Giant and Composition-Dependent Optical Bowing Coefficient in GaAsN Alloys

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Using first-principles supercell calculations we find a giant (7–16 eV) and composition-dependent optical bowing coefficient in $\mathrm{GaAs}_{1-x}\mathrm{N}_x$ alloys. We show that both effects are due to the formation in the alloy of spatially separated and sharply localized band edge states. Our analysis suggests that in semiconductor alloys band gap variation as a function of x can be divided into two regions: (i) a bandlike region where the bowing coefficient is relatively small and nearly constant, and (ii) an impuritylike region where the bowing coefficient is relatively larger and composition dependent. For $\mathrm{GaAs}_{1-x}\mathrm{N}_x$ the impuritylike behavior persists even for concentrated alloys.

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The band gap $E_g(x)$ of an $A_{1-x}B_x$ semiconductor alloy usually deviates from the average gap $\overline{E}_g(x) = (1 - x)E_g(A) + xE_g(B)$ of the constituents solids A and B. Measurements [1] and calculation [2–5] for isovalent semiconductor alloys show that the deviation $\Delta E_g(x) = E_g(x) - \overline{E}_g(x)$ can often be described by

$$\Delta E_g(x) = bx(x - 1)\,, \qquad (1)$$

where b is the bowing coefficient, typically a fraction of an eV, and composition independent (last column of Table I). We show here, via first-principles local density approximation (LDA) calculations, that in $\mathrm{GaAs}_{1-x}\mathrm{N}_x$ alloys b is giant and composition dependent (larger at dilute concentration). The calculated bowing coefficients of 16 eV for the bulk and 17 eV for epitaxially strained dilute alloy agree with the range in recent experimental determination by Kondow *et al.* [6] ($b = 20$ eV at $x < 1.6\%$) and Weyer, Sato, and Ando [7] ($b = 14$ eV at $x < 1.5\%$). We find that in the dilute $\mathrm{GaAs}_{1-x}\mathrm{N}_x$ alloy the band edge wave functions are localized *impuritylike* states: The valence band is strongly localized on the As sublattice, and the conduction band is strongly localized on the nitrogen sublattice. This localization, previously noticed by Rubio and Cohen [8] and by Neugebauer and Van de Walle [9], reflects the large differences between atomic orbital energies and sizes of the alloyed As and N atoms. Our analysis of the results provide new insights into the electronic behavior of isovalent semiconductor alloys, suggesting that the band gap variation as a function of x can be divided into two regions: (i) a bandlike region where the bowing coefficient is relatively small and nearly constant, and (ii) an impuritylike region where the bowing coefficient is considerably larger and composition dependent. For most isovalent semiconductor alloys made of chemically similar elements (e.g., $\mathrm{Ga\underline{As}{:}P}$ or $\mathrm{\underline{Ga}As{:}Al}$) the concentration range for impuritylike behavior (ii) is negligibly low ($x \ll 1\%$). However, for isovalent alloys exhibiting in the impurity-limit localized “deep” levels (e.g., $\mathrm{Ga\underline{As}{:}N}$, $\mathrm{Zn\underline{Te}{:}S}$, and Si:C) the impuritylike region can persists even at significant (~10%–20%) concentrations. This classification into impuritylike and bandlike alloy bowing characteristics could be useful in analyzing carrier dynamics and optical properties of semiconductor alloys [10].

Disorder alloys at $x = \frac{1}{2}$ and $x = \frac{1}{4}$ are represented in this study using the “special quasirandom structure” (SQS) approach [11] with 16 atoms per cell. The SQS’s are rather small unit cell periodic structures whose lattice sites are occupied by A and B atoms so as to mimic the atom-atom correlation functions of much larger $A_{1-x}B_x$ supercells with random occupations. Atomic relaxations and charge fluctuations needed to describe real alloys are naturally included in this approach. At the 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. For composition $x = \frac{1}{8}$ we use the impurity supercell [12] $D1$.

TABLE I. Decomposition of the bowing parameters (in eV) for the direct band gaps of various semiconductors, as calculated from LDA. The calculated bowing parameters in the ordered CuPt structure are 0.48 and 11.5 eV for $\mathrm{Ga_2AsP}$ and $\mathrm{Ga_2AsN}$, respectively.

