Theoretical study of the effects of isovalent coalloying of Bi and N in GaAs

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$GaAs_{1-x}N_x$ alloys have unique properties among the III-V systems to simultaneously lower both the lattice constant and the band gap. Therefore, it has a strong potential for optoelectronic device applications. However, due to the large size mismatch between N and As, the growth of high-quality GaAsN alloy on GaAs substrates is difficult. To overcome this problem, we propose here a material, the $GaAs_{1-x-y}N_xBi_y$ alloy, which can be lattice matched to GaAs with the appropriate ratio between the concentration of Bi and N ($y = 1.7x$). Based on band structure and total-energy calculations we show that coalloying of Bi and N in GaAs lowers the alloy-formation energy and drastically reduces the amount of N needed to reach the 1-eV band gap, which is important for high-efficiency solar cell and infrared-laser applications.

I. INTRODUCTION

Recent advances in optoelectronic device applications require design and growth of materials with specific structural and optical properties. For example, it is highly desirable to have a good quality ~ 1 eV material that is lattice matched to GaAs for application in 1.3-μm solid-state lasers[1] and high-efficiency multijunction solar cells.[2–5] A GaAs alloy containing a few percent of N is a strong candidate for this purpose. Due to the giant bowing coefficient,[6] $GaAs_{1-x}N_x$ alloys provide the rare opportunity among the III-V systems to simultaneously lower both the lattice constant and the band gap. However, due to the large size mismatch between N and As, the growth of high-quality $GaAs_{1-x}N_x$ alloy on GaAs substrates is difficult. In order to overcome this problem the coalloying approach is proposed. By substituting large-atom X (e.g., $X = $ In on the cation site or $X = $ Sb on the anion site), the new alloy XGaAsN can be made lattice matched to GaAs and has a band gap close to 1 eV. Most of the previous efforts focused on the growth of $In_yGa_{1-y}As_{1-x}N_x$ on a GaAs substrate. However, it appears that when the N concentration increases, the alloy quality deteriorates very fast as reflected by very low photoluminescence efficiency and very short diffusion length, impeding the use of $In_xGa_{1-x}As_{1-y}N_y$ in device applications.[4,5] Furthermore, experimental observations show that the presence of In does not significantly affect the incorporation of N in GaAs.[7] This is consistent with the fact that for this quaternary $Ga_{1-x}In_xAs_{1-y}N_y$ alloy with both mixed anions and mixed cations, the reduction of strain by forming (Ga-As) $+$(In-N) type of bonds is compensated by the weakening of the bonds when compared with the formation of the (Ga-N)$+$(In-As)-type bonds. Thus, in this case, coalloying of a large atom (In) with a smaller atom (N) does not significantly reduce the total alloy-formation energies.

In this paper we investigate a III-V alloy, $GaAs_{1-x-y}N_xBi_y$, as a potential candidate for the 1-eV band-gap material that is lattice matched to GaAs. Compared to the $Ga_{1-x}In_xAs_{1-y}N_y$ alloy, $GaAs_{1-x-y}N_xBi_y$ offers the following advantages.

(i) There is only one type of cation, Ga; thus, the strain reduction of coalloying N and Bi in GaAs is not compen-

sated by the weakening of the chemical bond energy. This can possibly increase the crystal quality of the alloy.[7]

(ii) The alloy-stabilized zinc-blende GaBi is expected to have a very negative band gap due to the large size of Bi; thus, it is possible that only a small amount of N is needed to lower the alloy band gap to 1 eV. This can possibly improve the optical and transport properties of the alloy.

(iii) Relative to GaAs, $GaAs_{1-x-y}N_xBi_y$ has a higher valence-band maximum (VBM), whereas $Ga_{1-x}In_xAs_{1-y}N_y$ has a lower conduction-band minimum. Thus, according to the doping limit rule,[8] $GaAs_{1-x-y}N_xBi_y$ can be doped more easily p type, whereas $Ga_{1-x}In_xAs_{1-y}N_y$ can be doped more easily n type. Therefore, $GaAs_{1-x-y}N_xBi_y$ alloys can be used as a complementary material to form p-n junctions with $Ga_{1-x}In_xAs_{1-y}N_y$ alloys.

II. METHODS OF CALCULATION

We have calculated the electronic and structural properties of the $GaAs_{1-x-y}N_xBi_y$ alloy and its binary constituents GaN, GaAs, and GaBi in the zinc-blende phase.[9] The calculations are performed using the density-functional formalism[10] and the local-density approximation (LDA) as implemented by the full-potential linearized augmented plane-wave method.[11] We use the Ceperley-Alder exchange correlation potentials as parametrized by Perdew and Zunger.[12,13] The Ga $3d$ electrons were treated as valence electrons.

