Tight binding modeling of electronic properties of III-V based heterostructures

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In this work, we present second nearest neighbour (2NN) sp3s* and nearest neighbour (NN) sp3d5s* tight binding calculations, with spin-orbit coupling to calculate the composition, temperature, pressure and strain effects on the electronic properties (e.g., band structure, density of states, band gaps and band widths) of GaAs, GaP, GaAN and AlN III-V binaries and ternary GaPN. The results are compared with those of density functional theory for GaN. Our results are in good agreement with experiment for fundamental band gaps and electron effective masses.

1 Introduction

Experimental and theoretical studies show that III-V based semiconductors and their alloys have great potential in the electronic and optoelectronic device industry as high-performance devices [1,2]. Meanwhile, development of computer technologies and computing methods have lead to an increase in the theoretical studies of past decades, and make it possible to calculate the properties of heterostructures and nanoscaled devices [3-7]. First principles calculations are computationally intensive and cannot be easily implemented for low dimensional optoelectronic devices [6,7]. In contrast, the semi-empirical tight binding model (ETB) is known as not only simple but also reliable and easily implemented in the calculation of electronic properties such as band structure, density of states, band gaps of the heterostructures [8-18].

In this article, we employ the second nearest neighbor (2NN) sp3s* [12] and nearest neighbour (NN) sp3d5s* [2, 17, 18] tight binding (TB) models to calculate the composition, temperature, pressure and strain effects on the electronic properties (e.g., band structure, density of states, band gaps and band widths) of group III-V binaries and ternaries. We will present the results of our 2NN tight binding calculations, with spin-orbit coupling [3-5] to calculate the effects on the electronic properties of Ga based III-V binaries (e.g., GaAs, GaP and GaN) and their ternaries (e.g., GaP). Our results are in good agreement with experimental data [8] for the fundamental bandgap energies and electron effective mass.

2 Tight binding modelling

In the semi-empirical sp3s* tight binding model Hamiltonian, each cation atom and anion atom are described by their outer valence s orbital, the three outer p orbitals and a fictitious excited s* orbital added to mimic the effects of higher lying d-states. In the semi-empirical tight binding model, Schrödinger equation written in matrix form as

\[ \sum_{m} \left[ H_{mn}(k) - S_{mn}(k)E \right] u_{m} = 0 \]  

where E is the energy eigenvalue of the Hamiltonian matrix \( H_{mn} \) and \( S_{mn} \) is the overlap integral between the atomic-like orbitals, with \( m \) and \( n \) that correspond to a cation and anion s (p, d, s*) orbitals, and \( H_{m} \) is the wave function coefficient. In the 2NN sp3s* TB model, there are thirteen independent matrix elements; six of them are known as diagonal elements or on-site atomic energies and seven of them are called off-diagonal elements or interaction integrals, also known as hopping terms. The spin orbit effects are included by different spin states of different on-site p orbitals through the spin-orbit interaction. Adding 2NN interactions to the sp3s* TB modeling adds two additional interaction parameters to orbitals basis set [19], and
that the size of the 10x10 Hamiltonian matrix becomes a 20x20 one for the cubic structure that is diagonalized for each k vector to obtain electronic band structure [7]. Jancu et al. [2] overcomes the problems at X high symmetry points by adding d orbitals to the basis set of sp3s* nearest neighbor tight binding modeling with the size of 20x20 Hamiltonian matrix.

Tight binding parameterization of the matrix elements for sp3s* 2NN interaction have been done as explained in our previous work [20]. Jancu et al. [2, 17] parameters are used to get sp3d5s* tight binding dispersion curves. The bands at the high symmetry points are shown in Table 1 for sp3s* 2NN and sp3d5s* NN TB models. Figure 1 shows electronic band structure and density of states of the GaAs calculated by using sp3s* 2NN and sp3d5s* TB models. Due to the inherent property of TB model, the excellent agreement at Γ (0,0,0) point between the two TB models, there is deviation towards X and L points; the latter model is more accurate than former away from the lowest lying energy levels. It is concluded that the inclusion of d-orbitals in the TB Hamiltonian improves the symmetry character of the Bloch function at the X point.

