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STRUCTURAL AND ELECTRONIC PROPERTIES OF GaAsBi

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Abstract

The structural and electronic properties of the GaAs$_{1-x}$Bi$_x$ ternary alloy are investigated by means of two first principles and full potential methods, the linear augmented plane waves (FPLAPW) method and a recent version of the full potential linear muffin-tin orbitals method (FPLMTO) which enables an accurate treatment of the interstitial regions. In particular, we have found that the maximal GaBi mole fraction $x$ for which GaBi$_x$As$_{1-x}$ remains a semiconductor is probably around $x = 0.5$. The electronic properties of (GaAs)$_m$/(GaBi)$_n$ quantum well superlattices (SLs) have also been calculated and it is found that such SLs are semiconductors when $m$ is larger or equal to $n$. 
1. Introduction

The GaAsBi alloy made of a semimetallic GaBi and a semiconducting GaAs has been successfully grown [1, 2, 3]. The advantage of this ternary and similar alloys combining semi–metals and semiconductors is the possibility of obtaining bandgaps insensitive to temperature. For example, the measurements show that the temperature coefficient of the bandgap of GaAs$_{0.974}$Bi$_{0.026}$ is only a third that of the GaAs at room temperature [4]. The peak energy of photoluminescence (PL) was demonstrated to be temperature-insensitive compared with that of GaAs [1]. Nitrogen can also be incorporated in this alloy to form the GaNAsBi quaternary which is suitable for LASER applications. GaNAsBi has also been obtained by molecular beam epitaxy [5, 6] and its bandgap has been found more temperature insensitive than the InGaAsP. Huang et al [6] have confirmed that the temperature coefficients of GaAsBi and GaNAsBi band gaps are governed by the GaBi molar fraction and that they decrease with increasing GaBi molar fraction. However, few theoretical results are available on such systems. This is probably due to the fact that compared to other III-V materials, less is known about GaBi, AlBi and InBi binaries. Few studies have addressed the problem of the equilibrium phase of these materials and the effect of the pressure has not received more attention. Using the first principles FPLAPW method, Ferhat et al [7, 8] have found that the zinc-blende structure is the most stable for AlBi and GaBi while InBi prefers the tetragonal PbO structure. In the zinc blende (B3) phase, first principle calculations show that GaBi and InBi are conductors, while AlBi is found to be a semiconductor with a small direct band gap of 42 meV at Γ and a linear relation between the bulk modulus and the cell volume for the zinc blende phase was found [9]. The results of ref [9] confirm those of ref [7] except that the second reference does not show the InBi band structure in the zinc blende phase but in the PbO phase.

The purpose of this work is to investigate the structural and the opto-electronic properties of the GaAsBi ternary materials and also of the binaries constituting it, especially GaBi and to calculate the maximal GaBi mole fraction $x$ for which GaBi$_x$As$_{1-x}$ remains a semiconductor. The problem of SLs made of both GaBi and GaAs binaries is discussed.

The paper is organized as follows. The properties of bulk GaBi binary are presented in section 2 then the GaAsBi ternary and GaAs/GaBi SLs are discussed in sections 3 and 4 respectively. Conclusions are summarized in section 5.

2. Bulk GaBi

Because there are few theoretical results in literature about GaBi in its zinc blende ground state phase, we have employed two first principles methods in the framework of the density functional theory [10, 11].
The first one being the Savrasov version of the full potential linear muffin-tin orbitals (FPLMTO) method [12] as implemented in the lmART code [13] and the second one the full potential linear augmented plane wave (FPLAPW) method [14] as implemented in the WIEN97 code [15]. The exchange and correlation effects are described within the parameterization of Perdew et al [16]. In both methods, the unit cell is divided into non overlapping muffin-tin spheres of radius RMTS and an interstitial region, the Kohn-Sham wave functions being expressed in spherical harmonics within spheres.

At the reverse of the previous LMTO methods, the present FPLMTO treats the interstitial regions on the same footing with the core regions. The non overlapping muffin tin spheres potential is expanded in spherical harmonics inside the spheres and Fourier transformed in the interstitial regions [12]. In the FPLAPW method, the relative Kohn-Sham wave functions are expressed in plane waves in the interstitial regions so that they are treated correctly. RMTS of Ga was fixed to 2.44 a.u in FPLMTO and to 2.3 in FPLAPW while RMTS of Bi was taken equal to 2.752 in FPLMTO and 2.5 in FPLAPW. In FPLMTO, the Fourier divisions, the K-mesh and consequently the cut-off energies and the plane waves involved in calculations have been chosen so that \( l_{\text{max}} = 6 \) was sufficient to reach accurate eigenvalues while \( l_{\text{max}} \) was taken equal to 10 in FPLAPW. The comparison of the FPLMTO and FPLAPW results for GaBi is a supplementary test to check the accuracy of our results and parameters involved in the calculations, so that, in the case of the GaAsBi ternary alloy and of the GaAs/GaBi superlattice, we need only to use the FPLMTO method.