III. RESULTS AND DISCUSSIONS

A. Binary compounds

In order to analyze the electronic and structural properties of the $Ga_{1-x}As_xN_{1-y}Bi_y$ alloys, it is essential to know the lattice constant and band gap of the binary constituents, such as the alloy-stabilized zinc-blende phase of GaBi. Table I presents our calculated equilibrium lattice constant a, bulk modulus B, and the pressure coefficient of the bulk modulus B' for GaN, GaAs, and GaBi. For completeness, the results for InBi are also included. The calculated LDA structural parameters for GaAs and GaN are in very good agreement with experimental values.[14–16] For GaBi, the experimentally

TABLE I. Calculated equilibrium lattice constant a, bulk modulus B, and the pressure derivative of the bulk modulus for InBi, GaBi, GaAs, and GaN in the zinc-blende phase. The calculated values are compared with available experimental values (Ref. 14).

Properties	InBi	GaBi	GaAs		GaN	
	Calc.	Calc.	Calc.	Exp.	Calc.	Exp.
a (Å)	6.686	6.324	5.649	5.653	4.488	4.50
B (Mbar)	0.383	0.451	0.742	0.756	2.063	2.05
B'	5.0	4.9	4.8	4.67	4.6	

estimated[17] lattice constant is 6.234 Å, smaller than our calculated value of $a = 6.324$ Å. The difference is possibly due to the large uncertainty in the experimental value, because it was obtained by extrapolation of the $GaAs_{1-x}Bi_x$ alloy data with $x \leq 0.03$. For InBi, and for the same reason, the experimentally estimated lattice constants range from 6.5 to 7.204 Å.[18] Our calculated value is 6.686 Å.

For the electronic structures, we need to overcome the well-known problem that LDA underestimates the band gap. For example, the calculated relativistic LDA band gaps (including spin-orbit coupling) are 1.60 eV and 0.09 eV for GaN and GaAs, which compare to the experimental values[14,15] of 3.30 eV and 1.52 eV, respectively. To correct this LDA error and to have a reliable prediction of the band structure of the alloy-stabilized zinc-blende GaBi (and InBi), we adopt a simple procedure[19] by adding to the LDA potential an atom-dependent, spherical potential inside the muffin-tin spheres centered at each atomic and interstitial sites α. The potential has the form

$$V^\alpha = \bar{V}^\alpha + V_0^\alpha \left(\frac{r_0^\alpha}{r}\right) e^{-(r/r_0^\alpha)^2},\qquad(1)$$

where the parameters $\bar{V}^\alpha$, V_0^α, and r_0^α for atom α (Table II) were fitted, so the LDA-corrected (LDA+C) band structures of GaAs are similar to experimental data.[14,15] The same parameters are then used to calculate the band structure of GaSb, GaBi, and InBi. Table III gives the predicted band gaps for GaAs, GaSb, GaBi, and InBi. For GaSb, the predicted band gaps are in good agreement with experimental data. Similar accuracy is expected for GaBi and InBi. Figure

TABLE II. Fitted parameters $\bar{V}$, V_0, and r_0 for the cations (Ga, In), anions (As, Sb, Bi) and empty spheres $(E)_{cation}$ (next to cation site), and $(E)_{anion}$ (next to the anion site) for the LDA corrections. The muffin-tin sphere radii used in our calculation are $R_{MT} = 2.2$ a.u. for Ga, As, and $R_{MT} = 2.5$ a.u for In, Sb, and Bi, respectively. For the empty spheres centered at the interstitial site, $R_{MT} = 2.05$ a.u.

Atom	$\bar{V}$ (Ry)	V_0 (Ry)	r_0 (a.u)
Ga, In	0.0	270	0.025
As, Sb, Bi	0.0	120	0.025
$(E)_{cation}$	0.24	100	0.025
$(E)_{anion}$	0.40	100	0.025

1 shows the calculated relativistic band structures of zinc-blende GaBi and InBi. We find that both GaBi and InBi have the inverted band structure, i.e., the Γ_{6c} state is below the Γ_{8v} state. The predicted band gaps $E_g(\Gamma_{6c} - \Gamma_{8v})$ are -1.45 and -1.63 eV for GaBi and InBi, respectively.