Furthermore, since the inclusion of d-orbitals in the TB Hamiltonian improves the symmetry character of the Bloch function at the X point, comparison is made only between the sp3d5s* tight binding method [18] and density functional theory [21] and is shown in Fig. 2 for the calculations of band structure and DOS of GaN.

Effective masses calculated by using sp3s* 2NN [21] and sp3d5s* [1, 18] tight binding models are given in Table 2.

In the framework of 2NN sp3s* and sp3d5s* TB models, the effect of the allow composition on electronic band structure of group III-V nitrides based heterostructures are calculated by using the called modified virtual crystal approximation (MVCA) [15-17, 21, 23]. MVCA makes possible to calculate the disorder nonlinear variation of the lattice constant and tight binding parameters to figure out the electronic structure properties such as band gaps, conduction and valence band offsets. The bond length of ternary $A_{1-x}B_xC$ as [14-16]:

$$d(x) = (1-x)d_{AC}^0 + (x)d_{BC}^0 + x(1-x)\delta(E_{iC}(x) - E_{iB}(x))$$  \hspace{1cm} (2)

where first two terms are the undistorted part of the bond length, the last one is the distorted part of the bond length due to cation-anion relaxation in the $A_{1-x}B_xC$ ternary. $d_{AC}^0$ and $d_{BC}^0$ are the distorted bond lengths of the host AC and BC materials, $d_{AC}(x)$ and $d_{BC}(x)$ are the bond lengths of AC and BC binaries in the $A_{1-x}B_xC$ ternary as

$$d_{AC}(x) = (1-x)d_{AC}^0 + (x)d_{BC}^0 + (1-x)\xi_{AC,B} \left( d_{AC} - d_{BC} \right)$$  \hspace{1cm} (3)

$$d_{BC}(x) = (1-x)d_{AC}^0 + (x)d_{BC}^0 + (x)\xi_{BC,A} \left( d_{BC} - d_{AC} \right)$$  \hspace{1cm} (4)

![Figure 1](https://example.com/figure1.png)

**Figure 1** Electronic band structure and density of states of GaAs calculated by using sp3s* 2NN (dashed) [20, 21] and sp3d5s* (solid) [2] TB methods.

In Eq. (2), $\delta_i$ is the difference between the dimensionless relaxation parameters $\xi_{AC,B}$ and $\xi_{BC,A}$ [23, 24]

$$\delta_i = \xi_{AC,B} - \xi_{BC,A} = \frac{1}{1 + \frac{\alpha_{AC}}{\alpha_{BC}}} \left[ 1 + 10 \frac{\beta_{AC}}{\alpha_{AC}} \right] - \frac{1}{1 + \frac{\alpha_{BC}}{\alpha_{AC}}} \left[ 1 + 10 \frac{\beta_{BC}}{\alpha_{BC}} \right]$$  \hspace{1cm} (5)

The off-site and on-site cation and anion atomic energies of the $A_{1-x}B_xC$ group III-V ternary semiconductor is written as [14-16]

$$E_i(x) = (1-x)E_{iC}^AC + (x)E_{iC}^BC + x(1-x)\delta_i (E_{iC}^AC - E_{iC}^BC)$$  \hspace{1cm} (6)

<table>
<thead>
<tr>
<th>eV</th>
<th>GaAs (sp3s*)</th>
<th>GaP (sp3s*)</th>
<th>GaN (sp3s*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_x^c$</td>
<td>1.519</td>
<td>1.519</td>
<td>2.878</td>
</tr>
<tr>
<td>$E_g^s$</td>
<td>1.980</td>
<td>1.980</td>
<td>2.349</td>
</tr>
<tr>
<td>$E_g^c$</td>
<td>1.818</td>
<td>1.830</td>
<td>2.563</td>
</tr>
</tbody>
</table>

Table 1 Calculated band gaps of GaAs, GaP and GaN by using sp3s* 2NN [21] and sp3d5s* [1, 18] TB parameters.

