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First-principles study of cubic $B_xIn_{1-x}N$ alloys

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Abstract

The first ab-initio calculations were carried out for the electronic and structural properties of BInN boron ternary alloys. The full potential linearized augmented plane wave (FP-LAPW) method was employed within density functional theory (DFT). We have investigated the lattice parameters and band gap energies. The lattice constant a exhibits a small downward bowing. The calculated band gap variation gives a small bowing in good agreement with the experimental reports. We notice a direct to indirect band gap crossover at $x = 0.83$.

Key Words: Lattice parameter, bulk modulus, pressure derivative and band gap, FP-LAPW, WIEN (2k) code.

1. Introduction

The III-nitride semiconductor has received much attention in the past few years since they have important applications in light emitting diodes (LEDs) and short wavelength laser diodes (LD), due mainly to their relatively wide band gap corresponding to the visible region to the near ultraviolet region of the spectrum and high emission efficiency. In addition, bright blue LEDs based on III-nitride semiconductors have already paved the way for full-color displays and for mixing three primary colors to obtain white light for illumination [1]. As well as, the hardness and large bulk modulus make them ideal protective coating materials. It is well-known that the binary zinc blend BN is an indirect band-gap alloy and the binary zinc blend InN is a direct band-gap alloy. Therefore, the ternary zinc blend BInN alloy with an increase of the aluminum composition exhibits a crossover point where the direct-to-indirect band-gap transition occurs. It is an interesting and important topic to define the crossover point. The emitting wavelength is dependent on the band gap energy of material, and the band gap bowing parameter is important for calculating the band gap energy of III-nitride ternary material.

The objective of this work is to investigate the electronic and structural properties of ternary zinc blend BInN alloy by using first-principles calculations. The method is based on the FP-LAPW based density functional

theory (DFT) in the local density approximation (LDA). The electronic properties, including the band gap energy obtained from band structure, the band gap bowing, and the crossover point of the direct-to-indirect band-gap transition, will be discussed. Furthermore, the structural properties, such as the equilibrium lattice constant, total energy, bulk modulus, and the pressure derivative of bulk modulus, will be calculated.

2. Computational method

Total energy calculations are performed using the full potential linearized augmented plane wave (FP-LAPW). In this method, the unit cell is partitioned into non-overlapping muffin-tin spheres around the atomic sites, and an interstitial region. Among these two types of regions different basis sets are used: the Kohn-Sham equation which is based on the density functional theory (DFT) [2–3] is solved in a self consistent scheme.

For the exchange-correlation potential we use the local density approximation (LDA) [4–5] In the following calculations, we distinguish the B ($1s^2$), In ($1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $4s^2$ $4p^6$ $3d^{10}$) and N ($1s^2$) inner-shell electrons from the valence electrons of B ($2\ s^2 2p^1$), In ($4d^{10} 5s^2\ 5p^1$) and N ($2s^2\ 2p^3$) shells. For these calculations the existing WIEN2k code [6] is used and applied to large unit cells.

The muffin-tin radii adopted were 1.45 Å (B), 1.99 (In) and 1.7 5 Å (N). In the following, we use the full-potential LAPW (FPLAPW) method to study the electronic properties under pressure for the binaries zinc blend, BN and InN. The maximum l value for the wave function expansion inside the atomic spheres was confined to l_{max}=10. In order to achieve energy eigenvalues convergence, the wave functions in the interstitial region are expanded in plane waves with a cutoff of $R_{MT} * K_{max} = 8$ (where is $K_{max} = 10$ the maximum modulus for the reciprocal lattice vector, and R_{MT} is the average radius of the MT spheres). The k integration over the Brillouin zone is performed using Monkhorst and Pack [7] mesh, yielding to 73 k points in the irreducible wedge of the Brillouin zone for both zinc blend structures. The iteration process is repeated until the calculated total energy of the crystal converges to less than 0.1 mRy.

