Calculation of the Bandgap of Dilute Nitride GaAsSbN Alloys

S Georgiev¹, V Donchev¹, M Milanova²

¹ Faculty of Physics, Sofia University, 5 J. Bourchier Blvd., BG-1164, Sofia, Bulgaria
² Central Laboratory of Applied Physics, Bulgarian Academy of Sciences, 61 St. Petersburg Blvd., BG-4000 Plovdiv, Bulgaria

E-mail: vtd@phys.uni-sofia.bg

Abstract. Dilute nitrides are semiconductor alloys, obtained from the conventional III-V compounds by incorporating a small amount of nitrogen. In this work, we focus on GaAsSbN considered as a perspective material for incorporation in multijunction solar cells. Nitrogen creates a localized level inside the conduction band continuum. The interaction of this level with the conduction band is usually described by the single band anti-crossing (BAC) model. The double BAC model of GaAsSbN considers both the N and the Sb localized levels in the conduction and the valence band, respectively. We calculate the bandgap energy of GaAsSbN employing the double BAC model for different concentrations of Sb and N. Parameters of the BAC model taken from different literature sources are used in the calculations and their influence on the final result is explored. Finally, the calculated bandgap energies are compared to experimental data of GaAsSbN layers grown on n-GaAs substrates by low-temperature liquid phase epitaxy. These data include the optical absorption edge of the material determined by surface photovoltage spectroscopy and the energy position of the photoluminescence peak at room temperature.

1. Introduction

The semiconductor materials based on III-V compounds by incorporating small amount of nitrogen (N), dilute nitrides, are a subject of a great attention in the recent more than 20 years. This was provoked by some interesting and unusual properties like huge bandgap reducing and lattice matching to GaAs substrate in the same time. That makes the dilute nitrides applicable in different types of devices for the optoelectronics – solar cells, photodetectors, light emitting diodes and others [1]. Talking about photovoltaics extensive studies have been performed on the quaternary and quinary compounds like InGaAsN, InGaAsSbN and GaAsSbN. Their high value is mostly as sub-cells in the multijunction solar cells [2, 3].

Generally the addition of indium (In) in the alloy facilitates the incorporation of N, while antimony (Sb) act as a surfactant that reduces the strain-induced defect formation, favours 2D growth and further decreases the bandgap [4]. However, GaAsSbN has advantages over the rest ones when used in solar cell and photo-detecting applications. This is due to the absence of In-related defects and lower N content to achieve the same bandgap. Furthermore, the conduction and valence band energies can be adjusted independently while it is lattice-matched to GaAs [5, 7]. Another favourable aspect concerns the fabrication. Good quality GaAsSbN layers can be grown with the low-cost liquid phase epitaxy. The efficiency of a single junction solar cell is based on closely compensated GaAsSbN has been recently reported to exceed 4% in [7], which is very promising in comparison to the 6% achieved in cells grown by the more expensive molecular beam epitaxy (MBE) technique [8].
In this work we calculate the bandgap behavior of GaAsSbN layers grown by liquid phase epitaxy. The theoretical model adopts the valence band anti-crossing (valence BAC) and conduction band anti-crossing (conduction BAC) models as described in [9] and [10] respectively. Valence BAC considers the interaction between the localized antimony states and the valence band (VB), while the conduction BAC describes the interaction between the localized nitrogen states and the conduction band (CB). The combination of both represent the so called double band anti-crossing model [11].

2. Bandgap calculations

Before performing the calculation, the following assumptions are made. The initial host crystal is GaAs and its valence band level is accepted to be the zero of the energy scale. All other energy levels are calculated with respect to it. The theoretical model is valid for dilute regime of both Sb and N contents.

We first calculate the effect of antimony, on the bands of GaAs. Initially virtual crystal approximation (VCA) is used to account for the linear change of the valence and conduction bands of GaAs\(_{1-y}\)Sb\(_y\) as a function of the antimony mole fraction \(y\):

\[
E_{V_B}^{GaAsSb} = E_{V_B}^{GaAs} + y \cdot V_{B\text{offset}}, \quad E_{C_B}^{GaAsSb} = E_{C_B}^{GaAs} + y \cdot C_{B\text{offset}}
\]  

In (1) \(E_{g}^{GaAs}=1.423 \text{ eV}\) is the bandgap energy of GaAs, \(V_{B\text{offset}}=0.5 \text{ eV}\) and \(C_{B\text{offset}}=-0.2 \text{ eV}\) are the valence and conduction band offsets between the endpoint compounds GaAs and GaSb.

The hybridization of the localized states of Sb and the extended states of the host semiconductor matrix is well described by the valence BAC model. More detailed mathematical formulation can be found in the work of Alberi [9]. At the \(\Gamma\) point, where \(k=0\), the eigenvalues of the Hamiltonian matrix are represented by (2):

\[
E_{V_B}^{GaAs_{1-y-x}Sb_\chi N_x} = 0.5 \left[ E_{Sb} + E_{V_B}^{GaAsSb} \pm \left( (E_{V_B}^{GaAsSb} - E_{Sb})^2 + 4 \cdot C_{Sb}^2 \cdot y \right)^{1/2} \right]
\]  

The above equation gives two values \(E_{V_B}^+\) and \(E_{V_B}^-\) where the higher one, \(E_{V_B}^+\), stands for the valence band maximum of GaAsSbN. The level \(E_{Sb}=-1 \text{ eV}\) is the energy position of the antimony in the host crystal GaAs. The coefficient \(C_{Sb}=1.05 \text{ eV}\) is the interaction potential between the localized and the extended states. These parameters are well established in the literature [11, 12].