<table>
<thead>
<tr>
<th>(m*)</th>
<th>sp3s*</th>
<th>sp3d5s*</th>
<th>Exp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaAs</td>
<td>0.163</td>
<td>0.067</td>
<td>0.066 (T=1.6 K)</td>
</tr>
<tr>
<td>GaN</td>
<td>0.269</td>
<td>0.199</td>
<td>0.220 (T=6 K)</td>
</tr>
<tr>
<td>GaP</td>
<td>0.184</td>
<td>0.129</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 2 Effective mass of GaAs, GaN and GaP calculated with sp3s* 2NN and sp3d5s* TB models.
where \( i \) represents the fitted energy of s, p and d states of anion and cation atoms for \( AC \) and \( BC \) binaries. Using the optimized \( \text{sp}^3\text{s}^* \text{2NN} \) [20] and \( \text{sp}^3\text{d}^5\text{s}^* \) [2, 17] TB parameters, the calculated band gaps of GaAs, GaP and GaN binaries are given in Table 1. The effects of pressure and temperature on band gaps shall be discussed next section.

3 Results and discussion

As pointed out in Section 1, development of the crystal growth technologies permits to control dimensions of the layers, allowing to control material properties of the semiconductors and their heterostructures. Materials with different compositions can be grown on the suitable lattice matched substrate. However, large lattice mismatch strain across the binary/ternary heterostructures causes major obstacles [25]. The performance of nanoscale devices depends on the composition and strain variation of their electronic energy band structure and the energy band offsets across the interface.

\[
E_i(T,P) = E_i(0,P_0) + C_i(T)(1 - \ln T) - \frac{a_i}{B} \left[ P - \frac{P^2}{2B} - \frac{(1 + B')}{6B^2} P^3 \right]
\]

Figure 2

Electronic band structure and density of states of GaN calculated by using \( \text{sp}^3\text{d}^5\text{s}^* \text{NN} \) tight binding method (solid) [18] and density functional theory (DFT) (dashed) [22].

Since nanoscale devices run under different high pressure and temperature environments, device performance of the heterostructures should be defined for various temperature and pressure conditions. Standard state chemical potentials, at any temperature and pressure, define the pressure effects on valence and conduction band energy levels can be written as [25, 26]

\[
E_i(T,P) = E_i(0,P_0) + C_i(T)(1 - \ln T) - \frac{a_i}{B} \left[ P - \frac{P^2}{2B} - \frac{(1 + B')}{6B^2} P^3 \right]
\]

where \( i \) represents the conduction (c) or valence (v) band energy levels, \( P \) is the applied pressure, \( T \) is the temperature, \( E_i(0,P_0) \) is conduction or valence band edges at \( \Gamma \), \( L \) and \( X \) symmetry points with deformation potentials \( a_i = -B \left( \partial E_i / \partial P \right) \). \( B \) is bulk modulus with \( B' = \partial B / \partial P \) its derivative, \( C_i^0 \) is standard heat capacity of conduction electrons and valence holes. The pressure and temperature effects on the band gap can be written as

\[
E_g(T,P) = E_g(0,P_0) + \Delta C^0_g(T)(1 - \ln T) - \frac{a_g}{B} \left[ P - \frac{P^2}{2B} - \frac{(1 + B')}{6B^2} P^3 \right]
\]

where \( \Delta C^0_g \), called the heat capacity of reaction for the formation of free electrons and holes [14-16], is obtained from fitting the band gap to the optical experimental data [8, 28, 29]. Equation (8) is used to calculate the temperature effects on the band gaps of the semiconductor at \( P=1 \) atm pressure and the results are presented in Figure 3. The 0 K values of the fundamental band gaps at \( \Gamma \), \( X \) and \( L \) high symmetry points are calculated by using the nearest neighbor (NN) \( \text{sp}^3\text{d}^5\text{s}^* \) tight binding model [1, 18].

