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$_{1-x}$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$_{1-x}$N$_x$ for $x\to1$! 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$_{1-x}$N$_x$ with the weakly perturbed alloy system GaAs$_{1-x}$P$_x$ having no deep gap levels in the impurity limits, and find that the concentrated GaAs$_{1-x}$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., Al-GaAs ~Refs. 3 and 4! and AlGaAsP ~Refs. 5–8!#, physical properties $P(x)$ were traditionally assumed[9] 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:

$$P(x) = xP(A) + (1-x)P(B) - bx(1-x), \qquad (1)$$

where $P(A)$ and $P(B)$ are the properties of the constituents A and B of the alloy A_xB_{1-x}, and b is the ''bowing coefficient.'' Examples[9] of Eq. ~1! include $P=$ lattice parameters, band gaps ~b is then called ''optical bowing coefficient''!, and mixing enthalpy ~b is then called ''interaction parameter''!. In all cases, b is composition independent. The optical bowing coefficient of conventional semiconductor alloys is known[9] to be small ~lower than 1 eV!.

Exceptions to this analytic and regular behavior are known to occur in some *metallic alloys*, when changes in composition move the Fermi level through a Van-Hove singularity ~i.e., ''electronic topological transitions''[10,11]!, and in some *semiconductor alloys* ~e.g., PbCdTe, PbSnTe, and PbGeTe! ~Ref. 12! showing some irregularities in microhardness, Hall mobility, and charge-carrier concentration at very dilute alloys. Because of the tediousness of measuring alloy properties on a sufficiently dense mesh of compositions, and because of the prevailing paradigm of the continuity and smoothness of $P(x)$, irregularities in P,(lectio11270±8.3,)-45 n¬Tf 8[(N(zTj /F12¬1all)]125¬TmcuAs)-13(bsy-0810¬TD [(w

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-

Atom	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

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 $R_{Ga-As}(x)$ and $R_{Ga-N}(x)$ versus x in GaAs$_{12x}$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 GaAs$_{12x}$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 $R_{Ga-N}(x)$ 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 $x_p 5 0.19$, close to the more accurate result of $x_p 5 0.198$ ~Ref. 43! obtained in previous fcc percolation simulations. Thus, at x_p; 0.19, one forms a continuous chain of *stiff* Ga-N-Ga-N{{{ bonds in a soft alloy medium ~$a_{VFF} 5 96.30$ N/m for GaN, compared to $a_{VFF} 5 41.19$ 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 $1 \gtrless x_{p.}$ 0.81! is also accompanied by a small bond length anomaly @see Fig. 1~c!#. In GaAs$_{12x}$P$_x$, we find again that the formation of a continuous chain of given

TABLE IX. The difference DR, at $x \approx 0.06$, between the A-C bond length in $AB_{1-x}C_x$ alloys as obtained in actual VFF simulations and the value obtained by fitting $R_{A\text{-}C}(x)$ for the composition domain $x \lesssim x_p$, where regular behavior is found. Da_{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 Da_{VFF}.

Impurity bond	Host	DR (Å)	Da_{VFF} (N/m)
Ga-N	GaAs	-0.003 (-0.15%)	-55.11
Ga-As	GaN	$+0.006$ $(+0.26\%)$	$+55.11$
Ga-P	GaAs	-0.001 (-0.04%)	-6.13
Ga-As	GaP	$+0.001$ $(+0.04\%)$	6.13

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 GaAs$_{1-x}$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 GaAs$_{1-x}$N$_x$ alloys ($x \lesssim 0.02$).[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 $x \to 1$. In this region, the band gap of the *random* alloy can be small (~ 0.4 eV for $x \approx 0.5$), 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 GaAs$_{1-x}$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 $x \to 0$ (no-gap level for N impurity in GaAs) and $x \to 1$ (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-
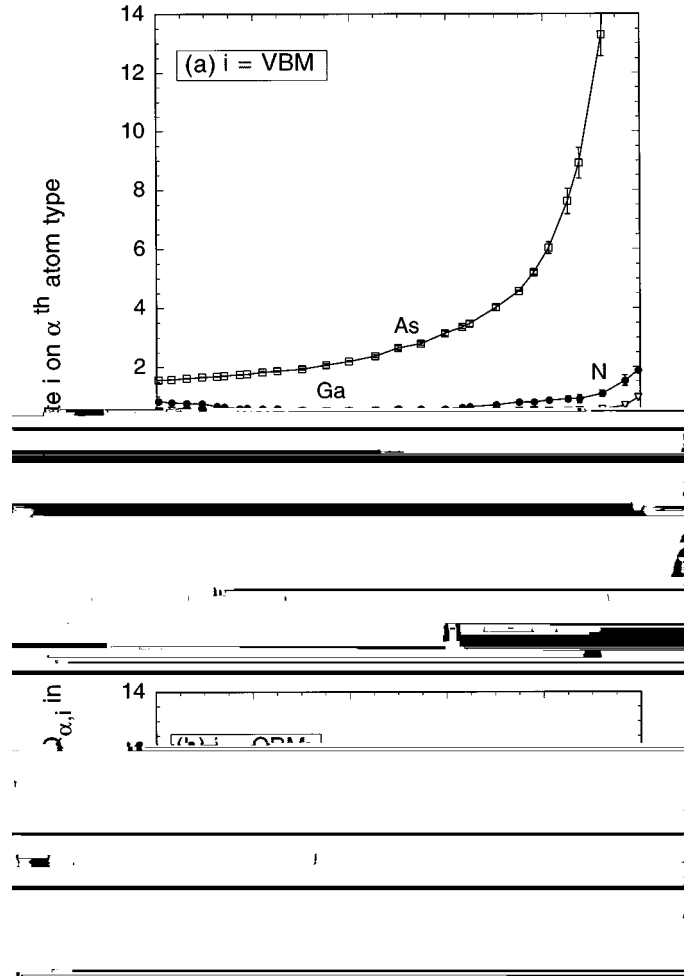

FIG. 3. Variation of the charge localization $Q_{a,i}$ of Eq. (3) for the highest occupied alloy level ($i=$VBM) and lowest empty alloy level ($i=$CBM) of atoms $a=$As,N,Ga of the random GaAs$_{1-x}$N$_x$ alloys as a function of x. The bars are statistical fluctuations in configurational sampling.

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 ($Dx \approx 0.6$) of the As-impurity region, compared to the N-impurity region ($Dx \approx 0.1$).

3. The electronic properties of GaAs$_{1-x}$P$_x$: A ''normal'' alloy

We now study the alloy properties of the weakly perturbed GaAs$_{1-x}$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 GaAs$_{1-x}$P$_x$. The direct to indirect (Γ_c to X_c) crossover occurs in the CBM at $x \approx 0.50$ [Fig. 6(c)], in good agreement with the experimental results[5-8] 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 $x \approx 0.5$, reflect the possibility of the CBM wave functions to have an X_c or Γ_c character at the transition point. We thus report in Fig. 6(b) the optical bowing coefficient for the Γ_{1c} state up to $x \approx 0.4$, and for the X_{1c} state for x higher than 0.6.

We see that in $GaAs_{1-x}P_x$ the impurity region occurs only in the extreme P-rich alloys -approximately between $x \gtrsim 0.97$ 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 Γ/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 experiment[6–8] and LDA-calculated[14,47] results of 0.18–0.28 eV.

IV. DISCUSSION

In studying the $GaAs_{1-x}N$

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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[2] R. T. Delves and B. Levis, J. Phys. Chem. Solids