Structural and electronic properties of GaN$_x$As$_{1-x}$ alloys

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Received: 15 April 2011 / Accepted: 24 October 2011 / Published online: 18 November 2011
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Abstract The structural and electronic properties of cubic GaN$_x$As$_{1-x}$ with N-concentration varying between 0.0 and 1.0 with step of 0.25 were investigated using the full potential–linearized augmented plane wave (FP-LAPW) method. We have used the local density approximation (LDA) and the generalized gradient approximation (GGA) for the exchange and correlation potential. In addition the Engel-Vosko generalized gradient approximation (EVGGA) was used for the band-structure calculations. The structural properties of the binary and ternary alloys were investigated. The electronic band structure, total and partial density of states as well as the electron charge density were determined for both the binary and their related ternary alloys. The energy gap of the alloys decreases when we move from $x=0.0$ to 0.25; then it increases by a factor of about 1.8 when we move from 0.25 to 0.5, 0.75 and 1.0 using EVGGA. For both LDA and GGA moving from $x=0.0$ to 0.25 causes the band gap to close, showing the metallic nature of the GaN$_{0.25}$As$_{0.75}$ alloy. When the composition of N moves through $x=0.25, 0.5, 0.75$ and 1, the band gap increases.

1 Introduction

III–V nitrogen doped ternary alloys such as GaN$_x$As$_{1-x}$ have attracted a great deal of interest due to their significance in potential applications such as optoelectronic, semiconductor lasers, and optical detectors [1–8]. Doping GaAs compound by a low concentration of nitrogen is found to have a dramatic effect on electronic structure and optical properties of these compounds. Weyers et al. [9] have observed a huge reduction in the band gap that reaches about 0.2 eV by replacing just one percent of the arsenic by nitrogen. This red shift is characterized by the optical bowing parameter that reaches 18–20 eV for N concentration less than 5%, which is about an order of magnitude larger than other III–V ternary alloys that exhibit a bowing of about 1.0 eV [10, 11].

Even since this discovery, intensive efforts have been made to investigate the effect of increasing nitrogen concentration on the properties of such doped alloys. The reason behind the huge bowing parameter of GaN$_x$As$_{1-x}$ ternary alloys has been interpreted differently. In dilute GaNAs, where the N atoms are considered as impurities, one study has related that to the band anticrossing caused by the strong interaction between the extended conduction band states and localized N resonant states [12]. Another has interpreted this anomaly by the band formation of N within the band gap [13]. Tisch et al., however, have suggested three compositional regions [14]. The first is the impurity region where N cluster states form within the band gap and cause a rapid decrease of the band gap. In the second region, the cluster...
states are within the conduction band and strongly interact with the conduction band states. Finally, the third region is suggested to be the alloy formation, which may occur at high compositions.

In order to understand the strange behavior of the variation of the band gap and the dependence of the bowing parameter with the concentration of N we have investigated the structural and electronic properties of GaN$_x$As$_{1-x}$ ternary alloys. The rest of this paper is organized as follows: Sect. 2 is devoted for the method of calculation. The results and discussion are presented in Sect. 3 and Sect. 4 summarizes the main concluding points.

2 Method of calculation

The total energy calculations are performed for GaN$_x$As$_{1-x}$ for $x$ varying from 0.0 to 1.0 by step of 0.25. In this work, we have used the ‘special quasirandom structures’ (SQS) approach of Zunger et al. [15] to reproduce the randomness of the alloys for the first few shells around a given site. This approach is reasonably sufficient to describe the alloys for many physical properties that are not affected by the errors introduced by using the concept of periodicity beyond the first few shells. The SQS are small unit cell periodic structures whose lattice sites are occupied by A and B atoms so as to mimic the atom-atom correlation function of much larger A$_{1-x}$B$_x$ supercells with random occupations. Charge fluctuations needed to describe real alloy are naturally included in this approach. At low concentration limit the SQS is similar to the ‘impurity supercell’ with one nitrogen atom per cell and a maximum N–N distance between impurity in adjacent cells [55].

