Band structure parameters of the nitrides: The origin of the small band gap of InN

Pierre Carrier* and Su-Huai Wei*

*National Renewable Energy Laboratory, Golden, CO 80401

Abstract. Using the full-potential linear augmented plane waves (FLAPW) method and adding Christensen's gaussian potential to the standard Kohn-Sham equations that allows to correct the band gap in the local density approximation (LDA), we study the chemical trends of the band gap variation in III-V semiconductors and predict that the band gap for InN is 0.8 (± 0.1 eV), which is much smaller than previous experimental value of 1.9 eV. The unusually small band gap of InN, that is even smaller than the band gap of InP, is explained in terms of the high electronegativity of nitrogen and consequently the small band gap deformation potential of InN. To understand the possible origin of the measured large band gap, we have calculated the absorption coefficients and effective masses of wurtzite InN and compared the results to the one of GaN. We show that, due to the non-parabolicity of the bands, using the standard linear interpolation scheme as in the experiments, the derived apparent band gap depends on the choice of the scale used in the measurements. The difference between the apparent band gap and the true band gap could be as large as 0.4 eV for InN, overestimating the true band gap. From the calculated effective masses we have calculated the Moss-Burstein shift of the band gap as a function of the carrier density. We find that due to the Moss-Burstein shift, the apparent band gap of InN can reach to 2.0 eV if the electron density in the conduction band is in the order of 10^{20}. Our observations are consistent with recent experiments, where a low band gap of 0.8 eV in InN is reported. This establishes the low value for the band gap in InN.

Recent measurements suggest that the band gap of wurtzite (WZ) InN is below 1.0 eV [1, 2, 3], much smaller than the 1.89 eV band gap [4] widely accepted in the past to interpret experimental data [5]. With a band gap less than 1.0 eV, InN and its III-nitride alloys could be suitable for a wide range of optoelectronic device applications such as future-generation solar cells. However, the recent observation also provides a challenge to our understanding of semiconductor band gaps: For common-anion (or cation) III-V semiconductors, the direct band gap at Γ usually increases as the cation (or anion) atomic number decreases [6]. This trend would hold for common-cation InX (X=N, P, As, Sb) compounds if $E_g(\text{InN}) = 1.9$ eV, as previously reported [4]. However, the rule will be broken if $E_g(\text{InN}) \sim 0.8$ eV.

In this paper, we have performed fully relativistic band structure calculations using linearized augmented plane wave (LAPW) method[7] within the local density approximation (LDA) [8]. We used a well established approach by adding to the LDA potential a δ-function-like external potentials [9] inside the muffin-tin (MT) spheres centered at each atomic site [10] to correct the LDA band gap error. This functional form is based on the observation that the LDA band gap error is orbital dependent. To correct the band gap error, one needs to have a potential that is more repulsive to the s orbital than to the p orbital (such as the δ-function-like potential).
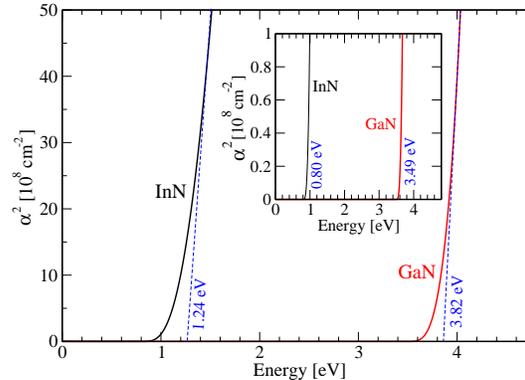

FIGURE 1. Calculated absorption coefficients of InN and GaN. We show that using the linear extrapolation technique the apparent measured band gaps depend on the scale used in the extrapolation.

Using this approach (described in details in Ref. [11]) we find that the band gap of WZ InN is 0.8 ± 0.1 eV, in good agreement with recent experimental measurements. The reason that InN has a smaller band gap than InP is due to the much larger electronegativity of nitrogen and the much smaller band gap deformation potential for InN. Due to the large electronegativity of nitrogen, the band gap of InN is much smaller than that of InP at fixed

lattice constant. For example, at a=5.87 Å, the band gap of InN is about 2.7 eV smaller than that of InP. Although the volume of InN is about 49% smaller than InP, its band gap deformation potential $a_g = dE_g/dlnV$ is small due to the high ionicity of InN [12]. (For instance, $a_g(\text{InN}) = -3.7$ eV, versus $a_g(\text{GaAs}) = -8.2$ eV). Because of its small $|a_g|$, the contribution due to the size or deformation potential in InN is not sufficient to reverse the order of the band gap due to the contribution of the chemical effect. This explains why InN has a much smaller band gap than InP (about 0.6 eV below). We notice that a similar situation occurs in II-VI semiconductors; for instance, experimental data [6] show that the ZnO band gap of 3.4 eV is smaller than the ZnS band gap of 3.8 eV.

