Empirical pseudo potential method for the energy gaps and optical properties of XN (X = Al, Ga, B) and their alloys materials Journal of Physics: Conference Series

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Abstract. The pseudo potential method associated with the improved virtual crystal approximation (VCA) is used to calculate symmetric and anti-symmetric form factors for BN, AlN, GaN and to predict the electronic band structure of the zinc-blende B_{x}Al_{y}Ga_{1-x-y}N alloys lattice matched to AlN. The optical properties of these alloys are calculated. The range of compositions for which the alloys are lattice-matched to AlN substrate is determined. We find that the addition of boron to the AlGaN alloys decreases the direct gap (E_{\Gamma}) and a direct to indirect transition occurs at a Al concentration of about 0.5 (y = 0.5), which corresponds to a band gap energy of about 4.75 eV.

1. Introduction

The III-nitride semiconductor, AlN, GaN, and their alloys have wide direct band gaps, which vary from 3.3 eV for GaN to 6 eV for AlN and are indispensable for the development of optoelectronic and electronic devices. Their alloys have been exploited to develop the high-power microwave transistors and the deep ultraviolet (DUV) optical devices operating at wavelength in the range of (344nm - 200nm), including light-emitting diodes and laser diodes ranging from the visible spectrum [1-4], optically pumped lasers, and photo detectors [5-8]. BN, on the other hand, has features of high thermal conductivity suitable for applications in electronics devices [9]. All these materials also have potential for high-temperature, high-power, and high-frequency electronic devices, due to their wide band gaps [10]. The (BAIGaN) quaternary system can be lattice matched to 6H–SiC and AlN substrates [11], whereas the band-gap energy (Eg) of the BAIGaN lattice matched to AlN and 6H–SiC substrates respectively is in the range of (3.6 eV–6.2 eV) and (3.8 eV– 6.2 eV) [12].
Some groups have studied the BaIGaN system. Takano et al. [13] have used Low-Pressure Metal-Organic Vapor-Phase Epitaxy (LP-MOVPE) to grow (BaIGaN) and (BaIGaN/AlN) where triethylboron (TEB), trimethylaluminium (TMAI), trimethylgallium (TMGa) and ammonia (NH3) were used as the source materials for boron, aluminium, gallium and nitrogen, respectively, and used Auger electron spectroscopy (AES) and X-ray diffraction (XRD) to determine the compositions of BxAlyGa1-x-yN. Here the boron composition was found to increase from 1% to 13%. Djoudi et al [14] have used the Full potential linearized augmented plane wave (FP-LAPW) to study the structural and electronic properties of the quaternary BxAlyGa1-x-yN, lattice matched to AlN substrate. Djoudi et al reported that B compositions in a BxAlyGa1-x-yN/AlN vary in a range of 0% to 14.2% and the band gaps are, on the whole, underestimated by about 51% to 56% compared with experimental data [14, 15]. In order to understand and control the materials and device properties, we have carried out another theoretical study of the energy band gaps and optical properties of the quaternary BxAlyGa1-x-yN, lattice matched to AlN substrate. We use the empirical pseudo potential method (EPM) within the virtual crystal approximation (VCA) to calculate the electronic structure of the quaternary alloy system. The empirical pseudo potential method (EPM) was developed in the 1960’s [16-18] as a way to solve Schrödinger’s equation for bulk crystals without knowing exactly the potential experienced by an electron in the lattice. The EPM has been one of the most popular methods to calculate the full band structure for device simulation. In this study, we considered the zinc-blend polytype as a model system. Calculations are performed over the entire composition range of x and y.

The plan of the present paper is as follows: a description of the method as well as some details of the calculations in section 2. In Section 3, the energy band gaps and optical properties of quaternary BxAlyGa1-x-yN matched to AlN substrate are presented and discussed. Conclusion of the present study will be given in section 4.

2. Calculation Method

The electronic structure of the quaternary BxAlyGa1-x-yN, lattice matched to AlN substrate is calculated using the empirical pseudo potential method (EPM) within the virtual crystal approximation (VCA). The fundamental concept involved in a pseudo-potential calculation is that the ion core can be omitted. Computationally this is crucial for it means that the deep core potential has been removed and a simple plane wave basis will yield rapid convergence [19]. The main advantage of using pseudopotentials is that only valence electrons have to be considered. The core electrons are treated as if they are frozen in an atomic-like configuration. As a result, the valence electrons are thought to move in a weak one-electron potential. The pseudopotential method is based on the orthogonalized plane wave (OPW) method due to Herring [20]. In this method, the crystal wave function is constructed to be orthogonal to the core states. Here the pseudo potentials is based by a set of atomic form factors V(G) (G is a reciprocal lattice vector). The form factors are treated as adjustable parameters that can be fit to experimental data, hence the name empirical pseudopotential method. Another advantage of the empirical pseudopotential method is that only six form factors are needed to describe the band structure, where the prefactors are referred to as the symmetric (Vs(3), Vs(8) and Vs(11)) and antisymmetric (Vs(3), Vs(4) and Vs(11)) structure factors. More details about the approach has been described in Ref. [19, 21, 22]. The band gap energies, lattice constants and form factors (symmetric (Vs) and antisymmetric (Vs)) for BN, AlN and GaN compounds are shown in Table 1 and Table 2, respectively. Generally, the experimental values used in the study are selected among the more recent measured band gap energies. When the experimental data are not available, we have taken instead of them the existing theoretical data in the literature.
Table 1. Band gaps of the zinc-blende structure, for BN, AlN and GaN used in the calculation.