3. Result and discussion

To model the ternary zinc blend $B_x In_{1-x}$ N alloys, we employ an 8-atom $B_n In_{4-n}$ N_4 super cell with periodic boundary conditions. Once the ratio between the B and In atoms is specified, the geometrical arrangement of B-In atoms is determined by translation of primitive vector of the primitive cell. The configuration utilized in this specific study is a fixed atomic configuration and the statistics and configuration average have not been taken into account. The minimization of the total energy with respect to the lattice constant in the ground state is performed for $n = 0$ to 4, which represents the boron composition x of 0, 0.25, 0.5, 0.75 and 1. Figure 1 shows the equilibrium lattice constant relation to the boron composition x. By fitting the results shown in Figure 1 with a quadratic equation of the boron composition x, the coefficient of x^2 is -0.014. It indicates that lattice constant of zinc blend $B_x In_{1-x} N$ exhibits a small deviation from the linear Vegard's law. In addition, the lattice constant of BN obtained by our calculation is 3.585 Å, which is in agreement with the experimental result of 3.615 Å [8–10]. It is worth noting that the lattice constants of both InN and BN obtained in this study are smaller than the experimental ones. The lattice constant is underestimated as a result of the over binding effect from LDA method. Underestimation of the band gap energy but accurate estimation of the

valence band is a well-known consequence of using LDA calculations. To amend these band gap energies, the results are calculated using scissors operator with a rigid upward shift of the conduction band with respect to the valence band from the known band gap energy of InN (0.9 eV) [11] and BN (9.09 eV) [12], as shown in Table 1.

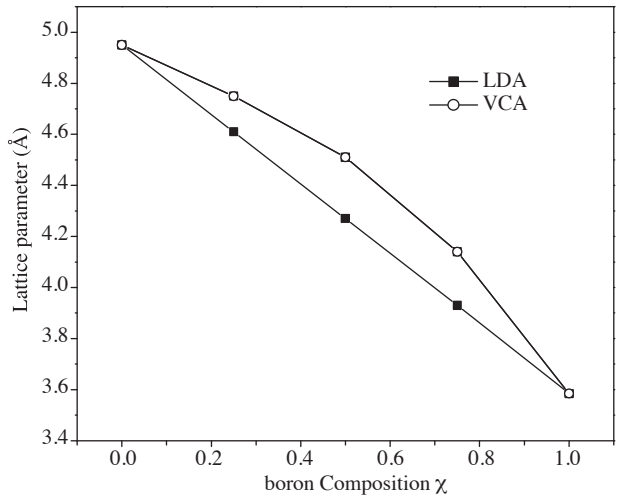

Figure 1. Lattice constant of $B_x In_{1-x} N$ as a function of boron composition x.

Table 1. Direct $\Gamma - \Gamma$ and indirect Γ-X band gaps of BN and InN and their alloys at equilibrium volume (all energies are in eV).

	$E_{\Gamma\Gamma}$ (eV)	$E_{\Gamma X}$ (eV)
InN		
Our.cal (LDA)	0.0	5.16
Other. Cal	0.7[13]	
Experiment	0.9[11]	
$B_{0.25}In_{0.75}N$		
Our.cal (LDA)	0.16	4.52
$B_{0.5}In_{0.5}N$		
Our.cal (LDA)	1.1	5.37
$B_{0.75}In_{0.25}N$		
Our.cal (LDA)	3.15	5.4
BN		
Our.cal (LDA)	8.81	4.44
Other. Cal	8.6 [12] 9.09 [12]	4.24[12]

The difference between the corrected and LDA energies of the ternary alloys is obtained from the linear combination of the differences of the InN and BN. The band gap energy of the zinc blend $B_x In_{1-x} N$ obtained with the equilibrium lattice constant is plotted in Figure 2. The band gap energy of $B_x In_{1-x} N$ can be depicted as a function of the boron composition x, and be expressed using the following formula:

