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Citation: *Applied Physics Letters* **74**, 1842 (1999); doi: 10.1063/1.123687

View online: <http://dx.doi.org/10.1063/1.123687>

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# Resonant hole localization and anomalous optical bowing in InGaN alloys

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(Received 19 October 1998; accepted for publication 1 February 1999)

Using large supercell empirical pseudopotential calculations, we show that alloying of GaN with In induces localization in the hole wave function, resonating within the valence band. This occurs even with perfectly homogeneous In distribution (i.e., no clustering). This unusual effect can explain simultaneously exciton localization and a large, composition-dependent band gap bowing coefficient in InGaN alloys. This is in contrast to conventional alloys such as InGaAs that show a small and nearly composition-independent bowing coefficient. We further predict that (i) the hole wave function localization dramatically affects the photoluminescence intensity in InGaN alloys and (ii) the optical properties of InGaN alloys depend strongly on the microscopic arrangement of In atoms. © 1999 American Institute of Physics. [S0003-6951(99)00613-0]

Low-In content ( $x < 0.1$ )  $\text{In}_x\text{Ga}_{1-x}\text{N}$  alloys exhibit (i) localized excitons<sup>1-3</sup> as well as (ii) large ( $b > 3$  eV) and composition-dependent band gap bowing coefficients.<sup>4,5</sup> The first anomaly is usually explained in terms of the existence of In clustering,<sup>1,2</sup> while the second is explained in terms of the large Ga-In size mismatch.<sup>5</sup> Both explanations seem problematic: (a) indium clustering was initially expected on the basis of calculations<sup>6</sup> of limited *bulk* solubility, but more refined calculations<sup>7</sup> have shown that *surface* solubility (which is more relevant for vapor-phase growth) is far more extensive than bulk solubility, so clustering is not expected thermodynamically in *low-In content* alloys. (b)  $\text{In}_x\text{Ga}_{1-x}\text{As}$  also has a large size mismatch, yet its bowing parameter is much smaller ( $< 0.5$  eV) and composition independent<sup>8</sup> relative to  $\text{In}_x\text{Ga}_{1-x}\text{N}$ . Therefore, size mismatch is unlikely to be the full answer for the anomalous bowing in InGaN. Here we show theoretically that even perfectly homogeneous, random  $\text{In}_x\text{Ga}_{1-x}\text{N}$  alloys without *chemical* clustering exhibit “*electronic clustering*” in the form of *In-localized hole wave functions*, and that this unusual effect can explain simultaneously both exciton localization and a large, composition-dependent bowing coefficient. To clarify the underlying physics, we carry out calculations, in parallel, for  $\text{In}_x\text{Ga}_{1-x}\text{N}$  and  $\text{In}_x\text{Ga}_{1-x}\text{As}$  alloys, demonstrating that hole wave function localization is present in the first case and absent in the second. This result is important as it suggests a different way of analyzing the data on low-In content  $\text{In}_x\text{Ga}_{1-x}\text{N}$  alloy, i.e., in terms of electronic clustering, instead of (or, when appropriate, in addition to) “chemical clustering.”

Technically, we model the random alloys by randomly occupying the zinc-blende cation sites of a  $\sim 4000$  atom periodic supercell by the alloyed Ga and In species. We permit all atoms in the random configuration to locally relax to their minimum strain energy positions. The strain energy is modeled via the valence force field approach.<sup>9</sup> The lattice constant  $a(x)$  is assumed here to vary linearly as a function of the composition  $x$ . To obtain the electronic structure for

each relaxed supercell configuration we solve the Schrödinger equation

$$\left\{ -\frac{1}{2}\nabla^2 + \sum_{\alpha,m} v_{\alpha}(\mathbf{r}-\mathbf{R}_{\alpha,m}; \mathcal{E}_{ij}) \right\} \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}), \quad (1)$$

where  $\mathbf{R}_{\alpha,m}$  are the strain-minimizing positions of atom species  $\alpha$  ( $m$  running over individual atoms) and  $v_{\alpha}$  is the screened atomic pseudopotentials which have explicit dependence on the *local strain tensor*  $\mathcal{E}_{ij}$ .<sup>10</sup> The local strain is calculated as in Ref. 11. Using the strain dependence we are able to accurately fit the pseudopotentials to reproduce, in addition to bulk band structures, the hydrostatic and biaxial deformation potentials separately for conduction and valence band states. The wave functions  $\psi_i$  are expanded in plane waves and Eq. (1) is diagonalized via the folded spectrum method.<sup>12</sup>

