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First-principles investigation of BAs and $B_xGa_{1-x}As$ alloys*

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Using first-principles calculations in the generalized gradient approximation, the electronic properties of BAs and $B_xGa_{1-x}As$ alloys are studied. At the Brillouin-zone centre, the lowest conduction band is the three-degenerate p-like Γ_{15c} state rather than s-like Γ_{1c} state, and the conduction band minimum (CBM) is along the Δ line between the Γ and X points-at approximately $11/14(1,0,0)2\pi/a$. With boron content at 0%–18.75%, $B_xGa_{1-x}As$ alloys have a small (2.6 eV) and relatively composition-independent band-gap bowing parameter, the band-gap increases monotonically by ∼18 meV/B% with increasing boron content. In addition, the formation enthalpies of mixing for $B_xGa_{1-x}As$ alloys with boron content at 6.25% and 12.5% are calculated, and the large formation enthalpies may explain the difficulty in alloying boron to GaAs.

Keywords: bowing parameter, formation enthalpy, band-gap, boride alloys
PACC: 7280E, 7115A, 7125R

1. Introduction

Recently, boron compounds are gaining much interest because they offer a new class of materials and open new possibilities for band-gap engineering in III–V related materials.[1−6] In 2006, Ren *et al*[7] systematically predicted that four boride III–V quaternary alloys may reach the range of 1.55μm emissions while the lattice matches to that of GaAs; among them $B_xGa_yIn_{1-x-y}As$ is especially notable, which is commonly expected to be another material with its direct transition band-gap below 1eV, while its lattice matches to that of GaAs, just as $Ga_xIn_{1-x}As_yN_{1-y}$.[8]

However, in BAs and $B_xGa_{1-x}As$ alloys, as the most important binary and ternary components in $B_xGa_yIn_{1-x-y}As$, their electronic properties are still not clear very much due to the difficulty in synthesizing them; at present there are some research papers on them both in theory and experiment, which mainly focus on how alloying with BAs affects the band-gap as well as other properties of GaAs.[9−12] In this paper, the electronic properties of zinc-blende $B_xGa_{1-x}As$ alloys with boron content as high as 18.75% are calculated using 32-atom special quasi-random structure (SQS-16) supercells, which corresponds to 2×2×1 conventional cells, of which the band-gaps are obtained to determine the bowing parameters; in addition, the formation enthalpies of mixing with boron content at 6.25% and 12.5% are calculated.

2. Calculation details

The electronic properties of BAs and $B_xGa_{1-x}As$ alloys are investigated using the CASTEP simulation program.[13] In this simulation program, the calculation is performed using the Kohn–Sham formation,[14] which is based on the density functional theory (DFT). Generalized gradient approximation (GGA) is made for the electronic exchange-correlation potential energy. The Coulomb potential energy caused by electron-ion interaction is described using ultra-

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soft scheme,[15] in which the orbitals of B ($2s^22p^1$), Ga ($3d^{10}4s^24p^1$), and As ($4s^24p^3$) are treated as valence electrons. Under the norm-conservation condition, the pseudo-wave function related to pseudopotential matches the plane-wave function expanded with Kohn–Sham formation beyond a cutoff energy. Ultrasoft pseudopotentials allow the calculation to be performed at a lower cutoff energy; in this calculation a cutoff energy of 295 eV is used.

3. Results and discussion

3.1. BAs electronic properties

Because the band structure of supercell shows zone folding,[16] we employ a two-atom primitive cell to calculate the electronic properties of BAs, the lattice constant of its corresponding zinc-blende conventional cell is the experimental value of 0.4777 nm.[17,18] Figure 1 is the calculated band structure along principal high-symmetry points as a function of k. It shows that the conduction band minimum (CBM) is along the Δ line between the Γ and X points-at approximately $11/14(1,0,0)2\pi/a$; at the Brillouin-zone centre, the lowest conduction band is the three-degenerate p-like Γ_{15c} state rather than s-like Γ_{1c} state. This reversal relative to most other Group-III-V compounds can be explained by the tight-binding model of Harrison.[19] Figure 2 shows the corresponding partial density of state (PDOS) in Fig.1, in which the upper parts of the valence bands are dominated by p states and the lower parts are dominated by s states with little mixing between them, while the p and s states are strongly mixed in the conduction band.

