Band Anti-Crossing Modelling on Tailored Ga$_{1-x}$In$_x$N$_y$As$_{1-y}$ Band Gap Energy Based Nitrogen Fraction

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Abstract This paper deals with a Band Anti-Crossing (BAC) modelling to investigate the tailoring of band gap energy of Ga$_{1-x}$In$_x$N$_y$As$_{1-y}$ alloy based on nitrogen fractions. Three different numerical methods have been adopted to estimate the extended state of conduction band ($E_M$) parameters. The first two methods used Vegard’s law and Varshni’s equation to estimate $E_M$ by considering Ga$_{1-x}$In$_x$As ternary alloy as ternary alloy based on temperature dependence, with values of bowing parameter of 0.475 and 0.477, respectively. The third method used excitonic band gap theory for Ga$_{1-x}$In$_x$As alloy temperature dependence by considering Passler fitting ($p$) and average phonon temperature ($\theta$). Results depict that optimum nitrogen fraction was in the range of 0.012 to 0.018% to achieve the device response at 1.3 μm wavelength, with an energy band gap in range of 0.955 ± 0.005 eV. Future work shows a potential study on influence of indium fractions in tailored energy band gap of Ga$_{1-x}$In$_x$N$_y$As$_{1-y}$ alloy and compressive strain of material.

Keywords Band Anti-Crossing, Dilute Nitride, Gallium Arsenide, Ga$_{1-x}$In$_x$N$_y$As$_{1-y}$ Alloy, Band Gap, 1.3 μm Wavelength

1. Introduction

Modern Ga$_{1-x}$In$_x$N$_y$As$_{1-y}$ semiconductor devices outperform silicon and germanium based on electronics due to their ability to operate at longer wavelengths and direct band gap properties [1]. Ga$_{1-x}$In$_x$N$_y$As$_{1-y}$/GaAs offers a much larger conduction band offset due to decreased curvature of the new conduction band in dilute nitrides [2]. Therefore, Ga$_{1-x}$In$_x$N$_y$As$_{1-y}$ can provide better confinement carriers in quantized sub-bands. They also make a better match of the valence and conduction band densities of states with consequently increased electron effective mass [3]. Utilization of Ga$_{1-x}$In$_x$N$_y$As$_{1-y}$ based devices in telecommunication application in replacement a current GaInAs/InP-based device, due to their reduced temperature sensitivity and improve refractive index material [1].

An incorporation of a small amount nitrogen into Ga$_{1-x}$In$_x$N$_y$As$_{1-y}$ based device, offers the flexibility of tailoring energy band gap onto nearest 0.95 eV and lattice-match due to GaAs substrate [4]. Moreover, this addition of nitrogen affected the nonlinear pressure dependence of the band gap [5], a large redshift of the band gap [2], an increase in the electron effective mass [1] and the formation of new bands with strong line width broadened transitions [6]. Many analytical methods are used to understand the effect of nitrogen fraction in Ga$_{1-x}$In$_x$N$_y$As$_{1-y}$ alloy, such as virtual crystal approximation (VCA) and band anti-crossing (BAC) methods [4].

This study focuses on the dependence of energy band gap and operational wavelength on temperature. The BAC method has been adopted for Ga$_{1-x}$In$_x$N$_y$As$_{1-y}$ material with constant indium (In) at 0.32% and different nitrogen (N) concentrations ranging from 1.0 to 2.0% with 0.1% increments. BAC simulation method has been developed using MATLAB as a mathematical platform. There are three different numerical techniques to estimate the extended state of conduction band. The first two techniques...
use the Vegard’s law, while considering the Ga\textsubscript{1-x}In\textsubscript{x}As material as ternary alloy with different bowing parameters. The third technique uses excitonic band gap theory of Ga\textsubscript{1-x}In\textsubscript{x}As alloy on temperature dependence. All the numerical methods used the Varshni’s equation to determine the equivalent extended states in the conduction band parameter in calculating an eigenvalue of BAC method.

## 2. Materials and Methods

This is a theoretical approach method that explains the optical bowing in dilute nitride alloys. It describes a variety of experimental phenomena such as band edge energies [7], annealing effect [8], pressure dependence of band gap [5], properties of dilute nitrides and other mismatched alloys. In addition, it could be used to calculate the strength of optical transition in bulk materials and electronic states of quantum wells [3].