B. Alloys

Using our calculated values in Table I, the lattice mismatches of GaN and GaBi with respect to GaAs are -20.4% and $+12.0\%$, respectively, suggesting that both $GaAs_{1-x}N_x$ and $GaAs_{1-x}Bi_x$ alloys are highly strained and have a strong tendency to phase separate at high concentrations of x. Assuming Vegard's law,[20] the lattice parameter of the $GaAs_{1-x-y}N_xBi_y$ alloy is given by

$$a(x,y) = (1-x-y)a_{GaAs} + xa_{GaN} + ya_{GaBi}. \qquad(2)$$

Therefore, using our calculated lattice parameters, the requirements of alloys lattice matched to GaAs imply that $y = 1.7x$.

The band gap of the $GaAs_{1-x-y}N_xBi_y$ alloy also depends on concentrations x and y. For small x and y, the band gap can be described by an expansion up to second order in x and y.

$$E_g(x,y) = (1-x-y)E_g(GaAs) + xE_g(GaN) + yE_g(GaBi)$$
$$- b_{GaAsN}x(1-x) - b_{GaAsBi}y(1-y) - b_{GaAsNBi}xy,$$
$$(3)$$

where b are the bowing coefficients. To determine these parameters, we simulated the $GaAs_{1-x-y}N_xBi_y$ alloy using 32- and 64-atom supercells. We calculated the alloy band gaps with either $x=0$, $y=0$, or $x=y$. In the last case, we find that N and Bi have the largest binding energy (0.28 eV) when they occupy the fcc next-nearest-neighbor (nnn) sites.

The calculated bowing coefficients are given in Table IV. Using the calculated bowing coefficient and Eq. (3), we find that the concentration at which a freestanding $GaAs_{1-x}N_x$ alloy has a band gap of 1 eV is $x=0.056$. The required N concentration will be smaller if the $GaAs_{1-x}N_x$ alloy is coherently strained on GaAs substrate. About two-thirds of the band gap reduction is due to the lowering of the conduction-band minimum. A recent theoretical study[21] has shown that high N concentration in GaAs is problematic because it leads to N-induced midgap defect states that are responsible for the low PL efficiency and short diffusion length observed in this system.[4,5] However, if we coalloy GaAs with N and Bi to form the $GaAs_{1-2.7x}N_xBi_{1.7x}$ alloy that is lattice matched to GaAs, due to the very negative band gap of GaBi, a much smaller N concentration, $x=0.027$, is needed to reach the 1-eV band gap. Therefore, a 1-eV $GaAs_{1-2.7x}N_xBi_{1.7x}$ alloy is expected to have better optical and transport properties than pure strained $GaAs_{1-x}N_x$ or even $Ga_{1-y}In_yAs_{1-x}N_x$ alloys. Table IV also shows that the calculated bowing coefficient $b_{GaAsNBi} = 16.2$ eV [the last term on the right-hand side of Eq. (3)] is strongly positive, indicating that the interaction between N and Bi also contributes to the band gap reduction in the $GaAs_{1-x-y}N_xBi_y$ alloy. To understand this behavior,

TABLE III. Calculated band gap for GaAs, GaSb, GaBi, and InBi using the LDA+C approach. For GaN the calculated results are obtained using the same parameters as in Table II except that we used $\bar{V}=0.44$ for $(E)_{cation}$, which has a $R_{MT}=1.3$ a.u. The results for GaAs and GaSb are compared with experimental values (Ref. 14).

	GaAs		GaSb		GaBi	InBi	GaN
	LDA+C	Expt.	LDA+C	Expt.	LDA+C	LDA+C	LDA+C
$\Gamma_{6c}-\Gamma_{8v}$	1.51	1.52	0.85	0.81	-1.45	-1.63	3.22
$L_{6c}-\Gamma_{8v}$	1.82	1.82	0.97	1.10	-0.24	-0.19	6.07
$X_{7c}-\Gamma_{8v}$	1.99	2.03	1.51	1.3	0.81	0.82	4.64

we note that when N and Bi are introduced into GaAs, the interband coupling between the N-induced conduction-band minimum (CBM) and the Bi-induced VBM (Ref. 22) tends to increase the band gap, whereas the intraband coupling between the N- and Bi-induced valence states and between the N- and Bi-induced conduction states tend to reduce the band gap. We find that the intraband coupling is stronger than the interband coupling, and therefore the band gap is further reduced after coalloying N and Bi with GaAs. Due to the intraband level repulsions, the VBM and CBM of the GaAs$_{1-x-y}$N$_x$Bi$_y$ are mainly localized on Bi and N, respectively, as shown in Fig. 2.