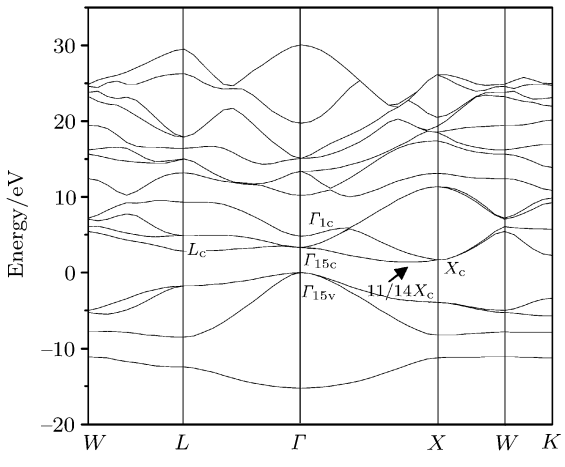


Fig.1. Band structure of BAs along principal high-symmetry points as a function of k.

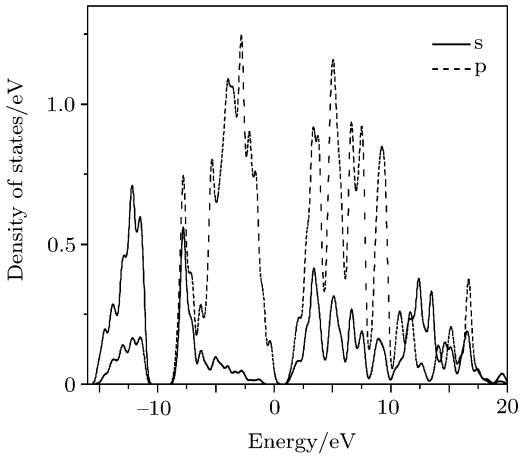


Fig.2. The partial densities-of-states for BAs, indicating that the p and s states are strongly mixed in the conduction band.

Table 1 lists the calculated direct and indirect transition energy-gaps. Due to no reliable experimental data, the GW (which evaluates the electron self-energy to the first order in the electron Green's function G and the screened Coulomb interaction W) calculations are considered to give energy-gaps in excellent agreement with experimental data for such semiconductors as BN, BP and BAs;[20,21] therefore, the GW calculations are also listed for comparison. From Table 1 it can be seen that compared to the GW calculations, the GGA band structures commonly underestimates the energy-gaps;[21–23] the magnitude of the error is $\sim 0.7- \sim 0.9$ eV for the direct transition $\Gamma_{15v} - \Gamma_{1c}$ and $\Gamma_{15v} - \Gamma_{15c}$ energy-gaps, and $\sim$0.2 eV for the indirect transition $\Gamma_{15v} - \Delta_{min}$ and $\Gamma_{15v} - X_{1c}$ energy-gaps. Obviously, compared to the local density approximation (LDA), GGA can reduce the error.[24]

3.2. The electronic properties of $B_xGa_{1-x}As$ alloys

GaAs is a direct band-gap semiconductor with the $\Gamma_{1c} - L_c - X_c - \Gamma_{15c}$ ordering of the conduction valley minima,[25] which is completely different from the band structure of BAs, therefore, the band structure of $B_xGa_{1-x}As$ is complicated very much; however, it must be GaAs-like in Ga-enriched condition and BAs-like in B-enriched condition. In Ref.[7] it was considered that the band-gap of $B_xGa_{1-x}As$ is the direct transition $\Gamma_{15v} - \Gamma_{1c}$ energy-gaps from x=0 (GaAs) to x=0.3. In this work, we use SQS-16 supercells to model a random alloy $B_xGa_{1-x}As$, of which the lattice parameter $a(x)$ is assumed to comply with a simple Vegard law. The band-gaps ($\Gamma_{15v} - \Gamma_{1c}$ energy-gap)

are calculated with their different configurations to mimic the atom random occupations. Tables 2 and 3 list the corresponding boron coordinates, as well as the weight and calculated results.

Table 1. Calculated and experimental direct and indirect energy-gaps (eV) of BAs.

	$\Gamma_{15v}-\Gamma_{15c}$	$\Gamma_{15v}-\Gamma_{1c}$	$\Gamma_{15v}-\Delta_{min}$	$\Gamma_{15v}-X_{1c}$	$\Gamma_{15v}-L_{1c}$
GGA[a)]	3.351	4.806	1.383	1.660	2.811
GW [b)]	4.2	5.5	1.6	1.86	
LDA[c)]	3.30		1.06 (0.8,0,0)	1.33	

[a)] This work, [b)] Ref.[20], [c)] Ref.[21].