The calculations were carried out using the full potential linearized augmented plane wave (FP-LAPW) method as implemented in WIEN2K code [16]. The exchange correlation potential was treated using three approximations, the local density approximation (LDA) [17], the generalized gradient approximation (GGA) [18] for the total energy calculations. Because of the shortcoming of both LDA and GGA in the underestimation of the energy gap [20], we also used the Engel-Vosko GGA (EVGGA) formalism [19] for band-structure calculations. This shortcoming is ascribed to the fact that they do not reproduce the exchange correlation energy and its charge derivative correctly. Therefore EVGGA is a modified form of GGA, which is able to better reproduce the exchange potential at the expense of less agreement in the exchange energy, which yields a better band splitting. However, the calculations of quantities that depend on an accurate description of the exchange potential as the equilibrium volume and bulk modulus using EVGGA are in poor agreement with experiment [20].

The spherical harmonics inside non-overlapping muffin-tin (MT) spheres surrounding the atoms are expanded up to $l_{\text{max}} = 10$. The muffin-tin radii were assumed to be 1.6 atomic units (a.u.) for N, whereas a 1.95 a.u. is used for both Ga, and As. The plane wave cut-off of $K_{\text{max}} = 9.0/R_{\text{MT}}$ was chosen for the expansion of the wavefunctions in the interstitial region for all the binary compounds GaAs, GaN and GaN$_x$As$_{1-x}$ ternary alloys, where $R_{\text{MT}}$ is the radius of the smallest muffin-tin sphere. The charge density was Fourier expanded up to $G_{\text{max}} = 14$ (Ryd)$^{1/2}$. The irreducible wedge of the Brillouin zone was described by a mesh of 35 special $k$-points for binary compounds and alloys except for the case of $x = 0.5$, where we used a mesh of 64 special $k$-points. In the case of band-structure calculations, we used denser meshes of 220 $k$-points for binary as well as ternary alloys of $x = 0.25$ and 0.75, whereas 216 $k$-points were used for $x = 0.5$. We have achieved convergence in the energy to within less than $10^{-6}$ Ry.

3 Results and discussion

3.1 Structural properties

In this section, we present the structural properties of the GaN$_x$As$_{1-x}$ compounds for compositions $x = 0.0$, 0.25, 0.5, 0.75 and 1.0. The zinc-blend structure is being used in the calculations for GaN and GaAs, whereas the ternary alloys are modeled using the SQS approach. For the composition $x = 0.25$ and 0.75 the simplest structure is an eight-atom simple cubic lattice (luzonite): the cations with the lower concentration form a regular simple cubic lattice. For $x = 0.5$, the smallest ordered structure is (001) supercell. The structures of all compounds were optimized by calculating the total energy as a function of volume, which was followed by fitting the results with Murnaghan’s equation of state [21]. From this fitting, we obtained the optimum lattice constant and bulk modulus. Table 1 presents our calculated values obtained after optimization compared with the estimated values using Vegard’s law [34]. From this table, one can notice that the optimized lattice constants agree well with the experimental ones and other theoretical calculations for the case of binary systems. However, in the case of the ternary alloys, the lattice constants deviate from the estimated values using Vegard’s law [34]:

$$a(A_xB_{1-x}C) = x a_{AC} + (1-x) a_{BC}, \quad (3.1)$$

where $a_{AC}$ and $a_{BC}$ are the equilibrium lattice constants of the binary compounds $AC$ and $BC$, respectively, and $a(A_xB_{1-x}C)$ is the alloy lattice constant. This is in agreement with previous experimental [35, 36] and theoretical investigations [37–40].
Table 1 Calculated lattice constant $a$ (in Å) and bulk modulus $B$ (in GPa) along with the experiment and theoretical ones for GaN$_x$As$_{1-x}$ compounds

