

Theoretical study of material parameters of InGaNP/GaP quantum structures

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This paper presents the theoretical calculations of the electronic properties of $\text{In}_x\text{Ga}_{1-x}\text{N}_y\text{P}_{1-y}$ quantum wells on GaP substrates which are expected to be advantageous for quantum well based light emitting diodes in visible range. We theoretically calculate the bandgap, the band offset, and effective mass of novel direct bandgap InGaNP/GaP structures to determine transition energies. Our calculations show that the incorporation of nitrogen into $\text{In}_x\text{Ga}_{1-x}\text{P}$ improves the band alignment. The band offsets and transition energies of InGaNP/GaP heterostructures are investigated for different indium (x) concentrations.

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1. Introduction

Dilute nitrides have emerged from conventional III-V semiconductors such as GaInAs or InGaP by addition of nitrogen into the group V sub lattice. The best known property of dilute nitrides is the very large band gap bowing [1, 2] introduced by incorporation of a small amount of nitrogen (N) allowing one to widely tune the band gap energy. In combination with the possibility of varying material parameters dilute nitrides have opened an interesting possibility of applications. The InGaNP/GaP structure can be investigated for optoelectronic devices, like GaPN/GaP and GaPNAs/GaP structures. The band structure of GaNP has been studied by Bellaiche et al, who, using 512-atom supercell pseudopotential band structure calculations and predicted the indirect-direct crossover at 3% N [3]. $\text{In}_x\text{Ga}_{1-x}\text{N}_y\text{P}_{1-y}$ alloys with different In and N concentrations can be grown lattice-matched to GaAs or GaP substrates for a variety of device applications such as light emitting diodes (LED) [4], semiconductor lasers [5, 6], heterojunction bipolar transistors (HBTs) [7, 8], and high efficiency tandem solar cells [9].

The unusual effects of nitride on the material parameters and characteristics of InGaNP is the objective of the present work. The determination of material parameters is interesting, necessary and important for theoretical predictions, modelling and better understanding of the physics of dilute nitrides. N incorporation into conventional III- N -V semiconductors causes a profound reduction of the fundamental band gap energy and this decrease does not adequately described by composition weighted linear average and quadratic correction for the dilute nitrides, such as the $\text{GaAs}_{1-y}\text{N}_y$ [10,11], $\text{GaP}_{1-y}\text{N}_y$ [12], and $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y$ alloys [13], which have recently attracted considerable attention. There are some published reports on the calculations of InGaNP bandgap

by using the bowing parameter and the band anti crossing (BAC) model [14-17]. In the literature it seems, so far, that the BAC model usually describes the average trend correctly and is well established as far as the macroscopic behaviour is concerned. An isolated N introduces highly localized states in these nitrides, which interact with the extended conduction-band states of the host semiconductor. The interaction splits the conduction band into an upper and a lower subband. The lower subband energy is taken as the bandgap of system and is used for calculating band alignment of InGaNP/GaP.

The relative band alignment of the band edges between the quantum well and barrier is the total band discontinuity distributed over the conduction band and valance band offsets, ΔE_C and ΔE_V , respectively. The band alignment of direct bandgap InGaNP/GaP system can be analyzed by means of Van de Walle's model solid theory (MST) [18] ignoring the presence of nitrogen in the average valence band energy values and taking into account the presence of nitrogen in all other parameters. The calculated results of band offsets in this study for InGaNP quantum wells on GaP substrates were in agreement with experimental results of Ref. [19, 20]. The theoretically calculated parameters were used to determine the influence of indium concentration in $\text{In}_x\text{Ga}_{1-x}\text{N}_{0.005}\text{P}_{0.995}$ /GaP quantum wells on the ground state and the transition energies.

2. Material parameters

2.1 Determination of bandgap

The BAC model manages to explain the basic properties of the material and to provide analytical expressions, such as conduction band edge dispersion

relations and electron effective mass. The BAC model has been successfully used to describe the dependences of the upper and lower subband energies on nitrogen concentration. The model is based on the interaction of the lowest conduction band with the highly localized N-induced energy level E_N .