The energy-gap bowing parameter is calculated by the following definition,

$$E_g(A_xB_{1-x}) = x\cdot E_g(A) + (1-x)\cdot E_g(B) - b(x)\cdot x\cdot(1-x), \quad (1)$$

where $E_g(A)$ and $E_g(B)$ are the calculated pure constituent energy-gaps, and $E_g(A_xB_{1-x})$ is the calculated alloy energy-gap at boron content x; in this case, the GGA errors can be neglected since only the relatively values are important.[4,9] Table 4 shows the calculated energy-gap ($\Gamma_{15v}-\Gamma_{1c}$) bowings, which are ∼2.4 eV, ∼2.6 eV and ∼2.7 eV for x=6.25%, 12.5% and 18.75% respectively. Thus, a small and relatively composition-independent band-gap bowing parameter of ∼2.6 eV is obtained with x in the 0%–18.75% range. In a recent experimental study,[2] optical bowing parameters of 1.6±0.3 eV and 2.3±0.3 eV for x=2%–4% are obtained using theoretical estimates of the direct-gap (direct transition $\Gamma_{15v}-\Gamma_{1c}$ energy-gaps) of cubic BAs of 3.56 eV and 4.23eV, respectively. As shown in Table 1, 4.23 eV is nearer to the experimental value than 3.56 eV for the direct-gap of BAs, but it is still underestimated. Therefore, the band-gap bowing parameter should be larger than 2.3eV, well coincided with the calculated value of 2.4 eV with x=6.25% in this work.

Table 2. Boron pair coordinates, symmetry group, weight, the calculated band-gaps ($\Gamma_{15v}-\Gamma_{1c}$ energy-gap), as well as the corresponding average band-gap for $B_2Ga_{14}As_{16}$, for a typified value x=12.5% in $B_xGa_{1-x}As$ alloys.

Boron coordinates	symmetry group	weight	E_g/eV
(0,0,0) (3/4,3/4,1)	$CMM2$	4	0.848
(0,0,0) (3/4,1/2,1/2)	$P21212$	4	0.860
(0,0,0) (1/2,1/2,0)	P-$4M2$	1	0.811
(0,0,0) (1,1/4,1/2)	$P2221$	4	0.835
(0,0,0) (0,0,1)	P-$42M$	2	0.808
			average E_g= 0.840

Table 3. Three-boron configuration coordinates, symmetry group, weight, the calculated band-gaps ($\Gamma_{15v}-\Gamma_{1c}$ energy-gap), as well as the corresponding average band-gap for a typified value x=18.75% in $B_3Ga_{13}As_{16}$.

Boron coordinates	symmetry group	weight	E_g/eV
(0,0,0) (3/4,1/4,0) (1/2,1/4,1/2)	$P1$	24	0.993
(0,0,0) (1/2,1/4,1/2) (1/2,3/4,1/2)	222	13	0.971
(0,0,0) (3/4,1/2,1/2) (1/2,3/4,1/2)	CM	24	1.023
(0,0,0) (1/4,3/4,1) (1/2,1/2,1)	$CMM2$	8	0.957
(0,0,0) (1/4,3/4,1) (3/4,3/4,1)	$P2$	33	0.946
(0,0,0) (0,1/2,1) (1/2,1/2,1)	P-$42M$	3	0.854
			average E_g = 0.976

Table 4. The calculated direct-gaps ($\Gamma_{15v} - \Gamma_{1c}$) for $B_xGa_{1-x}As$ alloys with boron content of x, as well as the corresponding bowing parameter.

System	x/%	$E_g(x)$	bowing, b/eV
$Ga_{16}As_{16}$	0	0.606	
$B_1Ga_{15}As_{16}$	6.25	0.727	2.4
$B_2Ga_{14}As_{16}$	12.5	0.840	2.6
$B_3Ga_{13}As_{16}$	18.75	0.976	2.7
$B_{16}As_{16}$	100	4.781	

To mimic the experimental band-gap of $B_xGa_{1-x}As$ with boron content ranging from 0% to 18.25%, we correct the calculated band-gaps at each composition using Eq.(1), the GW-estimated value (5.5 eV) for BAs and experimental value of 1.519 eV[24] for GaAs are used as their actual direct-gaps ($\Gamma_{15v} - \Gamma_{1c}$), $b(x)$ is the calculated bowing parameter listed in Table 4. The revised $B_xGa_{1-x}As$ band-gaps are 1.63, 1.73 and 1.85 eV with boron contents of 6.25%, 12.5% and 18.75%, respectively. Accordingly, addition of boron to GaAs will raise the band-gap, the average increment in the range of 0%–6.25%, 6.25%–12.5% and 12.5%–18.75% is about 18meV/%B,16meV/%B and 19 meV/%B, respectively, in good agreement with 14 meV/%B measured by photomodulation spectroscopic measurements with boron content ranging from 1% to 3%–5.6%,[10] a 1-eV-gap alloy cannot be realized with the addition of boron to GaAs, other than nitrogen to GaAs.[26]