On the other hand, the highly electronegative nitrogen atoms create band splitting of the conduction band. An equation similar to (2) can be written to reflect this coupling effect [10]:

\[
E_{C_B}^{GaAs_{1-y-x}Sb_\chi N_x} = 0.5 \left[ E_{N} + E_{C_B}^{GaAsSb} \pm \left( (E_{C_B}^{GaAsSb} - E_{N})^2 + 4 \cdot C_{N}^2 \cdot x \right)^{1/2} \right]
\]  

In (3) the parameters \(E_{N}\) and \(C_{N}\) are the nitrogen energy position with respect to GaAs VB and the interaction potential between the localized N and extended CB states, respectively. No clear consensus has been achieved about their exact values. They can vary with the growing technique or the post treatment. This is because the \(E_{C_B}\) energy of GaAsSbN has never been observed in the literature which plays an important role in determining the values of \(E_{N}\) and \(C_{N}\) [11]. In our calculations we used several documented pairs of parameters as shows in table 1.

| Reference | \(E_N\) [eV] | \(C_N\) [eV] |
|-----------|-------------|-------------|
| [11]      | 1.54        | 2.839       |
| [14]      | 1.65        | 3.9         |
| [15]      | 1.65        | 2.7         |
| [12, 13]  | 1.76        | 2.7         |
| [16]      | 1.76        | 2.7         |
| [17]      | 1.8         | 2.7         |
| [18]      | 1.65        | 2.68        |

The resulting band dependency of GaAsSbN on the nitrogen and antimony content is shown on figure 1. The calculations show that the antimony affects the CB very weakly, while the VB edge is significantly raised. The nitrogen strongly decreases the CB and has no effect on the valence band.
Figure 1. Calculated conduction and valence bands of GaAsSbN as a function of Sb and N content.

Figure 2. Bandgap dependency on N and Sb mole fraction. (a) and (b) present calculation with $E_N=1.65$ eV, $C_N=3.9$ eV; (c) and (d) present calculation with $E_N=1.54$ eV, $C_N=2.839$ eV.

Thus, the bandgap energy of GaAsSbN simply equals to $E_{GaAsSbN}^g = E_{CB}^- - E_{VB}^+$. Figure 2 represents two sets of bandgap calculations: (a) and (b) show $E_{GaAsSbN}^g$ dependency on N and Sb mole...
fraction respectively with $E_N=1.65$ eV, $C_N=3.9$ eV, while (c) and (d) show the same dependency with $E_N=1.54$ eV, $C_N=2.839$ eV. A closer observation of figure 2 unveils that small variations in the N related parameters can result in big differences in the final prediction.

3. Comparison with experimental results

The theoretical model in section 2 is used to describe the bandgap energies of four monocrystalline GaAsSbN samples – E355, E373, E384 and E404. They were grown by liquid phase epitaxy. The Sb mole fraction determined by energy dispersive x-ray spectroscopy (EDX) (Quantax, Bruker) is about 6.8%. The mole fraction of N is 0.1% as determined by x-ray photoelectron spectroscopy.

Two experimental methods are used to assess the bandgaps of our samples – photoluminescence (PL) and surface photovoltage spectroscopy (SPS) at room temperature. The PL spectra are shown in figure 3 (a), while figure 3 (b) presents the SPS results. The position of the PL peaks is an estimate of the bandgap. The SPS spectra reveal steep jumps of the signal, which correspond to the absorption edge of the semiconductor materials. The latter is determined by Tauc plot and can also be considered as an estimate of the bandgap energy.

![Figure 3](image.png)

Figure 3. Experimental results for GaAsSbN samples: (a) normalized photoluminescence spectra; (b) normalized surface photovoltage amplitude spectra.

A summary of the obtained energies is given in table 2. The SPS results typically show lower energy of the absorption edge as compared to those from PL [19].

| Sample | E355 | E373 | E384 | E404 |
|--------|------|------|------|------|
| SPS $E_g$ (eV) | 1.19 | 1.2  | 1.2  | 1.26 |
| PL $E_g$ (eV)  | 1.23 | 1.24 | 1.26 | 1.28 |

The values from table 2 are plotted on figure 4. For better readability, the energies from SPS are intentionally moved to 0.0011 nitrogen mole fraction. From the graph the best fitting pair N parameters appears to be $E_N=1.65$ eV, $C_N=3.9$ eV. The model is in a good agreement with the determined mole fraction for – Sb (= 6.8%) and N (=0.1%).
4. Conclusion
The bandgap of GaAsSbN alloy has been calculated using the double band anti-crossing model, which includes anti-crossing interactions for both valence and conduction bands. The model has shown that the impact of the nitrogen on the conduction band is very strong and the fitting parameters greatly affects the calculated bandgap. The comparison with the experimental results segregated $E_N=1.65$ eV, $C_N=3.9$ eV as best fitting pair. However, a deviation up to 30 meV is observed between the PL peaks and the predicted energies for some samples. A possible reason for the redshift of the experimental values is the existence of substitutional N pairs or clusters in the samples [15], or other effects that are not taken into account in the BAC model, e.g. –VB perturbations caused by N [20] or the density of states of the band tails of N [14]. This work reveals the need for achieving consensus concerning appropriate values of the N-related parameters $E_N$ and $C_N$. It also contributes to the better understanding of the applicability of the double BAC model to the dilute nitride materials, which are grown by liquid phase epitaxy.

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