System	b_{VD}	b_{CE}	b_{SR}	b_{total}
	Mixed anion			
$\mathrm{GaAs_{0.5}P_{0.5}}$ [a]	0.12	−0.01	0.08	0.19
$\mathrm{GaAs_{0.75}P_{0.25}}$	0.06	0.00	0.12	0.18
$\mathrm{GaAs_{0.875}P_{0.125}}$	0.06	0.01	0.16	0.23
$\mathrm{GaAs_{0.5}N_{0.5}}$	−0.66	2.02	5.48	6.84
$\mathrm{GaAs_{0.75}N_{0.25}}$	−0.76	1.96	6.40	7.60
$\mathrm{GaAs_{0.875}N_{0.125}}$	−0.78	8.07	8.40	15.69
$\mathrm{ZnSe_{0.5}S_{0.5}}$ [b]	0.03	0.09	0.38	0.50
$\mathrm{ZnTe_{0.5}Se_{0.5}}$ [b]	−0.20	0.43	0.91	1.14
$\mathrm{ZnTe_{0.5}S_{0.5}}$ [b]	−0.22	0.90	2.03	2.71
	Mixed cations			
$\mathrm{Ga_{0.5}In_{0.5}As}$ [a]	0.51	−0.04	−0.07	0.40
$\mathrm{Cd_{0.5}Zn_{0.5}Te}$ [c]	0.29	0.14	−0.08	0.35
$\mathrm{Hg_{0.5}Zn_{0.5}Te}$ [c]	0.40	−0.01	−0.16	0.23
$\mathrm{Hg_{0.5}Cd_{0.5}Te}$ [c]	0.00	−0.02	0.00	−0.02
$\mathrm{Ga_{0.5}Al_{0.5}As}$ [a]	0.00	0.20	0.00	0.20

[a] Ref. [3]; semirelativistic pseudopotential calculation.
[b] Ref. [4]; relativistic LAPW calculation.
[c] Ref. [5]; relativistic LAPW calculation.

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The electronic structures of the alloys are calculated by the LDA as implemented by the relativistic linearized augmented plane wave method [13]. The Ga $3d$ states are treated as valence bands. The calculated lattice constants of the end-point compounds $a_{\mathrm{GaAs}} = 5.64$ Å and $a_{\mathrm{GaN}} = 4.51$ Å are close to the experimental values [1]. For the relaxed alloys, we find that lattice constants vary linearly as function of composition x. The equilibrium bond lengths $R_{\text{Ga-As}}$ and $R_{\text{Ga-N}}$ show the typical bimodal distribution. The average bond length relaxation parameter [14] $\epsilon = [R_{\text{Ga-As}}(x) - R_{\text{Ga-N}}(x)]/[R^0_{\text{Ga-As}} - R^0_{\text{Ga-N}}]$ is close to 0.67 ($\epsilon = 0$ indicates no relaxation, while $\epsilon = 1$ indicates full relaxation).

The calculated band gaps of the supercells are then used along with the calculated values for GaAs and GaN to obtain the bowing coefficient b from Eq. (1). The LDA error is partially canceled [15] in the calculation since we consider here the band gap *difference* between the alloy and equal amount of the binary constituents. To demonstrate the quality of the supercells in determining the bowing parameter of disordered alloys, we first performed parallel calculations for $\mathrm{GaAs}_{1-x}\mathrm{P}_x$ alloys where accurate experimental data [1] and previous SQS type calculations [3] are available. The last column of Table I gives the calculated value of b. We find that $b(x = \frac{1}{4}) = 0.18$ eV and $b(x = \frac{1}{8}) = 0.23$ eV. These values indicate insignificant composition dependence and compare favorably with the experimental values [1] of 0.18 eV and previous pseudopotential SQS calculations of Magri *et al.* [3] ($b = 0.19$ eV). To provide perspective, the last column of Table I also gives values of b of some previously calculated isovalent semiconductors [3–5], and the corresponding values obtained here for $\mathrm{GaAs}_{1-x}\mathrm{N}_x$: $b(x) = 6.84$, 7.60, and 15.69 eV at $x = \frac{1}{2}, \frac{1}{4}$, and $\frac{1}{8}$ using the bulk equilibrium alloy lattice constants. For $\mathrm{GaAs}_{0.875}\mathrm{N}_{0.125}$ coherently strained on GaAs substrate, the calculated bowing coefficient [16] is 17.0 eV. We see that (i) the calculated value of b for the dilute $\mathrm{GaAs}_{1-x}\mathrm{N}_x$ alloy is in good agreement with the experimental range (14–20 eV for strained alloy), and (ii) in contrast to $\mathrm{GaAs}_{1-x}\mathrm{P}_x$ and other conventional III-V and II-VI alloys [11], we find $b(\mathrm{GaAs}_{1-x}\mathrm{N}_x)$ to be strongly composition dependent: The calculated bowing coefficient at $x = \frac{1}{8}$ is significantly larger than b calculated at $x = \frac{1}{2}$ and $\frac{1}{4}$, and is even much larger than the value for the CuPt ordered alloy ($b = 11.5$ eV).

