

Localization and percolation in semiconductor alloys: GaAsN vs GaAsP

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Tradition has it that in the absence of structural phase transition, or direct-to-indirect band-gap crossover, the properties of semiconductor alloys -bond lengths, band gaps, elastic constants, etc.! have simple and smooth -often parabolic! dependence on composition. We illustrate two types of violations of this almost universally expected behavior. First, at the percolation composition threshold where a continuous, wall-to-wall chain of given bonds -e.g., Ga-N-Ga-N! first forms in the alloy -e.g., GaAs_{1-2x}N_x!, we find an anomalous behavior in the corresponding bond length -e.g., Ga-N!. Second, we show that if the dilute alloy -e.g., GaAs_{1-2x}N_x for $x \ll 1$! shows a localized deep impurity level in the gap, then there will be a composition domain in the concentrated alloy where its electronic properties -e.g., optical bowing coefficient! become irregular: unusually large and composition dependent. We contrast GaAs_{1-2x}N_x with the weakly perturbed alloy system GaAs_{1-2x}P_x having no deep gap levels in the impurity limits, and find that the concentrated GaAs_{1-2x}P_x alloy behaves normally in this case. ©S0163-1829-96!10648-2#

I. INTRODUCTION

In the absence of composition-induced structural phase transitions in alloys @e.g., zinc-blende-to-wurtzite in CdTeSe -Ref. 1! and zinc-blende-to-NiAs in MnCdTe -Ref. 2!# or electronic direct-to-indirect band gap crossovers @e.g., AlGaAs -Refs. 3 and 4! and AlGaAsP -Refs. 5–8!#, physical properties $P(x)$ were traditionally assumed⁹ to be simple continuous functions of the composition x . This strongly held view is reflected by the almost universal depiction of the composition dependence of $P(x)$ by simple analytic form,⁹ e.g., a linear -Vegard-like! term, plus a small quadratic correction:

$$P(x) = P_A + x(P_B - P_A) + \frac{1}{2}x^2(P_C - P_A)$$

II. METHOD OF CALCULATION

We use a large ~

eigensolutions in a given energy window. At each composition, results are averaged over a few, randomly selected con-

TABLE V. Atomic pseudopotential parameters used in this study. The four rows for each atom correspond to the four Gaussians in Eq. -2!. These pseudopotentials must be used with a constant number of plane waves of 59 per zinc-blende cell, corresponding to the kinetic energy cutoff of 5 Ry for GaAs and GaP and of 7.87 Ry for GaN.

Atom	$a V_a$ -a.u.! ³	l	a_{la} -Ry!	b_{la} -a.u.! ²¹	c_{la} -a.u.! ²
Ga	131.4	1	21.244 980 0	1.527 480	0.0
		2	0.046 435 7	0.574 047	2.019 35
		3	0.036 651 7	0.959 082	2.097 82
		4	20.013 338 5	11.270 800	2.935 81
As	145.2	1	21.058 210 0	0.959 327	0.0
		2	20.043 431 2	2.946 790	0.851 64
		3	0.105 690 0	0.820 922	1.224 36
		4	20.002 176 3	6.531 450	2.468 08
N	75.0	1	20.226 280 0	1.816 013	0.0
		2	20.926 830 0	0.918 842	0.851 77
		3	0.237 280 0	0.909 593	1.555 91
		4	0.020 830 0	13.519 21	2.628 52
P	139.2	1	21.028 210 0	0.870 327	0.0
		2	20.049 431 0	3.186 790	0.889 64
		3	0.117 690 0	0.470 922	1.028 36
		4	0.012 176 0	5.811 450	2.400 80

TABLE VI. Structural and electronic properties of N impurity in GaAs -GaAs:N! and As impurity in GaN -GaN:As!. The charges Q are calculated from Eq. -3! using a 512-atom cell. $R_{\text{Ga-N}}$ and $R_{\text{Ga-As}}$ are the nearest-neighbor bond lengths. Note that GaAs:N has no gap level³⁸ while GaN:As has a deep, localized level.