Results show that there is good agreement between the theoretical approach and the experimental data for the fundamental bandgap \( E_{BG}^f \) of binary semiconductor. As lattice temperature increases the band gap energies decrease. In Table 3, we present the band gaps of GaAs, GaP, GaN and AlN at \( P=1 \) atm pressure. Star (*), triangle (\( \Delta \)), and square (\( \bullet \)), represent \( \Gamma \), \( X \) and \( L \) energy band gaps respectively. Solid line (-) represents the experimental data [28, 29].

Figure 3

Temperature effects on the band gaps for GaAs, GaP, GaN and AlN at \( P=1 \) atm pressure. Star (*), triangle (\( \Delta \)), and square (\( \bullet \)), represent \( \Gamma \), \( X \) and \( L \) energy band gaps respectively. Solid line (-) represents the experimental data [28, 29].
While increasing the pressure, band gaps of GaAs and GaP change from direct to indirect band gaps, but GaN and AlN both maintain the direct and indirect band gap properties.

<table>
<thead>
<tr>
<th>BG (eV)</th>
<th>GaAs</th>
<th>GaP</th>
<th>GaN</th>
<th>AlN</th>
</tr>
</thead>
<tbody>
<tr>
<td>E_g^\Gamma</td>
<td>1.28</td>
<td>2.39</td>
<td>2.73</td>
<td>3.30</td>
</tr>
<tr>
<td>E_g^X</td>
<td>1.82</td>
<td>1.68</td>
<td>2.13</td>
<td>1.80</td>
</tr>
<tr>
<td>E_g^L</td>
<td>1.55</td>
<td>2.07</td>
<td>2.57</td>
<td>3.17</td>
</tr>
</tbody>
</table>

Table 3: Band gaps (BG) of GaAs, GaP, GaN and AlN at Γ, X and L symmetry points at certain temperature and pressure values. The temperature and pressure values for the first columns is P=1 atm, T=600 K, and for the second columns is P=12 GPa and T=300 K.

Band gap of GaAs at Γ symmetry point crosses the one at X point at 4.469 GPa pressure. The direct band gap property of GaP becomes indirect at 8.531 GPa pressure.

**4 Conclusion**

We presented a 2NN sp3s* and nearest neighbor sp3d5s* tight binding models to study of band structure group III-V semiconductors. Using the optimized 2NN sp3s* [21] and NN sp3d5s* [1, 18] for GaAs, GaN, GaP and AlN III-V binary compounds, we have successfully calculated the electronic structures \( \text{GaP}_{1-x}\text{N}_x \) as a function of alloy composition for entire composition range.

Electronic band structure of GaAs and density of states were calculated by using sp3s* and sp3d5s* methods. GaN band structure and DOS result of sp3d5s* method was compared with and density functional theory [22]. The effective masses at Γ, X and L high symmetry points were also calculated and compared with available experimental
results. Applying modified virtual crystal approximation as nonlinear function of composition, we were able to calculate electronic band structure of ternary $\text{GaP}_{1-x}N_x$. We also applied standard state chemical potentials approach to figure out how temperature and pressure effect on the band gaps of the binaries. In addition, we showed that how energy band gap values of ternary $\text{GaP}_{1-x}N_x$ changes under certain pressure and temperature for various $x$ mole fractions. The physical parameters of ternary were assumed as linear combination of one of binaries, and the result were represented in the tables.

Figure 6 The temperature effects on the band gaps of $\text{GaP}_{1-x}N_x$ for $x=0.25$, 0.50 and 0.75 ternaries, respectively. The pressure value is $P=1$ atm.

**References**