$$Eg(x) = xE_{g,BN} + (1-x)E_{g,InN} - bx(1-x), \tag{1}$$

where $E_g(x)$ denotes the band gap energy of $B_xIn_{1-x}N$; $E_{g,BN}$ and $E_{g,InN}$ denote the band gap energy of BN and InN, respectively; and b is the band gap bowing parameter of B_xIn_{1-x} N. By fitting the results shown in Figure 2 with equation (1), the direct (Γ–Γ) bowing parameter of 13.84 eV and indirect (Γ–X) bowing parameter of -2.16 eV are obtained. There is a direct–indirect crossover at $x = 0.83$ for which the band gap energy is 5.07 eV. Some researchers are devoted to the study of both the bowing parameter and the crossover point of B_xIn_{1-x} N by theoretical calculations, but there are no experimental results available for the zinc blend structure. However, the results obtained by different researchers are quite diverging. For the direct bowing parameter the results are 11.18 eV [14]. Few studies about the indirect bowing parameter the available results are 6.736 eV [14]. For the direct–indirect crossover point the results are 0.35[14]. The physical origin of the band gap bowing can be attributed to the lattice mismatch between BN and InN. The larger lattice mismatch between the two binary alloys will result in the larger bowing. Qualitatively, the band gap bowing is larger for B_xIn_{1-x} N. The discrepancy of the bowing among the reports in the literature may be due to the partial ordering of alloy structures and the bond-length relaxation effect in the alloy crystal structures. The smaller lattice constant of BN in this study causes the larger lattice mismatch between BN and InN. Therefore, the larger bowing parameter is expected.

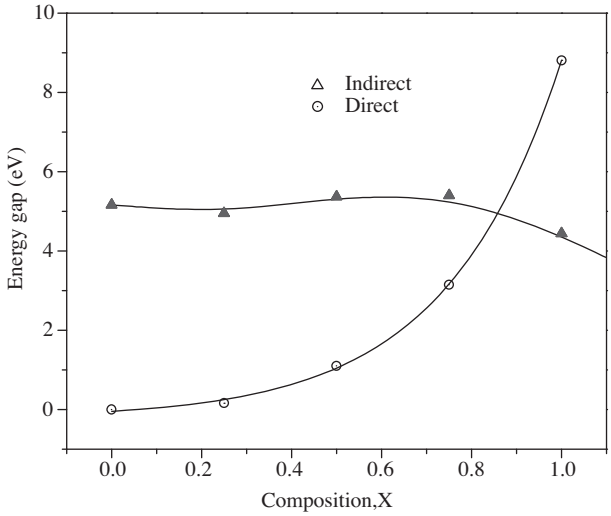

Figure 2. Band gap energy of $B_xIn_{1-x}N$ as a function of boron composition x.

For the calculation of bulk modulus of zinc blend $B_xIn_{1-x}N$, geometry optimizations are performed with the lattice constant fixed by a full relaxation of the internal coordinates. A more rigorous way to calculate this quantity would be to plot total energy versus cell volume for a variety of cell volumes and to fit a curve to this plot. The bulk modulus can then be calculated from the Murnaghan equation of state [15], and its third-order expansion of volume applied in this study is expressed as

$$E(V) - E(V_0) = \frac{B_0 \cdot V}{B_0'}\left[\frac{(V_0/V)^{B_0'}}{B_0' - 1} + 1\right] - \frac{B_0 V}{B_0' - 1}, \tag{2}$$

where E is the total energy at cell volume V, E_0 is the total energy at equilibrium volume V_0, B_0 is bulk modulus, and B_0' is the pressure derivative of the bulk modulus. The total energy of zinc blend $B_xIn_{1-x}N$ as a function of volume ratio V/V_0 for specific cases of $x = 0$, 0.5 and 1 is shown in Figures 3(a–c). By fitting the results shown in Figures 3(a–c) with equation (2), we obtain the bulk modulus and their pressure derivatives of zinc blend $B_xIn_{1-x}N$ as shown in Table 2, where the results of and $B_{0.75}In_{0.25}N$ are also included. For comparison, some results of binaries BN and InN reported in the literature are also shown in Table 2. For BN, $B_0 = 404$ GPa and $B_0' = 3.71$ obtained in this study are in good agreement with $B_0 = 386$ GPa and $B_0' = 3.6$ reported in [16–17]. The value is also in close agreement with the results of 397 GPa reported in [16] and 366 GPa reported in [17]. The larger bulk modulus obtained is due to the smaller lattice constant of BN obtained in this study.