It has been shown that an anticrossing interaction of the localized N states leads to a characteristic splitting of the conduction band into two non-parabolic subbands [13]. The BAC model gives the low energy edges of the subbands as follows:

$$E_{\pm} = \frac{1}{2} \left[(E_N + E_M) \pm \sqrt{(E_N - E_M)^2 + 4V_{MN}^2} \right] \quad (1)$$

where E_+ and E_- are the energy eigenvalues of the BAC Hamiltonian used to describe the level repulsion. In Eqn. (1), the E_M and E_N are the energies of the extended state and of the N level respectively. V_{MN} ($V_{MN} = C_{MN} \sqrt{y}$ eV) [21], is the matrix element of the term describing the interaction between localized N states and the extended states. The predicted splitting of the conduction band (CB) into subbands has been confirmed experimentally [21].

Buyanova et al. [14] investigated the BAC parameters for a direct transition $\text{In}_{0.5}\text{Ga}_{0.5}\text{P}_{1-y}\text{N}_y$ as $E_N = 2.1 \pm 0.1$ eV and $V = 1.7 \pm 0.2$ eV. On the other hand, Umeno et al, the estimated the BAC parameters $E_N = 2.125$ eV and $V = 1.769$ eV [12, 22, 23]. In this study, the BAC parameters are chosen as the parameters proposed by Buyanova et al. for the $\text{In}_x\text{Ga}_{1-x}\text{N}_y\text{P}_{1-y}$ alloy. Our theoretical results are agreed with the experimental PL band energies studied by different groups [20, 23-25]. Thus, the bandgap of the InGaNP/GaP QWs were estimated by the BAC model in this paper. For detailed analysis of this structure, the material parameters except for the band gap energy are linearly interpolated from those of the binary materials [26, 27] and tabulated in Table 1. The parameter $E_M = E_g(\text{InGaP})$ is the bandgap energy of the host materials and given as [28]:

$$E_g(\text{In}_x\text{Ga}_{1-x}\text{P}) = 1.351 + 0.643(1-x) + 0.786(1-x)^2 \quad (2)$$

where x is the indium concentration of the host semiconductor.

Table 1. The parameters are taken from Vurgaftman et al [29], except $E_{v,av}$ values [30] for calculating the parameters of InGaNP alloy.

Material	GaN	GaP	InP	InN
Lattice constant a_0 (Å)	4.50	5.4505	5.8697	4.98
Energy gap E_g (eV)	3.299	2.32	1.4236	0.78
Spin-orbit splitting Δ_0 (eV)	0.017	0.08	0.108	0.005
Valence band maximum, VBO (eV)	-2.64	-1.27	-0.94	-2.38
Hydrostatic deformation potential for CB, a_c (eV)	-6.71	-8.20	-6.0	-2.65
Hydrostatic deformation potential for VB, a_v (eV)	-0.69	-1.70	-0.6	-0.7
Elastic stiffness constant, C_{11} (GPa)	293.0	1405	1011.0	187.0
Elastic stiffness constant, C_{12} (GPa)	159.0	620	561.0	125.0
Deformation potential, b (eV)	-2.0	-1.6	-2.0	-1.2
Average Valence Band Position, $E_{v,av}$ (eV)	-	-7.4	-7.04	-

2. 2 Band offset ratios

The conduction- and valence-band offsets ($\Delta E_{c,v}$) of InGaNP versus N and In concentrations are calculated by means of the model solid theory (MST). The addition of N to InGaP causes substantial changes in the band alignments, adding small amount of N to InGaP decreases the bandgap, increases the CB offset and this results leading to a decrease in valence-band (VB) offsets. The calculated band alignments were shown in Figure 1. Our calculations indicate that the $\Delta E_c/\Delta E_v$ ratio changes from 1.9 to around 10.6 with an addition of 3% nitrogen. In addition, it is known that adding small amount of N which mainly affects the conduction band (CB) states leading to a small VB offsets (ΔE_v) [19]. The variation of the CB offset is a result of the combined effects of the variation of

Q_c and ΔE_g , since $\Delta E_c = Q_c \Delta E_g$ with ΔE_g is the difference between bandgap of the barrier and well. The other increase in ΔE_g ($= E_{g,barrier} - E_{g,well}$) with $E_{g,barrier}$ is the indirect gap of GaP and $E_{g,well}$ is the direct gap of InGaNP. As can be seen from Figure 1.a, the Q_c is increases with increasing N concentrations. On the other hand, in Figure 1.b, the increase in In concentrations results a decrease in the conduction band offset in the range of In concentrations between 0% to 25%. The offset of 300 meV is generally required for room temperature operation of semiconductor lasers [29-33]. Thus, it was clarified that the differences of the N composition of about 3% between the InGaNP well and the GaP barrier were required for a conduction band offset of 300 meV. The larger band offsets of InGaNP/GaP structures provide higher internal quantum efficiency at higher current densities.