|          | BN [23] | AlN[24] | GaN[25] |
|----------|---------|---------|---------|
| $E_g (\Gamma-\Gamma) \ (eV)$ | 9.09    | 6       | 3.3     |
| $E_g (\Gamma-X) \ (eV)$     | 4.24    | 4.9     | 4.57    |
| $E_g (\Gamma-L) \ (eV)$     | 8.10    | 9.3     | 6.04    |

Table 2. Symmetric ($V_S(G)$) and antisymmetric ($V_A(G)$) pseudopotential form factors and lattice constants ($a$) used in the calculation for BN, AlN and GaN alloys.

| Materials | $a$ (a.u.) | $V_S(3)$ | $V_S(8)$ | $V_S(11)$ | $V_A(3)$ | $V_A(4)$ | $V_A(11)$ |
|-----------|------------|----------|----------|-----------|----------|----------|-----------|
| BN [26]   | 6.8241     | -0.755   | 0.182    | 0.133     | 0.1755   | 0.1250   | 0.0251    |
| AlN [24]  | 8.26087    | -0.309603| 0.112783 | 0.067538  | 0.28     | 0.33     | 0.015     |
| GaN [25]  | 8.50662    | -0.347240| -0.016   | 0.21217   | 0.159988 | 0.2      | 0.135     |

3. Results and Discussions

3.1 Matching conditions

As starting point we have computed the lattice matching conditions for the $B_xA_l_{1-x}G_{1-y}N$ quaternary system on an AlN substrate. The lattice matching found is: $x = 0.146(1-y)$, for which Vegard’s rule has been assumed to calculate the lattice constant of the quaternary alloy under study.

$$a(x, y) = xa_{BN} + ya_{AlN} + (1-x-y)a_{GaN}$$  \hspace{1cm} (1)

Where $a(x, y)$, $a_{BN}$, $a_{AlN}$ and $a_{GaN}$ are the respective lattice constants of BAlGaN, BN, AlN and GaN. The composition range for which the lattice constants of $B_xA_l_{1-x}G_{1-y}N$ alloys are lattice matched to an AlN substrate is represented by the solid line in Figure 1. The calculated lattice matched of $B_xA_l_{1-x}G_{1-y}N$/AlN alloys is in good agreement with available experimental results [13]. Here the lattice mismatch of the material under study is given by: $(a_{BAlGaN} - a_{AlN}) / a_{AlN}$. In Table 3, we summarize the lattice mismatch for the $B_xA_l_{1-x}G_{1-y}N$ alloys for different B and Al compositions. The results clearly show that the lattice mismatch decreases when boron is incorporated with the small amounts.
Figure 1. Solid composition of boron versus solid composition of aluminium in the B₀.₃₆₆₄Ga₀.₆₄N quaternary system (14.69% boron is the maximum composition in the BAI GaN quaternary system lattice matched to AlN).

Table 3. Lattice mismatch for the BₓAlₓGa₁₋ₓ₋ₙN alloys for different B and Al compositions.

| Materials       | Lattice mismatch to AlN (%) |
|-----------------|----------------------------|
| B₀.₃₆₆₄Ga₀.₆₄N | 3.314                      |
| B₀.₀₃₆₆₄Ga₀.₉₁N | 2.185                      |
| B₀.₀₃₆₆₄Ga₀.₈₇₅N| 2.066                      |
| B₀.₀₆₆₆₄Ga₀.₇₄₅N| 1.158                      |

3.2 Form factors and Band gap energies

In the next step, we have computed the form factors of the BN, AlN, GaN and BₓAlₓGa₁₋ₓ₋ₙN alloys lattice matched to AlN. Therefore Vegard's rule has been assumed to calculate the form factors for quaternary BₓAlₓGa₁₋ₓ₋ₙN, so the form factors for quaternary BₓAlₓGa₁₋ₓ₋ₙN alloy are obtained as:

\[ F_{\text{Alloy}} = x F_{\text{BN}}(G) + y F_{\text{AlN}}(G) + z F_{\text{GaN}}(G) \]  