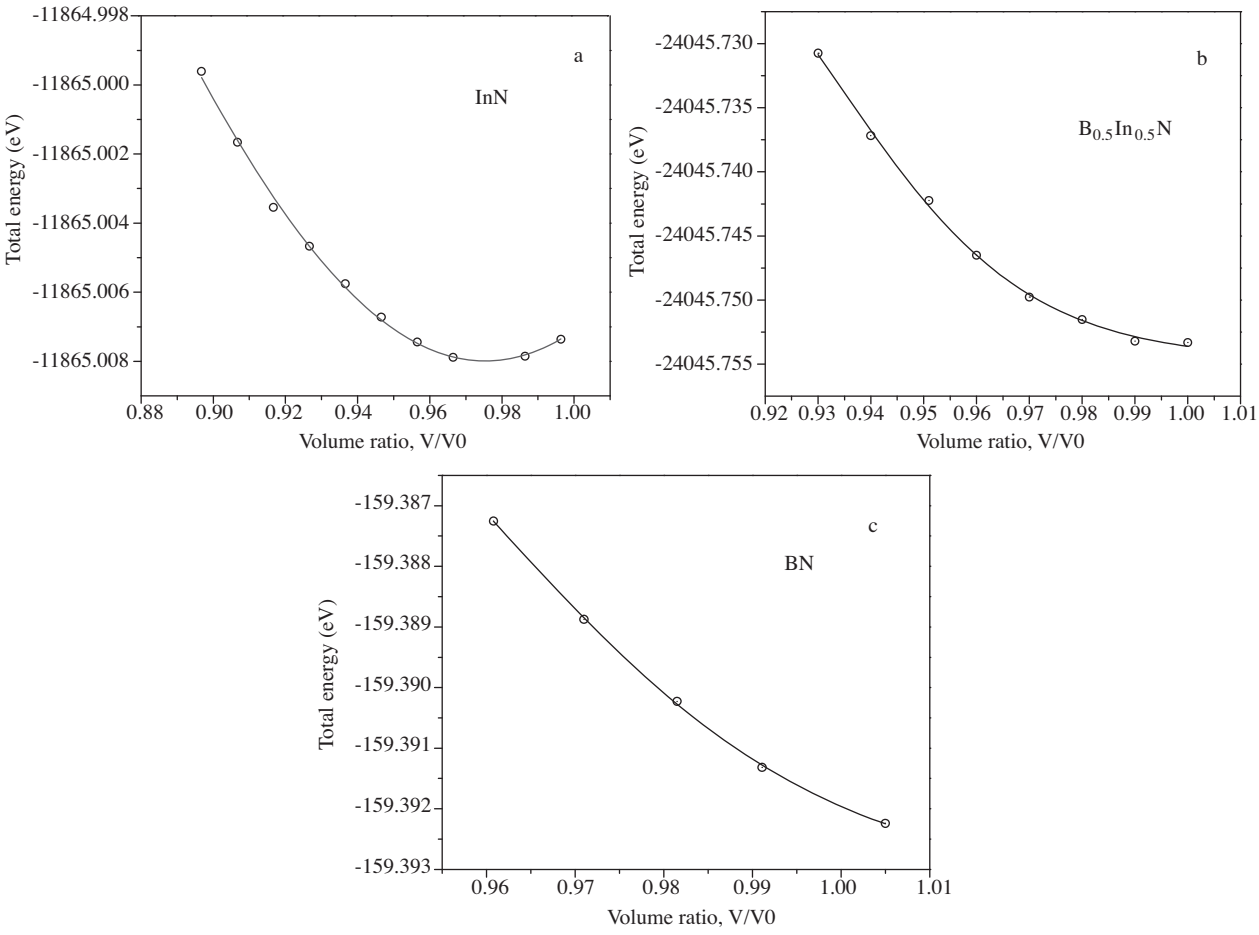

Figure 3. Total energy as a function of volume ratio. The line represents the fit of theoretical data to a third-order Murnaghan equation of state: (a) InN, (b) $B_{0.5}In_{0.5}N$, and (c) BN.