To understand the physical origins of the giant and composition-dependent bowing in $\mathrm{GaAs}_{1-x}\mathrm{N}_x$ alloys, we analyze b by decomposing it into physically distinct contributions [2]: (i) volume deformation (VD), (ii) charge exchange (CE), and (iii) structural relaxation (SR). The VD term represents changes in the band gaps due to compression of GaAs and dilation of GaN from their individual equilibrium lattice constants to the alloy value $a(x)$. The CE term is calculated from the change in gaps in bringing together GaAs with GaN, both already prepared at $a = a(x)$, thus forming $\mathrm{GaAs}_{1-x}\mathrm{N}_x$ at $a = a(x)$ with all atoms on unrelaxed zinc-blende lattice sites. Finally, the SR term represents the change in passing from the atomically unrelaxed to the relaxed alloy at $a(x)$. By construction, the total bowing is $b \equiv b_{\mathrm{VD}} + b_{\mathrm{CE}} + b_{\mathrm{SR}}$. Table I shows the breakdown for the disordered $\mathrm{GaAs}_{1-x}\mathrm{P}_x$ and $\mathrm{GaAs}_{1-x}\mathrm{N}_x$ alloys and some previously calculated [3–5] mixed-anion and mixed-cation alloys. We observe the following.

(i) The volume-deformation term b_{VD} of $\mathrm{GaAs}_{1-x}\mathrm{N}_x$ is relatively small and nearly constant, similar to the other semiconductor alloy systems [3–5]. In this system the increase in the direct gap due to compression of the material with the large lattice constant (GaAs) is slightly larger than the decrease in the direct gap due to expansion of the material with smaller lattice constant (GaN), thus the sum b_{VD} is negative.

(ii) Both b_{CE} and b_{SR} of $\mathrm{GaAs}_{1-x}\mathrm{N}_x$ are much larger than in other mixed-anion systems [3–5]. Thus charge exchange, proportional to the As-N *atomic orbital energy* differences, and structural relaxation, proportional to the As-N *atomic size* differences, appear to control the giant bowing in this alloy system.

To understand the origin of the large CE and SR effects in $\mathrm{GaAs}_{1-x}\mathrm{N}_x$, we present in Table II an analysis of the band edge wave functions in terms of their atomic character. We show results for the valence band maximum (VBM) and the conduction band maximum (CBM) at $x = \frac{1}{8}$ for (i) bulk equilibrium GaAs and GaN,

TABLE II. Normalized (e/ZB-cell-state) charge inside the muffin-tin (MT) spheres for the band edge states at $x = \frac{1}{8}$. Ga_1 has one N and three As as its nearest neighbors, while Ga_2 is surrounded only by As atoms. As_1 has fcc nearest neighbor N atoms, while As_2 has only second fcc nearest neighbors N atoms. The MT radii are 2.20, 1.56, and 2.10 a.u. for As, N, and Ga, respectively. The numbers in bold phase emphasize the significant *changes* of charge inside the MT sphere. The changes from the second column to the fifth column are due to VD, CE, and SR, respectively. For comparison, the last column gives the charge of relaxed alloy at $x = \frac{1}{4}$. It shows that at this composition the charge is not as localized as the one at $x = \frac{1}{8}$ in column five.