Formation enthalpies of mixing are determined by taking the difference between the energy of the alloy and that of the weighted sum of the constituents A and B:

$$\Delta H(x) = E_{A_xB_{1-x}} - [(1-x)\cdot E_A + x\cdot E_B]. \quad (2)$$

In this work, we calculate the formation enthalpies of mixing for $B_xGa_{1-x}As$ alloys with boron contents of 6.25% and 12.5%. Figure 3 illustrates the trends of variation for the calculated formation enthalpies of mixing: they are 77.2 and 146.5 meV/atom for x=6.25% and 12.5%, respectively. With increasing boron content the alloy exhibits a net increase of mixing enthalpy. Higher formation enthalpy implies a large strain energy, which may result in the deteriorating of alloy crystallinity if strain effects cannot be counterbalanced by chemical effects (i.e., enhanced bonding) during alloying.[4] To illustrate this point, the mixing enthalpies of $Al_xGa_{1-x}As$ and $In_xGa_{1-x}As$ alloys with $x = 6.25\%$ and 12.5% are also given in Fig.3. It can be seen that the two alloys have much smaller mixing enthalpy than $B_xGa_{1-x}As$. As is well known, $Al_xGa_{1-x}As$ and $In_xGa_{1-x}As$ alloys can exist for whole composition range, therefore, the large mixing enthalpies may be the main reason for the difficulty in alloying boron to GaAs.

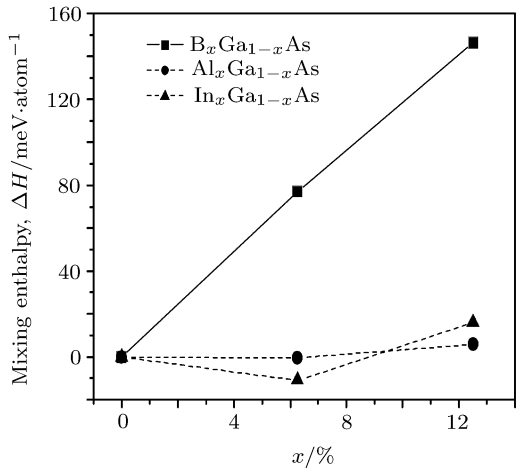


Fig.3. Comparison of formation enthalpies of mixing for $B_xGa_{1-x}As$, $Al_xGa_{1-x}As$, $In_xGa_{1-x}As$ alloys.

4. Conclusions

The electronic properties of zinc-blende BAs and $B_xGa_{1-x}As$ alloys are calculated using first-principles method in the GGA. At the Brillouin-zone centre, the lowest conduction band is the three degenerate p-likeΓ_{15c} state rather than s-likeΓ_{1c} state. The conduction band minimum is along the Δ line between the Γ and X points - at approximately $11/14(1,0,0)2\pi/a$. By using 32-atom special quasi-random structure (SQS-16) supercells to model a random alloy, the electronic properties of $B_xGa_{1-x}As$ with x=18.75% are studied; in this composition range a small (2.6 eV) and relatively composition-independent band-gap bowing parameter is obtained. The behaviour of $B_xGa_{1-x}As$ alloys is different from $GaAs_xN_{1-x}$, addition of boron to GaAs will raise its band-gap, the average increment in the ranges of x=0%–6.25%, 6.25%–12.5% and 12.5%–18.75% is about 18, 16 and 19 meV/%B, respectively. These results are in good accordance with the experimental values. In addition, the formation enthalpies of mixing for $B_xGa_{1-x}As$ alloys are calculated: they are 77.2 and 146.5 meV/atom for x=6.25% and 12.5%, respectively. With increasing boron content the alloys exhibit a net increase of mixing enthalpy. Compared to $Al_xGa_{1-x}As$ and $In_xGa_{1-x}As$ alloys, the large mixing enthalpies of $B_xGa_{1-x}As$ alloys may explain the difficulty in alloying boron in GaAs.

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