In addition, the bulk modulus of zinc blend $B_xIn_{1-x}N$ increases with boron composition x. This is because B–N is more tightly bound than In–N and results in a higher covalence for B–N than for In–N. On the contrary, B_0' monotonically decreased with increase in boron composition x. For InN, the $B_0 = 155$ GPa

and $B_0' = 3.76$ obtained in this study is smaller than 386 GPa reported in [18]. This is because the lattice constant of 4.7885 Å for InN, reported in [18], is smaller than that of 4.980 Å observed in this study. Moreover, the bulk modulus of as a function $B_x In_{1-x} N$ of the boron composition x are plotted in Figure 4. To proceed further into analysis of the amount of deviation from the linear relation between the bulk modulus and the boron composition x, the curve shown in Figure 5 can be approximated by the formula

$$B(x) = xB_{BN} + (1-x)B_{InN} - B_\delta x(1-x), \tag{3}$$

Table 2. The calculated lattice parameter a, bulk modulus B and its pressure derivatives $B\prime$ for $B_x In_{1-x}$ N and its binary compounds. Available experimental and theoretical data are also given for comparison.

	a(Å)	B (GPa)	B'
InN			
Our.cal (LDA)	4.94	155	3.76
Other calc	4.92 [19] 5.004[20]	139[19] 140 [20]	4.4[19] 4.38[20]
	4.947 [21] 4.968[22]	144[21] 147 [22]	4.561[21]
Experiment	4.986 [23]	137[24]	4.4 [22]
$B_{0.25}In_{0.75}N$			
Our.cal (LDA)	4.75	166	4.24
$B_{0.5}In_{0.5}N$			
Our.cal (LDA)	4.51	201	3.61
$B_{0.75}In_{0.25}N$			
Our.cal (LDA)	4.14	255	3.88
BN			
Our.cal (LDA)	3.585	404	3.71
Other calc	3.575 [16] 3.576 [16]	386 [16] 397[16]	3.6 [17] 2.91[18]
	3.649 [18]	366 [18]	3.94 [18]
Experiment	3.615[8][9][10]	369 [8]	4 [8]

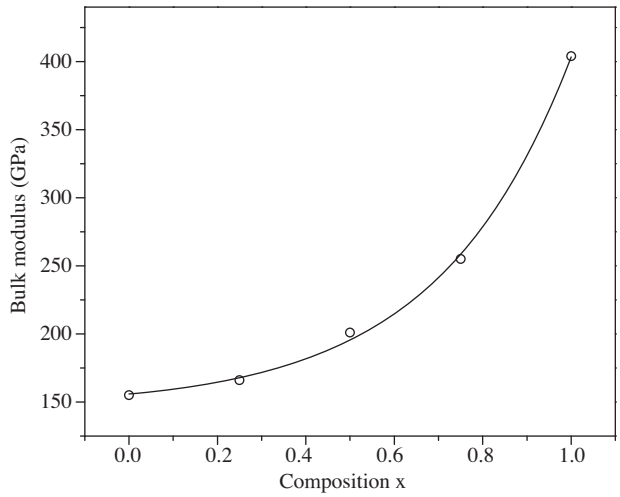

Figure 4. Bulk modulus of $B_x In_{1-x} N$ as a function of boron composition x.

where B_{BN} and B_{InN} denote the bulk modulus of BN and InN, respectively; and B_δ is the deviation parameter of bulk modulus for zinc blend. If we best fit the results shown in Figure 4 with equation (3), $B_\delta = 337.14$ GPa is obtained. This indicates that the bulk modulus of ternary zinc blend is s $B_x In_{1-x} N$ smaller than that obtained from a linear combination of the bulk modulus of binary BN and InN.

4. Conclusion

Numerical analysis based on first-principles calculations is utilized to investigate the electronic and structural properties of zinc blend $B_x In_{1-x} N$. From the calculated results, it is found that the lattice constant in $B_x In_{1-x} N$ the ground state has a small deviation from the linear Vegard's law. The deviation parameter that is the second order coefficient of the quadratic equation of Boron composition is 0.24 Å. The direct bowing parameter of 13.84 eV and indirect bowing parameter of -2.16 eV are obtained. There is a direct-indirect crossover near $x = 0.83$ for which the band gap energy is 5.07 eV. In addition, the bulk modulus of zinc blend $B_x In_{1-x} N$ monotonically increased with increase of composition x. The bulk modulus of 155 GPa for InN increases to that of 404 GPa for BN, and the deviation parameter of bulk modulus for zinc blend is 337.14 GPa $B_x In_{1-x} N$.

However, the pressure derivative of the bulk modulus monotonically decreased with increase of Boron composition x, decreasing from 3.76 for InN to 3.71 for BN.

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