	GaAs/GaN		GaAsN		
	a_{eq} $x = \frac{1}{8}$	$\bar{a}$ $x = \frac{1}{8}$	$\bar{a}$ $x = \frac{1}{8}$ unrelax	$\bar{a}$ $x = \frac{1}{8}$ relax	$\bar{a}$ $x = \frac{1}{4}$ relax
			VBM		
N	0.64	**0.59**	0.69	**0.16**	0.33
As_1	0.50	0.51	0.47	0.50	0.58
As_2	0.50	0.51	**0.64**	**0.83**	—
Ga_1	0.06	0.06	0.04	0.02	0.06
Ga_2	0.07	0.08	0.10	0.13	—
			CBM		
N	0.37	**0.22**	**0.72**	**0.84**	0.44
As_1	0.37	0.39	**0.10**	0.14	0.23
As_2	0.37	0.39	**0.00**	0.00	—
Ga_1	0.30	0.33	0.43	0.50	0.24
Ga_2	0.34	0.32	**0.00**	0.00	—

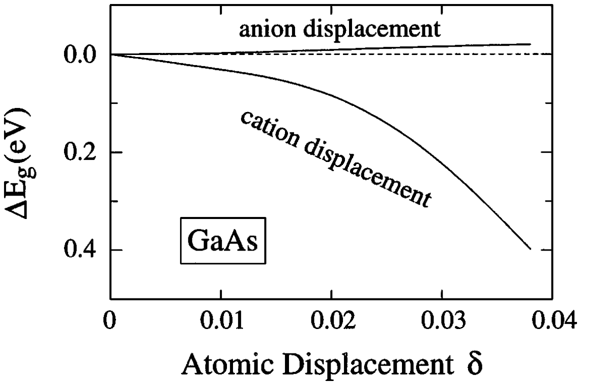

FIG. 1. Calculated band gap change ΔE_g as function of atomic displacement δ for GaAs. The results are calculated using a CuAu-like Ga_2As_2 structure, in which the two Ga-As bond lengths are given by $R_{\text{Ga-As}} = [0.125 + (0.25 \pm \delta)^2]^{1/2}a$, where a is the lattice constant. The crystal field averaged band gap increases when the anion is displaced, but decreases significantly when cation is displaced.

(ii) GaAs and GaN volume deformed to the value for the alloy, (iii) unrelaxed GaAsN, and (iv) relaxed GaAsN. We observe that (a) the VBM wave function becomes localized on As as we combine GaAs with GaN in the CE step, and that significant further localization on As takes place in the SR step. At the same time, the VBM wave-function amplitude on N is severely reduced at the SR step. (b) The CBM wave function becomes strongly localized on N upon forming the alloy in the CE and SR steps. Thus the formation of GaAsN from GaAs + GaN shifts valence charge from N to As, while the conduction charge shifts in the opposite direction from As to N. This creates large b_{CE} and b_{SR}.

To understand further the large SR term, we recall that [17] the principle static atomic displacement pattern in mixed-cation alloys (e.g., GaInP) is due to anion motion, while in mixed-anion alloys (e.g., GaAsN) the principal motion is due to the cation. We can separate the CE contribution from SR contribution by considering the changes in the band gap of *pure* GaAs (where $b_{\text{CE}} \equiv 0$) in response to displacing anions and separately cations (Fig. 1). We find that cation displacements lower the band gap considerably more than anion displacements, in accord with the trend in b_{SR} seen in Table I. This reflects the fact that cation displacements lead to strong intraband coupling *within* the conduction band and separately *within* the valence band. This coupling lowers the CBM and raises the VBM, thus reducing the band gap. We also find that when the cation are displaced, the CBM state becomes more localized on the anion with short bond [Fig. 2(a)], while the VBM state becomes more localized on the anion with longer bond [Fig. 2(b)]. In a mixed-anion alloy, if the larger atom has higher atomic p orbital energy and the smaller atom has lower atomic s orbital energy (e.g., $GaAs_{1-x}N_x$ or $ZnTe_{1-x}S_x$ [2,4]), lattice relaxation couples effectively to the chemical energy, thus greatly enhancing b_{SR}. This explains the large b_{SR} in $GaAs_{1-x}N_x$. In the case of anion displacements, the interband coupling *between* valence and conduction bands becomes dominant, thus the band gap *increases* [Fig. 1(b)]. Again, we find that the CBM state becomes more localized on the cation with a short bond [Fig. 2(c)], while the VBM state becomes more localized on the cation with a longer bond [Fig. 2(d)]. The effects, however, are much smaller than in the anion displacement case.