<table>
<thead>
<tr>
<th>$x$</th>
<th>Our work LDA</th>
<th>Exp.</th>
<th>Other calculations</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaN$<em>x$As$</em>{1-x}$</td>
<td>0</td>
<td>5.61</td>
<td>5.75</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>5.40</td>
<td>5.55</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>5.15</td>
<td>5.27</td>
</tr>
<tr>
<td></td>
<td>0.75</td>
<td>4.82</td>
<td>4.94</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>4.47</td>
<td>4.56</td>
</tr>
</tbody>
</table>

The relation of the lattice constant exhibits a quadratic term as a result of the mismatch between the constants of the extreme binary alloys, $A_C$ and $B_C$. Therefore, the lattice constant is better described as follows:

$$a(A_xB_{1-x}C) = x a_{AC} + (1-x)a_{BC} - x(1-x)b.$$  
(3.2)

Here, the constant $b$ is the bowing parameter. The bowing of GaN$_x$As$_{1-x}$ compounds is found to be $-0.42114$ Å (LDA) and $-0.49783$ Å (GGA) and is presented in Fig. 1 using the two approximations, LDA and GGA. To study the hardness of the alloy when we doped it by nitrogen, N, starting from $x = 0.0$ until $x = 1.0$, we calculated the bulk modulus of GaN$_x$As$_{1-x}$ alloy for different concentrations of N. The variation of bulk modulus with increasing concentration of N in GaN$_x$As$_{1-x}$ alloy is shown in Fig. 2. We notice the quadratic variation of this bulk modulus with the con-
Fig. 3 The ionicity of the bonds at different concentrations for GaN$_x$As$_{1-x}$ compounds using GGA.

The ionicity of the bonds at different concentrations for GaN$_x$As$_{1-x}$ compounds using GGA shows that concentration $x$ and the alloy becomes stronger (hard) than the parent GaAs when we add nitrogen. Adding nitrogen N to GaN$_x$As$_{1-x}$ gives a recommendation for optoelectronic devices applications [1–8]. It is clearly seen that using the two approximations GGA and LDA gives the same behavior for the lattice parameter and the bulk modulus with slight differences in the values.

It is well known that the ionicity factor is correlated to the total valance charge density; therefore our calculations of the ionicity parameter have been carried out on the basis of the empirical model described in [51]. In this approach, the total area occupied by the valence charge density is divided into two parts with respect to the center. $\lambda S_C$ and $\lambda S_A$ are the area of the cation (Ga ions) and anion (N ions) sides, respectively, and the ionicity factor is defined as

$$f_i = \left( \frac{S_A}{S_A + \lambda S_C} \right)^{\lambda},$$

(3.3)

Fig. 4 Electronic band structure of GaN$_x$As$_{1-x}$ compounds for different concentration $x$ of N using EVGGA.
where $\lambda$ is a parameter separating the strongly ionic elements from the weak ones. Thus $\lambda = -1$ for III–V compound semiconductors.

In Fig. 3, we display the ionicity of the bonds at different concentrations. It is relevant to note that for all the alloys the ionicity of the N–Ga bond increases from $x = 0.0$ until $x = 0.25$ and then it becomes approximately constant, and that of the Ga–As bond decreases, while the bulk modulus increases by going from $x = 0.0$ to $x = 1.0$, which is due to the increasing of nitrogen concentration.

3.2 Electronic properties

3.2.1 Band structures and densities of states

The calculated band-structure energies of binary compounds as well as for their alloys using EVGGA approximation in-

![Graphs showing total and partial density of states for different concentrations of N in GaN$_x$As$_{1-x}$ compounds using EVGGA.]
dicate a direct band gap located at the gamma point in the whole range of concentrations. The lattice parameters used to investigate the electronic properties are found using the GGA approximation. Figures 4 and 5 show electronic band structure and the density of state for $x = 0.0, 0.25, 0.5, 0.75$ and 1.0 using EVGGA. The energetic results are presented in Table 2. It is clearly seen that the band gap values given by EVGGA are in reasonable agreement with the experimental ones and confirm the variation of energy gap with concentration of N using LDA, GGA and EVGGA as shown in Fig. 6.