Property	GaAs and GaAs:N	GaN and GaN:As
Pure host:		
Q_{VBM} -anion!	1.55	4.16
Q_{VBM} -cation!	0.51	0.30
Q_{CBM} -anion!	3.19	4.81
Q_{CBM} -cation!	1.64	1.18
$R_{\text{Ga-As}}$ -Å!	2.45	
$R_{\text{Ga-N}}$ -Å!		1.95
Impurity:		
		1.0 -Ga!
$Q_{\text{impurity level}}$		178 -As!
		1.9 -N!
$R_{\text{Ga-N}}$ -Å!	2.03	1.95
$R_{\text{Ga-As}}$ -Å!	2.45	2.25
Energy level -eV		

B. The full alloy range

1. Alloy bond lengths and the appearance of percolation thresholds

We next raise gradually the composition from the dilute impurity limits to cover the full alloy range. Figure 1 shows the nearest-neighbor distances $R_{\text{Ga-As}}(x)$ and $R_{\text{Ga-N}}(x)$ versus x in $\text{GaAs}_{1-2x}\text{N}_x$, demonstrating a bimodal distribution. We are not aware of any experimental determination of these bond lengths in this alloy system. Figure 2 shows similar results for $\text{GaAs}_{1-2x}\text{P}_x$, and Table VIII compares our calculated results to the measured extended x-ray absorption fine structure -EXAFS! data of Ref. 41 for this system, showing good agreement. Figure 1-b! shows an enlarged section of $R_{\text{Ga-N}}(x)$ revealing a small slope discontinuity at x_p ; 0.19. To test whether this result is accidental or not, we have repeated the VFF calculation with a larger supercell containing 1000 atoms, taking an average of eight configurations at each composition. The calculated Ga-N bond length exhibits again a slight slope discontinuity near x_p . We interpret this anomaly as the appearance of a percolation threshold. In the site percolation model for a regular lattice,⁴² a property, which carries the statistical character of the problem, is randomly assigned to each site of the regular lattice, and the percolation threshold is defined as the minimum composition of the assigned sites forming an infinite connected cluster, which thus allows the propagation of the property through the whole sample. In line with this idea, we have analyzed our 512-atom supercell searching for the composition at which a connected chain of N-N bonds first forms on the fcc anion sublattice. We find $x_p \approx 0.19$, close to the more accurate result of $x_p \approx 0.198$ -Ref. 43! obtained in previous fcc percolation simulations. Thus, at $x_p \approx 0.19$, one forms a continuous chain of *stiff* Ga-N-Ga-N bonds in a soft alloy medium - $a_{\text{VFF}} \approx 96.30$ N/m for GaN, compared to $a_{\text{VFF}} \approx 41.19$ N/m for GaAs!. Interestingly, the formation of a continuous chain of *soft* Ga-As-Ga-As bonds in a stiffer al-

loy medium -at $12x_p \cdot 0.81!$ is also accompanied by a small bond length anomaly @see Fig. 1-cl#. In $\text{GaAs}_{1-2x}\text{P}_x$, we find again that the formation of a continuous chain of given

TABLE IX. The difference DR , at $x \leq 0.06$, between the A - C bond length in $AB_{1-2x}C_x$ alloys as obtained in actual VFF simulations and the value obtained by fitting $R_{A-C}(x)$ for the composition domain x . x_p , where regular behavior is found. $D\alpha_{VFF}$ is the difference between the bond-stretching force constants of the impurity and of the host bonds. Note that the value of DR is proportional to the value of $D\alpha_{VFF}$.

Impurity bond	Host	DR -Å!	$D\alpha_{VFF}$ -N/m!
Ga-N	GaAs	10.003 -0.15%!	155.11
Ga-As	GaN	20.006 -20.26%!	255.11
Ga-P	GaAs	10.001 -0.04%!	16.13
Ga-As	GaP	20.001 -20.04%!	26.13

Analysis of Figs. 3 and 4 suggests three composition regions.