First, we have calculated the total energy of the zinc blende GaBi as a function of the volume. Then, by fitting to the Murnaghan equation of state [17], the equilibrium volume, the equilibrium lattice constant, the bulk modulus \( B \) and its derivative have been calculated. The results are summarized in Table 1. The calculated lattice parameters and bulk modulus are in good agreement with the recent FPLAPW [7] and with the LDA first-principles pseudopotential [9] calculations.

Both FPLMTO and FPLAPW band structure calculations predict a semi–metallic behaviour for GaBi. Conduction bands (CB) being mixed with valence bands (VB) (Fig. 1). We notice that at \( \Gamma \), the gap is almost zero and we will see below that this is also the case in the alloy and SL systems involving GaBi.

3. GaAsBi ternary

All the following calculations were carried out using FPLMTO within the same above parameterization of Perdew et al. The equilibrium lattice constant, the bulk modulus and its derivative for zinc blende GaAs were found to be equal to 5.624 Å, 71.788 GPa and 4.641 respectively. Then, we have performed minimization calculations for several GaAs\(_{1-x}\)Bi\(_x\) alloys, i.e., for \( x = 0 \) (GaAs), 0.25, 0.5, 075 and 1 (GaBi).
We have made these calculations assuming that these alloys are obtained from GaBi and GaAs crystallizing in the zinc blende (B3) structure. However, their ternary alloy does not keep the symmetry of the binary “parents”. The ternaries present an elementary unit cell that is cubic with a lattice parameter \( a_0 \) and a volume \( a_0^3 \). Then, the equilibrium lattice parameter, the bulk modulus and its derivative have been deduced in the same way as for the bulk. Table 2 summarizes our results. We remark that the lattice parameter \( a_0 \) increases with the Bi mole fraction \( x \) while the bulk modulus decreases. Both of them follow approximately the virtual crystal approximation (VCA).

GaAs is known to have a direct fundamental gap at \( \Gamma \). Our calculations give 0.34 eV for this gap, of course underestimated by LDA (Fig. 2). The band structure calculations for the three cases \( (x=0.25, 0.5 \text{ and } 0.75) \) of the ternary have been performed (Fig. 3). We remark a direct but approximately zero \( \Gamma-\Gamma \) fundamental gap for \( \text{GaAs}_{0.75}\text{Bi}_{0.25} \) which is then expected to be a semiconductor since its experimental gap may be higher. In the case of \( \text{GaAs}_{0.50}\text{Bi}_{0.50} \), a semi–metallic gap is obtained. The CB bottom is crossed by the Fermi level. However, the negative gap which is obtained is so small that we expect that it is probably due to LDA and that this alloy may also be a semiconductor with an indirect gap. Similar remark holds for \( \text{GaAs}_{0.25}\text{Bi}_{0.75} \) but the negative gap becomes more severe so that the semi–metallic nature of the compound is more probable. A remarkable fact is that in all cases, the \( \Gamma-\Gamma \) gap remains approximately zero like in bulk GaBi and this is attributed to the prevailing of the contribution of Bi compared with that of As.

4. GaAs/GaBi superlattices

The SL has a different symmetry. For reasons of commodity, we restrict ourselves to \((\text{GaAs})_m/ (\text{GaBi})_n \) SLs with \( m+n \) even, \( m \) and \( n \) being the number of monolayers, each monolayer contains one cation and one anion. In Fig. 4, we show the direct lattice of a (001) growth axis zinc blende/zinc blende \((\text{GaAs})_{m-1}/(\text{GaBi})_{n-1}\) SL which has a tetragonal symmetry. The link between the bulk and the SL direct lattices is shown in the figure. The volume of the of the tetragonal SL is \( V_{\text{SL}}=2L.V_B \), with \( L=(m+n)/2 \), \( V_B \) being the volume of the bulk. The SL equilibrium volume \( V_0 \) is taken equal to \( V_{\text{SL}} \) divided by \( m+n \) (number of formula units). Results of the minimization calculation of \((\text{GaAs})_m/ (\text{GaBi})_n \) quantum well SLs with \((m, n)=(3,1), (2,2) \text{ and } (1,3) \) are summarized in Table 3. In particular, the lattice constants (multiplied by \( \sqrt{2} \)) and the bulk modulus were found to be the same in SLs than in ternaries for the same proportion of Bi (Figs. 5 and 6).

The band structure of our SLs is shown in Fig. 7. An approximately zero \( \Gamma-\Gamma \) fundamental gap is present for \((m, n)=(3,1), (2,2) \). Knowing that gaps are underestimated by LDA, these two SLs are probably semiconductors. On the other hand, \((\text{GaAs})_{m-1}/(\text{GaBi})_{n-3} \) is probably a semi-metal since the Fermi level crosses VB.
5. Conclusion

In summary, the structural and electronic properties of GaBi and its ternary alloys and SLs with GaAs have been investigated within both FPLAPW and PLW-FPLMTO methods. It has been found that these systems are probably semiconductors when there is at least the same proportion of GaAs than GaBi. For a lower proportion of GaAs, a semi-metallic behaviour is expected.