Where G is the reciprocal lattice vector, and \( F_{\text{BN}} \), \( F_{\text{AlN}} \), and \( F_{\text{GaN}} \) are the form factors for AlN, GaN and BN, respectively. Table 4 present the results found for the form factors for AlN, GaN, B₀.₆₆₆₄Ga₀.₉₁N, B₀.₀₆₆₄Ga₀.₈₇₅N and B₀.₀₆₆₄Ga₀.₇₄₅N. In Table 5, we summarize the Band gaps of the zinc-blende structure, for BN, AlN and GaN alloys found in the calculation.
A good knowledge of electronic band structure in semiconductors provides valuable information regarding their potential utility in fabricating electronic and optoelectronic devices. In this context we have calculated the electronic band structure properties of B\textsubscript{x}A\textsubscript{y}Ga\textsubscript{1-x-y}N alloys lattice matched to AlN in the zinc-blende structure at this equilibrium lattice constants using the pseudo potential method associated with the improved virtual crystal approximation. The energy variation of the conduction band edges at Γ, X and L with respect to the top of the valence band are obtained as a function of aluminium composition. The obtained direct and indirect band-gaps are presented and plotted in figure 2. The results shows the dependence of direct gap energy \(E_{\Gamma\Gamma}\) and indirect gap energies \(E_{\Gamma X}\) and \(E_{\Gamma L}\) for B\textsubscript{x}A\textsubscript{y}Ga\textsubscript{1-x-y}N/AlN, on the aluminium content, where the energy band gaps \(E_{\Gamma\Gamma}\) and \(E_{\Gamma L}\) increase monotonically with increasing the composition (y), but for the indirect gap energy \(E_{\Gamma X}\) varies non-monotonically with increasing the aluminium content. A direct to indirect transition occurs at an aluminium concentration of about 0.5 (y = 0.5), which corresponds to a band gap energy in the order of 4.75 eV. Above this concentration (y > 0.5), the alloy becomes an indirect gap semiconductor. The curves of figures obey the following variations:

\[
\begin{align*}
E_{\Gamma\Gamma}(eV) & = 4.002227 + 1.27108y + 0.74056y^2 \\
E_{\Gamma X}(eV) & = 5.12018 - 1.03021y + 0.811667y^2 \\
E_{\Gamma L}(eV) & = 6.50422 + 2.0324y + 0.7824y^2
\end{align*}
\]

These expressions may be useful for obtaining the direct and indirect band gaps for any y concentration in B\textsubscript{x}A\textsubscript{y}Ga\textsubscript{1-x-y}N alloy lattice matched to AlN. We see that the three equations are characterized by bowing parameter, for the first equation (3) the coefficient of \(y^2\) is 0.74056 eV and for the second equation (4) is 0.811667 eV and for the last equation (5) is 0.7824 eV. This indicates that the direct gap and indirect gaps of zinc-blende B\textsubscript{x}A\textsubscript{y}Ga\textsubscript{1-x-y}N/AlN has a very large deviation from the linear Vegard’s law.
In Table 6, we have listed the fundamental band gaps ($E_0$), at the high-symmetry point $\Gamma$ in the Brillouin zone, for the systems investigated and compared the results with available experimental data. The results clearly show that the band gaps are, on the whole, underestimated by about 11% to 17% compared with experimental data. We note that this method gives good results in comparison with other calculation method based on DFT [14, 15, 27].

### Table 6. Band gaps of the zinc-blende structure, for $B_{0.03}Al_{0.06}Ga_{0.91}N$, $B_{0.03}Al_{0.10}Ga_{0.87}N$ and $B_{0.06}Al_{0.20}Ga_{0.74}N$

| Material                  | $E_g (\Gamma-\Gamma)$ (eV) | Present calculations | Exp. [13] |
|---------------------------|-----------------------------|----------------------|-----------|
| $B_{0.03}Al_{0.06}Ga_{0.91}N$ | 4.081                       |                      | 4.92      |
| $B_{0.03}Al_{0.10}Ga_{0.87}N$ | 4.137                       |                      | 4.73      |
| $B_{0.06}Al_{0.20}Ga_{0.74}N$ | 4.286                       |                      | 4.84      |

### 3.3 Optical properties

In the last step, we have calculated the optical properties of $B_xAl_yGa_{1-x-y}N$. To really understand the optic properties of the semiconductors, it was necessary to know the electronic structure of these materials. The refractive index ($n$) for $B_xAl_yGa_{1-x-y}N$ has been calculated using the empirical expression proposed by Herve and Vandamme [28], the optical high frequency dielectric constant it is the square of a the refractive index of the material of interest and the static dielectric constant has been calculated using the empirical expression proposed by Harrison model [29]. We summarize in the
Table 7. Models used to calculate the refractive index (n), the optical high frequency dielectric constant and the static dielectric constant.