-i! A *nitrogen-impurity region* -for x smaller than 0.1!: according to Table VI, nitrogen poses a weak-to-medium perturbation on GaAs. Indeed, at small x in $\text{GaAs}_{1-2x}\text{N}_x$ we find intermediate localization of the CBM wave functions around the N atom @Fig. 3-b!#, an increase of the CBM energy @Fig. 4-c!#, and of the bowing coefficient @from 6.7 to 7.6 eV, Fig. 4-b!# when x decreases. The band gap in this region decreases rapidly as x increases. This is consistent with the observed rapid redshift of the band-edge photoluminescence with increasing N content in dilute $\text{GaAs}_{1-2x}\text{N}_x$ alloys (x , 0.02).^{45,46}

-ii! An *As-impurity region* for middle and high x -for x higher than 0.4!: since As poses a strong perturbation on GaN -viz., Table VI!, the effects here are more dramatic than in the nitrogen-impurity region: the arsenic-impurity region is characterized by a very strong localization of VBM wave functions around the As atom @Fig. 3-a!#, and a rapid increase of the bowing coefficient @Fig. 4-b!# as x increases. It is also characterized by a rapid decrease of the VBM energy @Fig. 4-c!# and increase of the band gap @Fig. 4-a!# when $x \rightarrow 1$. In this region, the band gap of the *random* alloy can be small -0.4 eV for x ; 0.5!, while the band gap of some *ordered* alloys could even be negative @see Fig. 4-a!#.

-iii! An *intermediate region* located around x_p , where the alloy properties vary smoothly as a function of composition x : we find that in this region, although still very large -; 7 eV! compared to conventional semiconductor alloys, the optical bowing coefficient is nearly composition independent @Fig. 4-b!#, and both the CBM and the VBM wave functions are delocalized -Fig. 3!.

Our large 512-atom supercell calculation thus confirmed the recent suggestion of Wei and Zunger,¹⁴ based on LDA calculations of smaller cells, that $\text{GaAs}_{1-2x}\text{N}_x$ alloy has one bandlike domain where alloy properties vary smoothly as a function of x -with a composition-independent bowing coefficient! and can be described well by Eq. -1!, and two impuritylike domains, where Eq. -1! is not satisfied.

The *basic asymmetry* of $x \neq 0$ -no-gap level for N impurity in GaAs! and $x \neq 1$ -deep level for As impurity in GaN! explains the different behaviors of the physical properties in the N-impurity and As-impurity regions: the N-impurity region shows weak localization of the CBM wave functions around the nitrogen, with an optical bowing coefficient slightly composition dependent, whereas the As-impurity re-