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References

Table 1: The structural parameters of GaBi ($V_0 = a_0^3/4$ is the equilibrium volume, $a_0$ the lattice constant, $B_0$ the bulk modulus and $B'_0$ is its pressure derivative). The volume per unit formula is taken into account.

<table>
<thead>
<tr>
<th>Material</th>
<th>$a_0$ (Å)</th>
<th>$V_0$ (Å$^3$)</th>
<th>$B_0$ (GPa)</th>
<th>$B'_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>FPLMTO: LDA + Perdew92</td>
<td>6.304</td>
<td>62.645</td>
<td>43.250</td>
<td>4.847</td>
</tr>
<tr>
<td>FPLAPW: LDA + Perdew92</td>
<td>6.275</td>
<td>61.758</td>
<td>46.260</td>
<td>4.371</td>
</tr>
</tbody>
</table>


Table 2: The structural parameters of GaAs$_{1-x}$Bi$_x$ in ZnS (B3) phase, calculated with FPLMTO: LDA + Perdew92.

<table>
<thead>
<tr>
<th>Material</th>
<th>$a_0$ (Å)</th>
<th>$V_0$ (Å$^3$)</th>
<th>$B_0$ (GPa)</th>
<th>$B'_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaAs$<em>{0.75}$Bi$</em>{0.25}$</td>
<td>5.8129 [*]</td>
<td>49.1053 [*]</td>
<td>62.2265 [*]</td>
<td>4.0438 [*]</td>
</tr>
<tr>
<td>GaAs$<em>{0.50}$Bi$</em>{0.50}$</td>
<td>5.9912 [*]</td>
<td>53.7636 [*]</td>
<td>53.9885 [*]</td>
<td>4.6326 [*]</td>
</tr>
<tr>
<td>GaAs$<em>{0.25}$Bi$</em>{0.75}$</td>
<td>6.1556 [*]</td>
<td>58.3115 [*]</td>
<td>46.6331 [*]</td>
<td>4.5722 [*]</td>
</tr>
</tbody>
</table>

Table 3: FPLMTO: LDA + Perdew92 results for the structural parameters of the zinc blende (GaAs)$_m$/(GaBi)$_n$ quantum well superlattices (SLs) for different values of $m$ and $n$. The volume of the of the tetragonal SLs is $V_{SL} = 2L V_0$, with $L = (m+n)/2$. $V_0$ is taken equal to $V_{SL}/(m+n)$ for SLs. The relation between the equilibrium lattice constants of SL and its bulk parents is: $a_0 = \sqrt{2} a_{SL}$.

<table>
<thead>
<tr>
<th>Material</th>
<th>$a_0$ (Å)</th>
<th>$a_{SL}$ (Å)</th>
<th>$V_0$ (Å$^3$)</th>
<th>$c_{eq}/a_{eq}$</th>
<th>$B_{eq}$ (GPa)</th>
<th>$B'_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(GaAs)$_1$/(GaBi)$_1$</td>
<td>5.8114</td>
<td>4.1093</td>
<td>49.0663</td>
<td>2. $\sqrt{2}$</td>
<td>58.5488</td>
<td>4.6561</td>
</tr>
<tr>
<td>(GaAs)$_2$/(GaBi)$_2$</td>
<td>5.9872</td>
<td>4.2336</td>
<td>53.6566</td>
<td>2. $\sqrt{2}$</td>
<td>53.2530</td>
<td>4.8614</td>
</tr>
<tr>
<td>(GaAs)$_3$/(GaBi)$_3$</td>
<td>6.1483</td>
<td>4.3475</td>
<td>58.1045</td>
<td>2. $\sqrt{2}$</td>
<td>44.7207</td>
<td>4.7884</td>
</tr>
<tr>
<td>Definitive</td>
<td></td>
<td></td>
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</table>

References:
Fig. 1: FPLMTO band structure of bulk GaBi in the zinc blende phase.

Fig. 2: The FPLMTO band structure of bulk GaAs
Fig. 3: The FPLMTO band structure of bulk GaBi and GaAs in the ZB phase and of their alloys.

Fig. 4: Bulk and (001) SL(1,1) primitive cells. \(X_{SL}, Y_{SL}\) and \(Z_{SL}\) are the primitive translation set for SL (1,1). Dots of different colours represent GaBi or GaAs nodes containing two atoms each. \(a_{SL}\) is the lattice constant of the SL.
Fig. 5: Lattice parameter variation with the Bi fraction in the alloys which corresponds to the GaBi monolayers number of SLs.

Fig. 6: Lattice parameter variation with the Bi fraction in the alloys which corresponds to the GaBi monolayers number of SLs.
Fig. 7: The FPLMTO band structure of $(\text{GaAs})_m(\text{GaBi})_n$ SLs.