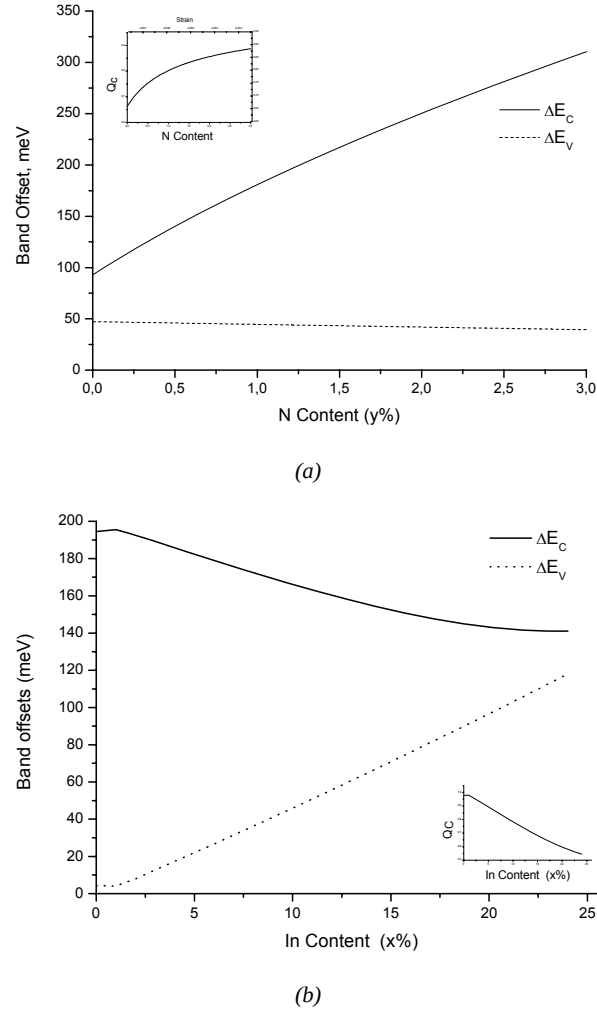


Fig. 1. According to the MST model, the variation of the conduction and valence band offsets of InGaNP/GaP hetero structures with various N and In concentrations. Band offsets of $\text{In}_x\text{Ga}_{1-x}\text{N}_y\text{P}_{1-y}/\text{GaP}$ a) as a function of y with $x=10\%$ and b) as a function of x with $y=0.5\%$.

Large conduction band offsets are essential for electron confinement, stability and any quantum effects. Therefore, increasing N concentration in the limits of direct transition of the InGaPN well, increase the conduction band offsets of InGaNP/GaP for light-emitting devices.

2.3 The effective masses

Our aim is at this point to determine the electron effective mass of InGaNP system by using the BAC model to determine transition energies. It should be noted that the BAC model provides an analytical equation that describes the effective mass of electrons as a function of the indium and nitrogen concentrations. A dramatic increase of m_e^* in III-V-N (for GaInNAs) has been predicted to increase with increasing N composition is explained well by using BAC [34]. This behaviour is rather unusual and is in fact, opposite to the conventional semiconductors, where the

value of m_e^* decreases with decrease of the band gap energy. The compositional dependence of an electron effective mass is described by the BAC model as

$$\frac{1}{m_e^*} = \frac{1}{2m_{III-V}^*} \left[1 - \frac{E_c - E_N}{\sqrt{(E_c - E_N)^2 + 4V_{mn}^2}} \right] \quad (3)$$

where m_{III-V}^* is the electron effective mass of the host semiconductor. E_c is the extended energy and taken as $E_c = E_M + VBO$ and VBO is unstrained valence band maximum. The electron effective mass decreases with increasing In concentration. The other method for determining the effective mass parameter is the interpolation technique. This technique is used by some groups, such as Kaewket et al. [35] and Umeno et al., [23].