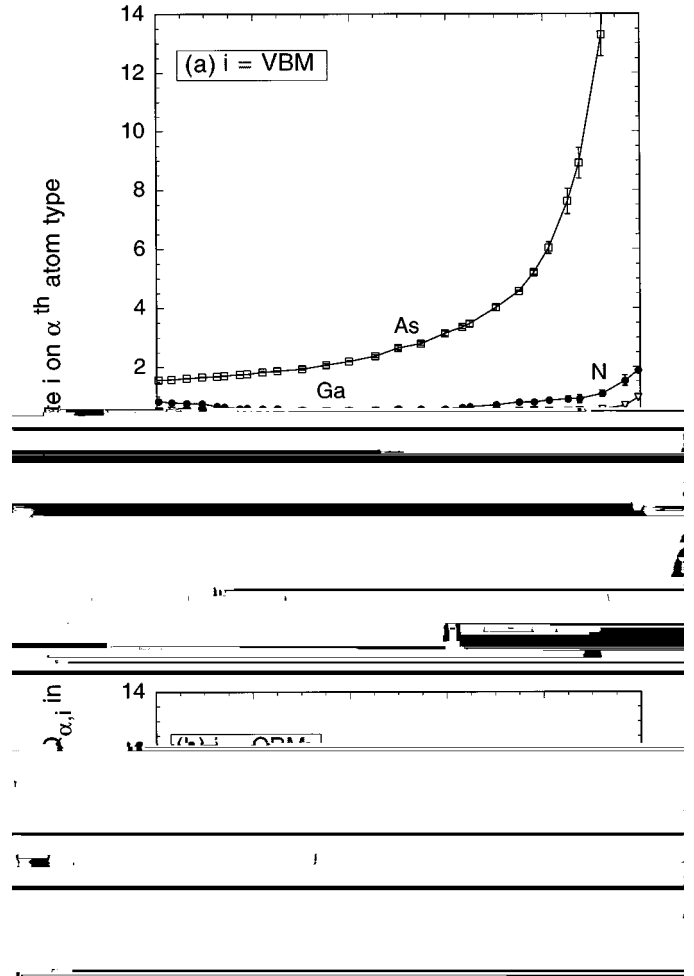


FIG. 3. Variation of the charge localization $Q_{a,i}$ of Eq. -3! for the highest occupied alloy level - $i \leq \text{VBM}$! and lowest empty alloy level - $i \leq \text{CBM}$! of atoms $a \in \{\text{As}, \text{N}, \text{Ga}\}$ of the random $\text{GaAs}_{1-2x}\text{N}_x$ alloys as a function of x . The bars are statistical fluctuations in configurational sampling.

gion shows a strong localization of the VBM wave functions around the arsenic, with a bowing coefficient that is very large and strongly dependent on the composition. This asymmetry in the single impurity limits explains also the large compositional range (Δx , 0.6) of the As-impurity region, compared to the N-impurity region (Δx , 0.1).

3. The electronic properties of $\text{GaAs}_{1-2x}\text{P}_x$: A “normal” alloy

We now study the alloy properties of the weakly perturbed $\text{GaAs}_{1-2x}\text{P}_x$ system in which no deep levels exist -Table VII!. Figure 5 shows, in analogy with Fig. 3, the VBM and CBM localization parameters, while Fig. 6 shows the composition variation of the band gap, bowing parameter and band-edge energies of $\text{GaAs}_{1-2x}\text{P}_x$. The direct to indirect (G_c to X_c) crossover occurs in the CBM at x , 0.50 @Fig. 6-c!#, in good agreement with the experimental results⁵⁻⁸ of 0.45-0.49, and leads to an abrupt change in the identity of the CBM wave functions @see Fig. 5-b!#. The large fluctuations of Fig. 5-b!, for x , 0.5, reflect the possibility of the CBM wave functions to have an X_c or G_c character at the transition point. We thus report in Fig. 6-b! the optical bowing coefficient for the G_{1c} state up to $x \leq 0.4$, and for the X_{1c} state for x higher than 0.6.

We see that in $\text{GaAs}_{1-2x}\text{P}_x$ the impurity region occurs only in the extreme P-rich alloys -approximately between $x \in 0.97$ and 1! where the optical X_{1c} -type bowing coefficient ranges from 0.3 to 1 eV and the CBM wave functions are weakly localized around the As impurity atoms. On the other hand, for all other compositions -outside the G/X crossover region!, this alloy system exhibits normal behavior with spatially extended wave functions, constant and small optical bowing coefficients of about 0.3 eV, in good agreement with experiment⁶⁻⁸ and LDA-calculated^{14,47} results of 0.18–0.28 eV.

IV. DISCUSSION

In studying the $\text{GaAs}_{1-2x}\text{N}$

trated alloy where its electronic properties -e.g., optical bowing coefficient and wave functions! become irregular: the optical bowing coefficient is large and composition-dependent and the wave functions are localized around the impurity atoms. Thus, on a more general note, this study points out that the properties of semiconductor alloys having deep isovalent impurity levels in the dilute alloy limit *may not* be describable by a smooth function of the type of Eq. -1!, as previously thought.

In what follows, we will briefly review the literature on *deep isovalent impurities* indicating which alloys are likely to have the anomalies discussed above.

-i! *II-VI alloys*. Optical fluorescence, absorption, surface photo-emf, photoconductivity, and photoluminescence measurements have shown that CdS

stiffness between the *A-C* and *A-B* bonds is larger. Second, if the dilute alloys shows a localized deep impurity level in the gap, there will be a composition domain in the concen-

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