The BAC method of Ga\textsubscript{1-x}In\textsubscript{x}N\textsubscript{y}As\textsubscript{1-y} alloy explained the electronic structure by interaction of elongated conduction-band and localized nitrogen impurity states. This resulted in the splitting of conduction band to blue-shift transition ($E_c$) and red-shift transition ($E_v$) bands as shown in Figure 1 [2]. It occurred when the extended states in the conduction band ($E_M$) and the nitrogen localized state ($E_N$) are empowered. The approximated solution of this coupling between the two states is established from the two-state-like eigenvalue as,

$$H_{BAC(y)} = \begin{pmatrix} E_M & V_{NM} \\ V_{NM} & E_N \end{pmatrix}$$

(1)

Under the assumption of low nitrogen concentration in the group V sub-lattice sites,

$$V_{NM} = C_{NM}\sqrt{y}$$

(2)

where $C_{NM}$ is the coupling parameter based on the combination of valance bands and conduction bands of extended heavy hole (HH), light hole (LH) and spin-orbit-split-off (SO) states. The variable $y$ represents nitrogen concentration in the dilute nitride alloy [9]. The parametric values of $C_{NM}$, $E_N$ and $E_M$ are required for BAC modelling, in order to obtain energy band gap equivalent of Ga\textsubscript{1-x}In\textsubscript{x}N\textsubscript{y}As\textsubscript{1-y} alloy up to 1.3 µm wavelength. Equation (3) and (4) are widely used in BAC modelling to calculate the value of $C_{NM}$ and $E_N$ for Ga\textsubscript{1-x}In\textsubscript{x}N\textsubscript{y}As\textsubscript{1-y} alloy [2, 5].

$$C_{NM} = 2.3(1-x) + 1.9x - 4.2x(1-x)$$

(3)

$$E_N = 1.7 + 3.89y$$

(4)

where $x$ is the In fraction and $y$ is the N fraction. Meanwhile, it is crucial to determine the extended state in the conduction band ($E_M$) of Ga\textsubscript{1-x}In\textsubscript{x}As, it will be determined through the temperature dependence of Ga\textsubscript{1-x}In\textsubscript{x}As alloy. There are three different numerical methods that are used to calculate the values of $E_M$, first two methods use empirical expressions for the ternary alloy composition and temperature dependence based on Vegard’s law and Varshni’s equations respectively [8]. The third numerical (TM) method utilizes excitonic band gap dependence on temperature for Ga\textsubscript{1-x}In\textsubscript{x}As alloys [7].

$$E_{a_{1-x}b_{x-c}} = A + Bx - Cx(1-x)$$

(5)

where $A = E_{BC}$ and $B = E_{AC} + E_{DC}$ and $C$ is bowing parameter. Equation (5) can be rewritten for Ga\textsubscript{1-x}In\textsubscript{x}As as a function of gallium fraction ($g$) with equivalent 1-x and temperature (T) as follows.

$$E_{Ga_{1-x}In_xAs} = E_{InAs}(T) + [E_{GaAs}(T) + E_{InAs}(T)]g - Cg(1-g)$$

(6)

Using Varshni’s equation to obtain an empirical expression with temperature dependence condition.

$$E_g(T) = E_g(T = 0) - \frac{\alpha T^2}{T + \beta}$$

(7)

$$E_{Ga_{1-x}In_xAs}(T) = E_{InAs}(0) - \frac{\alpha_{InAs}T^2}{T + \beta_{InAs}} + \left[E_{GaAs}(0) - \frac{\alpha_{GaAs}T^2}{T + \beta_{GaAs}} - E_{InAs}(0) + \frac{\alpha_{GaAs}T^2}{T + \beta_{GaAs}}\right]g - Cg(1-g)$$

(8)

where $\alpha$ is the limiting slope of band gap shift at high temperature, $E_g(T)$ is the band gap at a finite temperature, $E_g$ is the band gap at 0°C and $\beta$ is the Deybe temperature of material. The Deybe’s temperature values of (8) are listed in Table 1.

