap of 0.85 ± 0.1 eV. This result indicates that InN and its III-nitride alloys could be suitable for future PV applications. We have also calculated the structural and band parameters of the binary nitrides, as well as the valence-band offsets, alloy mixing energies and the optical bowing parameters of the nitride alloys. These properties can be used for modeling solar cells.

DOE supported this research under Contract No. DE-AC36-99GO10337. The author also would like to acknowledge X. Nie, I. G. Batyrev, P. Carrier and Shengbai Zhang for their helpful discussions.

REFERENCES

[1] H. Morkoc, *Nitride Semiconductors and Devices*, (Springer, New York, 1999).

[2] J. Wu et al., Appl. Phys. Lett. **80**, 3967 (2002); 4741 (2002).

[3] T. L. Tansley and C. P. Foley, J. Appl. Phys. **59**, 3241 (1986).

[4] L. Bellaiche et al., Appl. Phys. Lett. **74** 1842 (1999); P. R. C. Kent and A. Zunger, Appl. Phys. Lett. **79**, 1977 (2001).

[5] S.-H. Wei, X. Nie, I. G. Batyrev, and S. B. Zhang, unpublished.

[6] S.-H. Wei and H. Krakauer, Phys. Rev. Lett. **55**, 1200 (1985).

[7] *Intrinsic Properties of Group IV Elements and III-V, II-VI, and I-VII Compounds*, edited by O. Madelung, M. Schulz, and H. Weiss, Landolt-Bornstein, New Series, Group III, Vol. 22, Pt. a (Springer, Berlin, 1987).

[8] S. H. Wei and A. Zunger, Phys. Rev. B **57**, 8983 (1998).

[9] X. Zhu and S. G. Louie, Phys. Rev. B **43**, 14142 (1991).

[10] S.-H. Wei and A. Zunger, Phys. Rev. B **60**, 5404 (1999).

[11] S.-H. Wei and A. Zunger, Appl. Phys. Lett. 69, 2719 (1996).

[12] J. Li et al., unpublished.

REPORT DOCUMENTATION PAGE

Form Approved
OMB NO. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE May 2003	3. REPORT TYPE AND DATES COVERED Conference Paper

4. TITLE AND SUBTITLE III-Nitride Semiconductors for Photovoltaic Applications	5. FUNDING NUMBERS PVP2.2401
6. AUTHOR(S) S.-H. Wei	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) National Renewable Energy Laboratory 1617 Cole Blvd. Golden, CO 80401-3393	8. PERFORMING ORGANIZATION REPORT NUMBER NREL/CP-590-33560
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT National Technical Information Service U.S. Department of Commerce 5285 Port Royal Road Springfield, VA 22161	12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

Using a band-structure method that includes bandgap correction, we study the chemical trends of the bandgap variation in III-V semiconductors and predict that the bandgap for InN is 0.85 ± 0.1 eV. This result suggests that InN and its III-nitride alloys are suitable for photovoltaic applications. The unusually small bandgap for InN is explained in terms of the atomic energies and the bandgap deformation potentials. The electronic and structural properties of the nitrides and their alloys are also provided.

14. SUBJECT TERMS III-V semiconductor; band-structure method; InN; III-nitride alloys; bandgap variation; electronic properties; structural properties; photovoltaic applications	15. NUMBER OF PAGES
	16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	UL