It is clearly seen that the energy gap decreases until $x \cdot 0.25$ and after that it increases with increasing concentration $x$. The reduction in the band gap is explained due to the highly localized nature of the perturbation introduced by N atoms [52–57]. The largest contribution to the band
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Fig. 5 (Continued)

Table 2 Calculated energy gap (in eV) using LDA, GGA and EVGGA along with the experimental data and previous theoretical calculations for GaN$_x$As$_{1-x}$ compounds

<table>
<thead>
<tr>
<th>$E_g$ (eV)</th>
<th>LDA cal.</th>
<th>GGA cal.</th>
<th>EVGGA cal.</th>
<th>Experiment</th>
<th>Other work</th>
</tr>
</thead>
<tbody>
<tr>
<td>$X$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>0.4667</td>
<td>0.14517</td>
<td>0.6246</td>
<td>1.42$^a$</td>
<td>1.42$^c$</td>
</tr>
<tr>
<td>0.25</td>
<td>0</td>
<td>0</td>
<td>0.38</td>
<td></td>
<td>1.63$^b$</td>
</tr>
<tr>
<td>0.5</td>
<td>0</td>
<td>0.3281</td>
<td>0.16646</td>
<td>0.38</td>
<td></td>
</tr>
<tr>
<td>0.75</td>
<td>0</td>
<td>1.0087</td>
<td>0.6651</td>
<td>0.38</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>1.8959</td>
<td>1.5194</td>
<td>2.0470</td>
<td>3.38$^e$</td>
<td>3.82$^j$</td>
</tr>
</tbody>
</table>

a: ref. [41], b: ref. [42], c: ref. [43], d: ref. [24], e: ref. [44], f: ref. [45, 46], g: ref. [47], h: ref. [48], i: ref. [49], j: ref. [50]

gap reduction originate from structural relaxation of the alloy and charge exchange that are, respectively, proportional to the differences in the atomic orbital size and energy of the As and N atoms [52, 55].

Based on a very simple model, using a quantum dielectric theory, Munich and Pierret predicted a nearly linear monatomic increase in the band gap with increasing composition $x$ [58]. However, experimental results [59] show a strong red shift for small composition $x$ ($x < 0.015$).

Our results for the energy gap, obtained by quadratic fit, are presented and compared with the other available experimental and theoretical predictions in Table 2. The results are
shown in Fig. 6 and obey the following variations:

\[
\begin{align*}
E_{\text{LDA}}^{\text{Ga}}(x) &= 0.41 - 1.95x + 3.50x^2, \\
E_{\text{GGA}}^{\text{Ga}}(x) &= 0.14 - 1.29x + 2.66x^2, \\
E_{\text{EVGGA}}^{\text{Ga}}(x) &= 0.60 - 1.36x + 2.82x^2.
\end{align*}
\]

(3.4)

It has been seen that the main influence of the band gap energy is due to the lattice constant and the electronegativity mismatch of the parents’ atoms.