We have also studied the effects of coalloying of N and Bi on the alloy formation energy of the GaAs$_{1-x-y}$N$_x$Bi$_y$ alloy

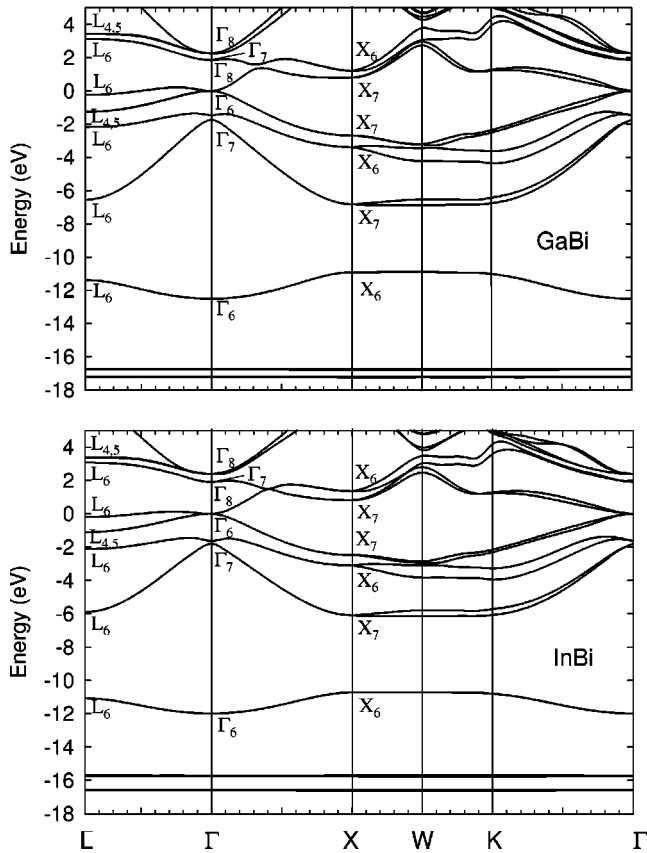

FIG. 1. Calculated relativistic band structure of GaBi and InBi using the LDA+C method. Both GaBi and InBi show inverted band structure, i.e., the Γ_{6c} is below the Γ_{8v} state.

lattice matched to GaAs ($y=1.7x$). In the small concentration regime, the formation energy $\Delta H_f(x)$ can be expressed as $\Delta H_f(x)=\Omega x$, where Ω is the interaction parameter. The calculated interaction parameters are given in Table IV. For a freestanding GaAs$_{1-x}$N$_x$ alloy, we find $\Omega_{GaAsN}=1.86$ eV/anion. For a freestanding GaAs$_{1-x}$Bi$_x$ alloy, we find $\Omega_{GaAsBi}=0.36$ eV/anion. The alloy formation energies will be much larger if they are constrained on the GaAs substrate. Furthermore, the large lattice mismatch between these alloys and GaAs also limits their applications. On the other hand, the coupling between the small-sized N and large-sized Bi in GaAs reduces the formation energy of the GaAs$_{1-x-y}$N$_x$Bi$_y$ alloy. For each N-Bi pair, the calculated interaction parameter can be as small as 1.94 eV per pair, smaller than the sum of the interaction parameters of pure GaAs$_{1-x}$N$_x$ and pure GaAs$_{1-x}$Bi$_x$, which is 2.22 eV per pair. For a GaAs$_{1-2.7x}$N$_x$Bi$_{1.7x}$ alloy that is lattice matched to GaAs, the alloy formation energy is calculated under two scenarios.

(i) All the N and Bi is far apart, thus there is no interaction between N and Bi. In this case, $\Omega_x=\Omega_{GaAsN}+1.7\Omega_{GaAsBi}$, i.e., $\Delta H_f(x)=2.47x$ (eV/anion). This is an upper limit of the alloy-formation energy.

(ii) All the N forms nnn pairs with Bi, and the excess Bi atoms occupy sites far away from the N-Bi pairs. In this case, $\Omega_x=2\Omega_{GaAsNBi}+0.7\Omega_{GaAsBi}$, i.e., $\Delta H_f(x)=2.19x$(eV/anion). This is close to the actual formation energy of the alloy. Figure 3 plots the alloy formation energy of the GaAs$_{1-2.7x}$N$_x$Bi$_{1.7x}$ and compares it to that for GaAs$_{1-x}$N$_x$ and GaAs$_{1-x}$Bi$_x$ alloys. In the GaAs$_{1-x}$N$_x$ alloy, to reach 1-eV band gap (at $x=0.056$), the formation energy is 104 meV/anion. After adding Bi to form a GaAs$_{1-2.7x}$N$_x$Bi$_{1.7x}$ alloy lattice matched to GaAs, the formation energy of the 1-eV alloy is reduced to 59 meV/anion. This large reduction of the alloy formation energy indicates that coalloying Bi with N in GaAs is a very effective way to reduce the alloy formation energy.