**Table 1.** Material parameters for first and second numerical methods [10].

| Material   | $E_g(T = 0)$ eV | $\alpha$ (meV/K) | $\beta$ (K) |
|------------|-----------------|------------------|-------------|
| GaAs      | 1.52            | 5.8              | 300         |
| InAs      | 0.42            | 4.9              | 271         |
\[ E_{GaInAs}(g, T) = 0.42 + 0.625. g - \left\{ \frac{5.8}{(T+300)} \cdot 10^{-4} \cdot T^2 \cdot (g) \right\} - \left\{ \frac{4.19 \times 10^{-4}}{(T+217)} \cdot T^2 + C \cdot (1 - x)^2 \right\} \] (9)

\[ E_{GaInAs}(1 - x, T) = 0.42 + 0.625. (1 - x) - \left\{ \frac{5.8}{(T+300)} \cdot 10^{-4} \cdot T^2 \cdot (1 - x) \right\} - \left\{ \frac{4.19 \times 10^{-4}}{(T+217)} \cdot T^2 + C \cdot (1 - x)^2 \right\} \] (10)

For the first method (FM), the value of 0.475 as the bowing parameter is used in the following [9].

\[ E_{GaInAs1}(x, T) = 0.42 + 0.625. (1 - x) - \left\{ \frac{5.8}{(T+300)} \cdot 10^{-4} \cdot T^2 \cdot (1 - x) \right\} - \left\{ \frac{4.19 \times 10^{-4}}{(T+217)} \cdot T^2 + 0.475. (1 - x)^2 \right\} \] (11)

The second method (SM) used the value of 0.477 as the bowing parameter for following [5].

\[ E_{GaInAs2}(x, T) = 0.42 + 0.625. (1 - x) - \left\{ \frac{5.8}{(T+300)} \cdot 10^{-4} \cdot T^2 \cdot (1 - x) \right\} - \left\{ \frac{4.19 \times 10^{-4}}{(T+217)} \cdot T^2 + 0.477. (1 - x)^2 \right\} \] (12)

The third numerical (TM) method utilized excitonic band gap in Ga\textsubscript{1-x}In\textsubscript{x}As alloy with temperature dependence as follows.

\[ E_g(T) = E_0(T = 0) - \frac{\alpha \theta}{2} \left[ \sqrt{\left( \frac{217}{\theta} \right)^p} - 1 \right] \] (13)

where \( p \) is Passler fitting parameter and \( \theta \) is a constant that is closely related with average phonon temperature. The values of \( p \) and \( \theta \) for (13) are listed in Table 2.

| Material | \( E_g(T = 0) \) (eV) | \( \alpha_g \) (meV/K) | \( \theta \) (K) | \( p \) |
|----------|---------------------|---------------------|----------------|-----|
| GaAs     | 1.52                | 5.8                 | 230            | 2.44|
| InAs     | 0.42                | 4.9                 | 143            | 2.10|

The values of \( C_{NM} \), \( E_N \) and \( E_M \) parameters have been calculated to solve the eigenvalue for (1), in order to predict the splitting of conduction band into two sub-bands, which are the upper \( E_u \), sub-band and lower \( E_s \) sub-band as the following [11].

\[ E_{\pm} = \frac{1}{2} \left\{ [E_M \pm E_N] \pm \sqrt{[E_M \pm E_N]^2 + 4V_{NM}^2} \right\} \] (14)

### 3. Result and Discussion

Figure 2 shows the nitrogen localized states \( (E_0) \) in the range of 0.01 to 0.02 % based on nitrogen fraction, by incrementing 0.001% through (4). The extended states of the conduction band have been obtained by using (12), (13) and (14) as shown in Figure 3.
Figure 4. Temperature dependence of Ga$_1$In$_x$N$_y$As$_{1-y}$ alloy (a) energy band gap (b) wavelength by using FM BAC method.

Figure 5. Temperature dependence of Ga$_1$In$_x$N$_y$As$_{1-y}$ alloy (a) energy band gap (b) wavelength by using SM BAC method.

Figure 6. Temperature dependence of Ga$_1$In$_x$N$_y$As$_{1-y}$ alloy (a) energy band gap (b) wavelength by using TM BAC method.
Figure 7. BAC results (a) energy band gap (b) wavelength of Ga$_{1-x}$In$_x$N$_y$As$_{1-y}$ alloy at 300K.

The energy band gap and wavelength at 300 K are shown in Figure 7 which visualizes the increment energy band gap and wavelength based on the nitrogen fraction for each method.