Now let us investigate the total and partial densities of states, Fig. 5 show the total density of states along with the Ga-s/p/d, N-s/p and As-s/p/d partial density of states for the binary and ternary alloys. Following the PDOS we are able to identify the angular momentum characters of various structures; from Fig. 5(a) for the parent compound GaAs one can see that As-p states is concentrated at the valence band maximum (VBM) whereas the conduction band minimum (CBM) is formed by As-s/p and Ga-s. When we replace one As atom by N atom (i.e; \(x = 0.25\)) we notice that replacing As atom by N atom cause to push Ga-s states in CBM toward Fermi energy \(E_F\) resulting in reduction the energy band gap \(E_g\) by around 0.244 eV keeping the VBM fix (see Fig. 5(b), (d)). After increasing the concentration of N to \(x = 0.5\) (replacing two As atoms by two N atoms), we notice that increasing the concentration of N atoms leads to pushing Ga-s (CBM) toward higher energies with respect to \(E_F\), resulting in increasing \(E_g\) by around 0.2757 eV (see Fig. 5(i)). Now we tried to replace three As atoms by N atoms (\(x = 0.75\)): we found that increasing the concentration of N atoms cause to push all of Ga-s and As-p toward higher energies with respect to \(E_F\) resulting in increasing the \(E_g\) by around 0.5272 eV (see Fig. 5(k–m)). Finally we replaced all As atoms by N atoms, and we notice that N-p states concentrated in both of VBM and CBM and cause significantly increasing the \(E_g\) by around 0.8641 eV (see Fig. 5(n), (o)). From above we should emphasize that by adding a low concentration of N one causes \(E_g\) to reduce with respect to the parent GaAs, while increasing the concentration of N leads to an increase of \(E_g\) by around double.

Pure ionic bonding is not known to exist. All ionic compounds have a degree of covalent bonding. The larger the difference in electronegativity between two atoms, the more ionic the bond. The ionic character of an alloy can be related to the charge transfer between the cationic and the

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**Fig. 6** Variation of energy gap with concentration \(x\) of N of Ga\(_{x}\)As\(_{1-x}\) compounds using LDA, GGA and EVGGA

**Fig. 7** Contour plot of total valence charge density in (110) plane for Ga\(_{x}\)As\(_{1-x}\) compounds for different concentration \(x\) of N
anionic sites. For this reason, we studied the nature of the bond for different concentrations of N in the GaN\(_{x}\)As\(_{1-x}\) compound. We have calculated the total charge density of GaN\(_{x}\)As\(_{1-x}\) compounds, in different planes and for different concentrations. Figure 7 illustrates all the bonds in the (110) plane containing Ga, As and N atoms. One can see clearly for the Ga-N bond that the bonding charge is displaced strongly toward the N atom, due to the difference between the electronegativity values of the two atoms, and the distributed of the charge are almost the same when we replace the As atoms by the N atoms (x = 0.25, 0.5, 0.75) in the alloy. However, the Ga–As bonds become more covalent when we substitute N in the place of As. This is in good agreement with the analysis done for Fig. 3. Generally speaking we conclude from the calculated electron charge distributions that the ionic character of GaN\(_{x}\)As\(_{1-x}\) tends to be more significant.

4 Conclusions

We have presented the results of FP-LAPW method and studied the composition dependence of the structural and electronic properties of GaN\(_{x}\)As\(_{1-x}\) compounds. The structural properties of these materials, in particular the composition dependence of the lattice constant, are found to be almost linear. The bulk modulus for the alloys of interest increases by increasing the N concentration. This indicates the effect of nitrogen when we add it to the parent GaAs; the compound becomes stronger. The electronic properties are very well described by calculating the band gap that exhibits non-linear behavior versus the concentration. The energy gap decreases until x = 0.25 and after that it increases with the concentration x. Finally, the densities of states and the band structure are also presented; we have found that the binary compound GaAs possesses a small and direct band gap, while the intermediate concentrations still possesses a direct band gap but the value of the band gap increase with increasing the concentration of N.

Acknowledgements Z.C, H.B and B.H would like to acknowledge Max-Planck institute for the financial support. For the author Ali Hussein Reshak this work was supported from the program RDI of the Czech Republic, the project CENAKVA (No. 1.05/2.1/0001.0024), the grant No. 152/2010/Z of the Grant Agency of the University of South Bohemia. School of Material Engineering, Malaysia University of Perlis, P.O. Box 77, d/a Pejabat Pos Besar, 01007 Kangar, Perlis, Malaysia. Y.A. work was supported from FRGS grants numbered: 9003-00249 & 9003-00255, and the author would like to acknowledge TWAS-Italy and JUST-Jordan for their financial and technical supports, respectively, within his scientific visit under TWAS UNESCO Associateship.

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