TABLE IV. Calculated bowing parameters b (in eV) and the interaction parameter Ω (in eV per anion) for the GaAs$_{1-x-y}$N$_x$Bi$_y$ alloys.

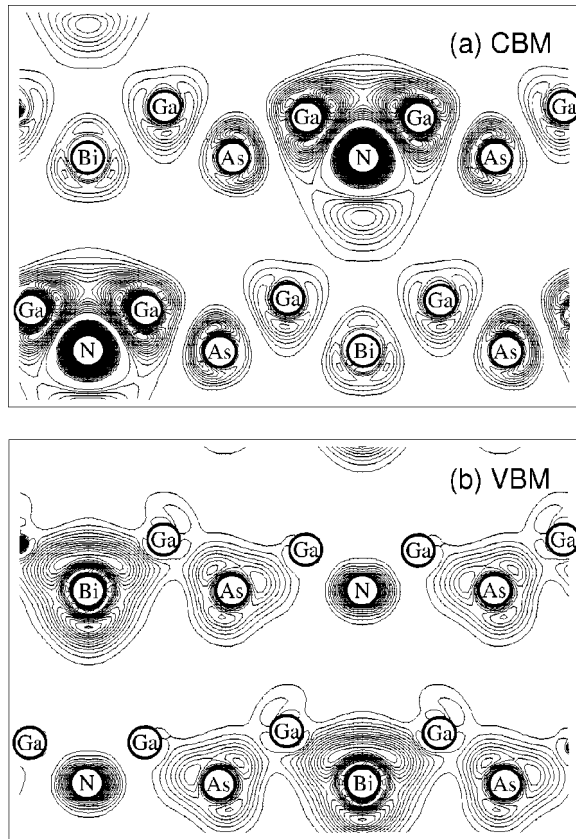|	b	Ω
GaAsN	11.5	1.86
GaAsBi	2.1	0.36
GaAsNBi	16.2	0.97

FIG. 2. Contour plot of electron charge density of (a) conduction-band minimum (CBM) and (b) valence-band maximum (VBM) states of $GaAs_{1-x-y}N_xBi_y$ alloy. The CBM is more localized on N, while the VBM is more localized on Bi.

FIG. 3. Calculated formation energy as a function of composition x for $GaAs_{1-2.7x}N_xBi_{1.7x}$ lattice matched to GaAs and for free-standing $GaAs_{1-x}N_x$ and $GaAs_{1-x}Bi_x$ alloys. The formation energy for 1-eV band-gap material is indicated as filled circles.

IV. SUMMARY

In summary, we have studied the electronic and structural properties of $GaAs_{1-x-y}N_xBi_y$ alloys as a novel 1-eV band-gap material that is lattice matched to GaAs. We find that coalloying Bi with N in GaAs can significantly lower the N concentration required to reduce the alloy band gap to 1 eV.
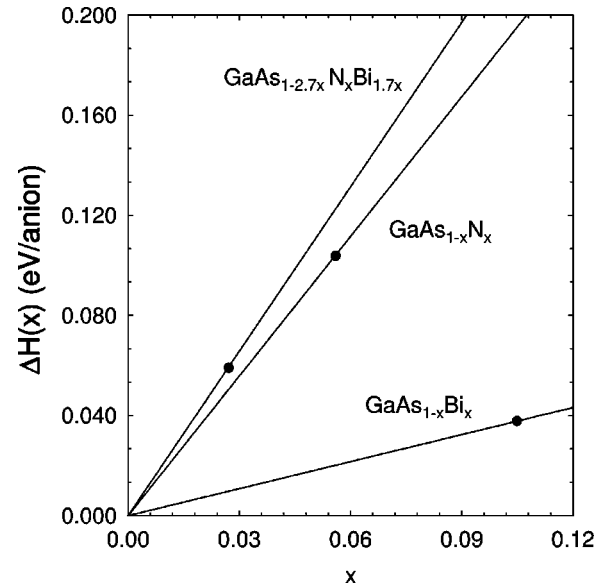
The strain compensation between the small-sized N and the large-sized Bi also reduces the alloy formation energies. Thus, the crystal quality of $GaAs_{1-x-y}N_xBi_y$ alloys are expected to be superior than other current 1-eV N-containing alloys that are lattice matched to GaAs. On the other hand, because Bi can diffuse easily from the bulk to the surface, alloys with large concentration of Bi cannot be grown under conditions too far from equilibrium. Experimental tests of our predictions are called for.

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