The facts that (i) bowing coefficient of $GaAs_{1-x}N_x$ at $x = \frac{1}{8}$ is significantly larger than that at higher concentrations and that (ii) the impuritylike band edge wave functions at $x = \frac{1}{8}$ are so localized as to make the overlap of the band edge wave functions between adjacent cells small

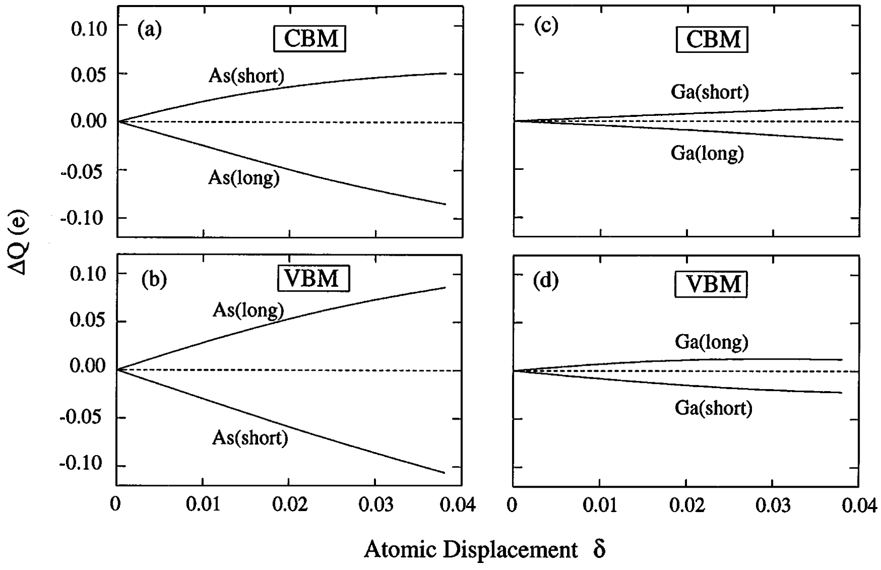

FIG. 2. Calculated change of the muffin-tin charges ΔQ as function of atomic displacement δ for GaAs. Results are for the CBM and VBM states. (a),(b) Cation displacement. (c),(d) Anion displacement.

suggest that in semiconductor alloys the band gap variation as function of x can be divided into two regions: (i) a bandlike region where the bowing coefficient is relatively small and $\Delta E_g(x)$ can be described by Eq. (1) with nearly constant b, and (ii) an impuritylike region where the bowing coefficient is relatively larger and composition dependent. We conjecture that the existence of localized band edge wave functions is unique to alloy systems exhibiting in the dilute limit a "deep" impurity state. As is well known [18], isovalent impurities such as $\underline{\text{Ga}}$As:Al, Ga$\underline{\text{As}}$:P, Si:Ge, or Zn$\underline{\text{Se}}$:S usually have a weak central-cell potential $\Delta V = V_{\text{host}} - V_{\text{impurity}}$ and produce energetically shallow and spatially extended states. In this case of weak ΔV, as the impurity concentration increases, the impurity wave functions start to overlap and the impurity energy level merges almost immediately with the band edges and both move rigidly and continuously with x, producing "optical bowing" of the type described by Eq. (1). Hence the impuritylike region is negligible for alloy systems with small ΔV. On the other hand, when the atomic potential and size of the impurity differ sufficiently from those of the host atom being replaced, ΔV is large enough to support a deep localized state at the dilute limit even in the isovalent alloy. In this case of strong ΔV, as the alloy concentration increases, the bound state initially persists and maintains spatial localization even for significant concentrations. In this limit, the composition dependence of the impurity gap does not follow Eq. (1) with a constant b, but rather with $b = b(x)$. Large bowing parameters are expected. We predict this to be the case for deep isovalent center systems such as Ga$\underline{\text{P}}$:N, Ga$\underline{\text{As}}$:N, Zn$\underline{\text{Te}}$:S, Cd$\underline{\text{Te}}$:S [19], and Si:C [20].

In summary, we find a giant and composition-dependent optical bowing coefficient in dilute $\text{GaAs}_{1-x}\text{N}_x$ alloys. We show that both effects are due to the formation in the alloy of spatially separated and sharply localized band edge states. This localization reflects the large differences between As and N in their atomic orbital energies and sizes. The effects of atomic bond relaxation on the optical bowing are studied systematically. We propose that in semiconductor alloys band gap variation as a function of x can be divided into two regions: (i) a bandlike region where the bowing coefficient is relatively small and nearly constant, and (ii) impuritylike region where the bowing coefficient is relatively larger and composition dependent.

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[16] This suggests that the band gap of $\text{GaAs}_{1-x}\text{N}_x$ is closed at composition $x = 12.5\%$. However, the alloy at this composition is unstable since our calculated spinodal decomposition limit at $T = 800$ K is only 1.85%.

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