| Models | Observation |
|--------|-------------|
| $n = \sqrt{1 + \left(\frac{A}{E_g + B}\right)^2}$ | Eg is the fundamental energy band-gap and $A$ and $B$ are constants with values of 13.6 and 3.4 eV, respectively. [30,31] |
| $\varepsilon_m = n^2$ | Harrison model. [29] |
| $s_0 - 1 = 1 + \nu$ | $\alpha_p$ is the polarity and $\alpha_c$ is the covalency of the material |
| $v = \frac{2\alpha^2}{V_r(3)}$ | $\alpha_p$ is the polarity proposed by Vogl [32] and $V_S(3)$ and $V_A(3)$ are the symmetric and antisymmetric pseudo potential form factors. |
| $\alpha_p = -\frac{V_r(3)}{V_A(3)}$ |
| $\alpha_c^2 = 1 - \alpha_p^2$ |

The variations of the refractive index, the high frequency dielectric constants and the static dielectric constant as a function of alloy composition are plotted in Figure 3. It is clearly seen that the static dielectric constant decreases rapidly, the high frequency dielectric constant decreases slowly and the refractive index decreases very slowly as a function of Al concentration, respectively. The curves of figures obey the following variations:

$$n = 2.0985 - 0.33809y$$  \hspace{1cm} (6)
$$\varepsilon_m = 4.38545 - 1.30255y$$  \hspace{1cm} (7)
$$s_0 = 7.42191 - 3.11473y$$  \hspace{1cm} (8)

These expressions may be useful for obtaining the refractive index, the high frequency dielectric constants and the static dielectric constant for any $y$ concentration in B$_x$Al$_y$Ga$_{1-x}$N alloy lattice matched to AlN. We see that the three equations are characterized by negative slope parameter, for the first equation (6) the coefficient of $y$ is $-0.33809$ and for the second equation (7) is $-1.30255$ and for the last equation (8) is $-3.11473$. This indicates that the refractive index, the high frequency dielectric constants and the static dielectric constant of zinc-blende B$_x$Al$_y$Ga$_{1-x}$N/AlN decreases as a function of Al concentration.

Table 8. Values of the refractive index, the static dielectric constant and the high frequency dielectric constant for different values of the Al concentration.
Aluminium (y) concentration | Refractive index | High frequency dielectric constant | Static dielectric constant |
--- | --- | --- | --- |
0 | 2.089 | 4.364 | 7.435 |
0.1 | 2.064 | 4.259 | 7.147 |
0.2 | 2.034 | 4.137 | 6.807 |
0.3 | 2.002 | 4.008 | 6.487 |
0.4 | 1.968 | 3.874 | 6.164 |
0.5 | 1.933 | 3.737 | 5.842 |
0.6 | 1.897 | 3.597 | 5.503 |
0.7 | 1.861 | 3.463 | 5.202 |
0.8 | 1.826 | 3.335 | 4.917 |
0.9 | 1.791 | 3.209 | 4.628 |
1.0 | 1.759 | 3.093 | 4.378 |

Figure 3. Variations of refractive index, the high frequency dielectric constants and the static dielectric constant as a function of alloy composition for various aluminium concentrations.

4. Conclusion

The pseudo potential method (EPM) associated with the improved virtual crystal approximation (VCA) is utilized to investigate the symmetric and anti-symmetric form factors and energies band gaps for BN, AlN, GaN and B_{x}Al_{y}Ga_{1-x-y}N alloys lattice matched to AlN and the optical properties of this material. From the calculated results, it is found that the band gaps of the zinc-blende structure of each binary (BN, AlN and GaN) is in reasonable agreement with the experimental values, and for zinc-blende B_{x}Al_{y}Ga_{1-x-y}N alloys lattice matched to AlN the band gaps are, on the whole, underestimated by about 11% to 17% compared with experimental data. The absorption at the optical gaps suggested that a transition from an direct to indirect band gap may occur in B_{x}Al_{y}Ga_{1-x-y}N alloys lattice matched to AlN at y equal 0.5. Therefore for this material to be useful in optical applications it is necessary to keep the concentration for Aluminium less than 50%. The calculated band-gap energy of B_{x}Al_{y}Ga_{1-x-y}N...
N alloys lattice matched to AlN is in the range of 4 eV to 4.3 eV, corresponding to the wavelength range of 310 nm to 288 nm. Therefore, the BAlGaN system is a promising material for use in semiconductor lasers that operate in the ultraviolet (UV) spectral region. Our findings indicate that the refractive index, the high frequency dielectric constants and the static dielectric constant of zinc-blende BxAlyGa1-x-yN/AlN decreases as a function of Al concentration. Finally our results are predictions and may serve as reference for future experimental work.

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