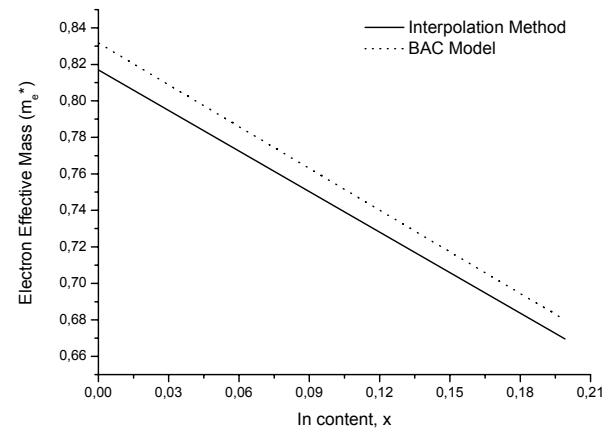


Fig. 2. The electron effective mass of $\text{In}_x\text{Ga}_{1-x}\text{N}_{0.005}\text{P}_{0.995}$ is calculated for different indium concentrations by interpolation method (the solid line) and by BAC model (dotted line).

These two methods were used to calculate the electron effective mass and the results give the similar trend as can be shown in Fig. 2. The decrease in electron effective mass is due to difference between binary parameters. This decreasing trend is also in agreement with experimental values of Ref. [34].

2.4 The transition energy

Indium concentration dependence of ground state and transition energy of $\text{In}_x\text{Ga}_{1-x}\text{NP}/\text{GaP}$ quantum wells with N concentrations of 0.5% and 1% were calculated. Fig. 3 shows the dependence of the quantum well transition and ground state energies versus In (x) concentration. The transition energy decreases and the ground state energy increases with increasing In concentration. In addition, the nitrogen concentration dependence was also seen on Fig. 3. Increase of nitrogen concentration in Fig. 3(a), leads to an increase of the electron ground state energy, whereas the transition energy starts to decrease in Fig. 3 (b). The ground state energy is very close to the bottom of the

conduction band due to small band offset results. The transition energy is determined by adding electron ground state and valence band energies to the band gap. Therefore, the effect of conduction and valence band energies on the transition energy is very small.

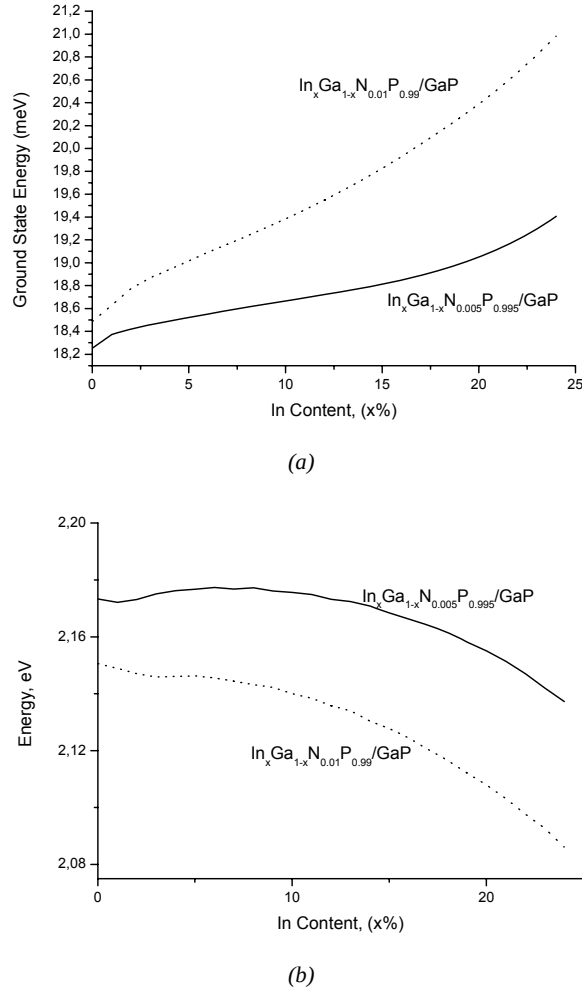


Fig. 3. The theoretically calculated a) ground state and b) transition energies versus indium concentrations of $\text{In}_x\text{Ga}_{1-x}\text{N}_y\text{P}_{1-y}/\text{GaP}$ QW with well width of $L_z = 4$ nm and nitrogen concentrations (y) of 1.0% and 0.5%.

3. Conclusions

In this paper are presented the material parameters of $\text{In}_x\text{Ga}_{1-x}\text{N}_y\text{P}_{1-y}/\text{GaP}$ structures with different indium concentrations are presented. It is shown that the BAC model for the large band bowing of the InGaNP alloy due to N incorporation can be used to calculate the band structure and the electron effective mass. We also calculated the conduction and valence band offsets for structures with different indium and nitrogen concentration by using the MST model to determine transition energies.

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