Table 3. The energy band gap of Ga$_{1-x}$In$_x$N$_y$As$_{1-y}$ alloy at 300 K for each method

| Nitrogen Fraction (%) | Energy Band Gap (eV) |
|-----------------------|----------------------|
|                       | FM       | SM       | TM       |
| 1.0                   | 0.964    | 0.973    | 0.980    |
| 1.1                   | 0.962    | 0.971    | 0.978    |
| 1.2                   | 0.960    | 0.969    | 0.976    |
| 1.3                   | 0.958    | 0.967    | 0.974    |
| 1.4                   | 0.957    | 0.965    | 0.972    |
| 1.5                   | 0.955    | 0.964    | 0.971    |
| 1.6                   | 0.953    | 0.962    | 0.969    |
| 1.7                   | 0.951    | 0.960    | 0.967    |
| 1.8                   | 0.950    | 0.958    | 0.965    |
| 1.9                   | 0.948    | 0.957    | 0.964    |
| 2.0                   | 0.946    | 0.955    | 0.962    |

As shown in Table 3, the energy band gap of Ga$_{1-x}$In$_x$N$_y$As$_{1-y}$ alloy at 300 K offers a lower deviation at 0.964 ± 0.01 eV based on the nitrogen fraction. The deviation of energy band gap for FM and SM is influenced by the bowing parameters of Vegard’s law used to accommodate the curvature of extended conduction band energy. The deviation of wavelength in Table 4 also depicts a similar trend with the energy band gap.

Table 4. The wavelength of Ga$_{1-x}$In$_x$N$_y$As$_{1-y}$ alloy at 300 K for each method

| Nitrogen Fraction (%) | Wavelength (nm) |
|-----------------------|-----------------|
|                       | FM   | SM   | TM   |
| 1.0                   | 1288 | 1276 | 1267 |
| 1.1                   | 1291 | 1279 | 1270 |
| 1.2                   | 1293 | 1281 | 1272 |
| 1.3                   | 1295 | 1284 | 1274 |
| 1.4                   | 1298 | 1286 | 1277 |
| 1.5                   | 1300 | 1288 | 1279 |
| 1.6                   | 1303 | 1291 | 1282 |
| 1.7                   | 1305 | 1293 | 1284 |
| 1.8                   | 1307 | 1295 | 1286 |
| 1.9                   | 1310 | 1298 | 1288 |
| 2.0                   | 1312 | 1300 | 1291 |

Based on the FM BAC modelling, it shows the optimum N fraction in range of 0.012% to 0.018% to achieve a response device at 1.3 μm wavelength with energy band gap 0.955 ± 0.005 eV with 1.3 ± 0.005 eV. Meanwhile, the SM and TM results were the outline data on the basic strategies to achieve 1.3 μm emission from Ga$_{1-x}$In$_x$N$_y$As$_{1-y}$ material with 1.5 ± 0.2 N% fraction [4]. Based on that fraction, the composition of Ga$_{1-x}$In$_x$N$_y$As$_{1-y}$ material with 32% In with 1.2%-1.8% N was promised the optimum lattice constant and compression strain [1]. In this case, the compression strain of material is dependent on the indium fraction and tensile strain of material is coming from the nitrogen fraction [4].

In other word, the increment of N fraction in host semiconductor material able decreases the material optical quality [3]. In fact, the increment of N fraction restructures the conduction band of the host semiconductor by rising the electron states density at edge conduction band [7]. Restructuring of the conduction band occurs by the delocalized conduction band and localized nitrogen level interaction in host semiconductor material. In addition, the N fraction influences the hole effective mass of material by strain-induced valance band non-parabolicity and it might affect the electrical and optical properties of material [4]. Therefore, there is a potential to study the influence of indium fraction in tailored energy band gap of Ga$_{1-x}$In$_x$N$_y$As alloy and compressive strain of material.
4. Conclusions

The effect of nitrogen fraction on tailored energy band gap of Ga$_{1-x}$In$_x$N$_y$As$_{1-y}$ alloy has been investigated by using band anti-crossing (BAC) method based on temperature dependence. This work adopted three numerical methods to determine $E_M$ parameter based on Vegard’s law, excitonic band gap and Varshni’s equation. Based on BAC results, the optimum nitrogen fraction has been evaluated in the range of 0.012 to 0.018% to achieve a device response at 1.3 $\mu$m wavelength with an energy band gap of 0.955 ± 0.005 eV. Thus, it has a potential to study the influence of indium fraction in tailoring energy band gap of Ga$_{1-x}$In$_x$N$_y$As$_{1-y}$ alloy and compressive strain of material.

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