Experimentally, one often assumes that the band edge states near Γ is parabolic and the dipole transition matrix element is nearly independent of **k**, therefore, the absorption coefficient squared, α^2, is a linear function of the absorption energy, E. The fundamental band gap, thus, can be obtained from the interception with the energy axis by drawing a straight line in the α^2 versus E plot [2, 3, 4]. Figure 1 shows our calculated absorption coefficients of InN, and GaN for comparison. Because of the large deviation from the parabolic band, the calculated α^2 is not a linear function of E (Fig. 1). Therefore, if one use the linear extrapolation technique to determine the band gap, the derived apparent band gaps depend on where the straight lines are drawn. For example, as shown in Fig. 1, for InN, using large values of the absorption coefficient to draw the straight line, one can obtain an apparent band gap that is about 0.4 eV larger than the fundamental band gap. The dependence is relatively smaller for GaN which has a larger effective mass than that of InN, thus a sharper increase of the absorption coefficient. Finally, we notice that InN samples that show large band gaps are often heavily n-type doped [2, 3, 4]. Besides the possible formation of InNO alloys as proposed in Ref. [2], this observation suggests that the measured absorption edge can be shifted by the Moss-Burstein effect [13]. Figure 2 shows our calculated absorption edge energy as a function of the carrier density. We see that the absorption edge increases with the carrier density from 0.8 eV for intrinsic InN to 1.9 eV for n-type samples with electron concentration of 3×10^{20} cm^3 (Fig. 2). These results are consistent with recent experimental observation [14], and could explain the higher band gap value reported in experiments for InN.

In summary, using an empirical LDA-based band structure method with band gap correction we have systematically studied the chemical trends of the band gap variation in III-V semiconductors. We find that InN has a band gap of 0.8 ± 0.1 eV, in good agreement with recent experimental measurements. We show that the previously accepted band gap-common-cation rule does not hold for ionic InN and the II-VI oxides.
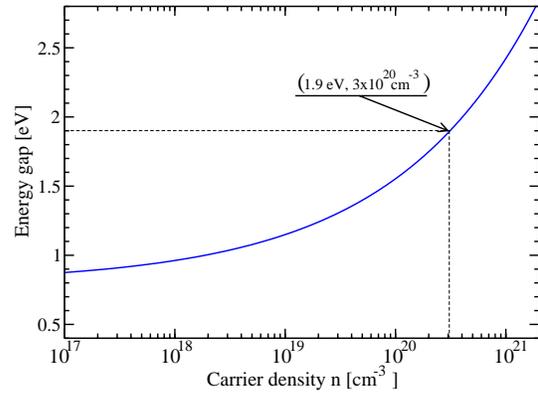
FIGURE 2. Calculated Moss-Burstein shift of the absorption edge energy as a function of the carrier density.

ACKNOWLEDGMENTS

REFERENCES

1. T. Inushima *et al.*, J. Cryst. Growth **227/228**, 481 (2001); V. Y. Davydov *et al.*, Phys. Stat. Sol. (b) **230**, R4 (2002); Phys. Stat. Sol. (b) **229**, R1 (2002); Phys. Stat. Sol. (b) **234**, 787 (2002); J. Wu *et al.*, Appl. Phys. Lett. **80**, 3967 (2002); Appl. Phys. Lett. **80**, 4741 (2002); A. Yamamoto *et al*, J. Cryst. Growth **261**, 275 (2004).
2. Motlan *et al.*, J. Cryst. Growth **241**, 165 (2002).
3. K. Osamura *et al.*, Solid State Commun. **11**, 617 (1972); J. Appl. Phys. **46**, 3432 (1975).
4. T. L. Tansley and C. P. Foley, J. Appl. Phys. **59**, 3241 (1986).
5. H. Morkoç, *Nitride Semiconductors and Devices* (Springer, New York, 1999).
6. *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).
7. S.-H. Wei and H. Krakauer, Phys. Rev. Lett. **55**, 1200 (1985); D. J. Singh, *Planewaves, Pseudopotentials, and the LAPW Method* (Kluwer, Boston, 1994); P. Blaha *et al.*, Comput. Phys. Commun. **59**, 399 (1990).
8. P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964); W. Kohn and L. J. Sham, *ibid.* **140**, A1133 (1965).
9. N. E. Christensen, Phys. Rev. B **30**, 5753 (1984); S.-H. Wei and A. Zunger, Phys. Rev. B **57**, 8983 (1998).
10. S.-H. Wei *et al.* Phys. Rev. B **67**, 165209 (2003).
11. S.-H. Wei and P. Carrier, submitted to J. Appl. Phys. (2004).
12. S.-H. Wei and A. Zunger, Phys. Rev. B **60**, 5404 (1999).
13. T. S. Moss, Proc. Phys. Soc. London B **67**, 775 (1954); E. Burstein, Phys. Rev. **93**, 632 (1954).
14. J. Wu *et al.*, Phys. Rev. B **66**, 201403 (2002).