*Wave function localization:* We find no states in the gap. Thus, we focus on the energy levels in the upper  $\sim 100$  meV from the alloy valence band maximum (VBM) down. Figure 1 shows iso-surface plots of the wave functions at the alloy

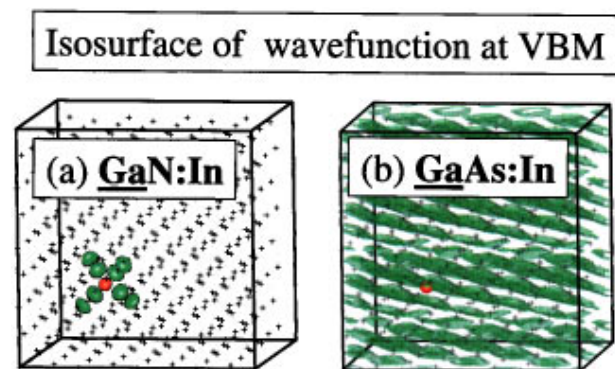


FIG. 1. The wave function squared of valence band maximum for a single In impurity in GaN (a) and GaAs (b). In atom is shown as a red sphere. The atomic positions of Ga,As,N are indicated by crosses. The green iso surface (constant-value surface) is drawn in both cases at 30% of the maximum value, which corresponds to the density  $0.001$  ( $0.00002$ )  $\text{e}/\text{Bohr}^3$  in  $\text{GaN:In}$  ( $\text{GaAs:In}$ ).

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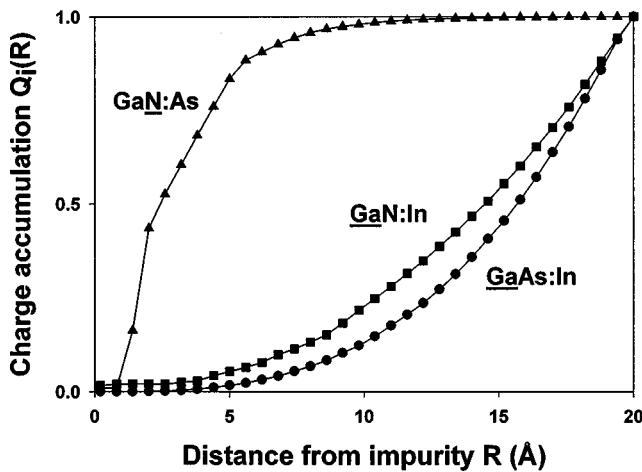


FIG. 2. The charge accumulation function  $Q_i(R) = 4\pi \int_0^R r^2 \psi_i^2 dr$  calculated for three impurity systems:  $\underline{\text{GaN}}:\text{In}$ ,  $\underline{\text{GaAs}}:\text{In}$ , and  $\underline{\text{GaN}}:\text{As}$ .  $R$  indicates the distance from the impurity atom.

valence band maximum in In-dilute  $\text{In}_x\text{Ga}_{1-x}\text{N}$  (part a) and  $\text{In}_x\text{Ga}_{1-x}\text{As}$  (part b). We see hole wave function localization around In in  $\text{In}_x\text{Ga}_{1-x}\text{N}$  but not in  $\text{In}_x\text{Ga}_{1-x}\text{As}$ . In fact, this localization exists not only for the alloy VBM state, but also extends for states below the alloy VBM ( $\sim 100$  meV range). Thus, the state shown in Fig. 1(a) has a *resonant* character. It can be thought of as a combination of the In ‘‘impurity’’ wave functions hybridized with a continuum of GaN valence bands. In this regard  $\underline{\text{GaN}}:\text{In}$  is different from the cases of isovalent *traps* of  $\underline{\text{GaN}}:\text{As}$ <sup>13</sup> that show localized states *inside the band gap*, with exponentially decaying wave function. As a result, there is strong localization on a small number of

atomic shells around  $\underline{\text{GaN}}:\text{In}$ , and at larger distance the wave function is extended. To see this, we calculate the charge enclosed within a sphere of radius  $R$  from the impurity  $Q_i(R) = 4\pi \int_0^R r^2 \psi_i^2 dr$  for electronic level  $i$  (Fig. 2). We see that (i)  $\underline{\text{GaN}}:\text{As}$  has a deep *gap* level with exponentially localized  $\psi_i$ , so  $Q_i(R)$  increases rapidly, reaching 90% already at a radius of 5 Å from the impurity. (ii)  $\underline{\text{GaAs}}:\text{In}$  has a wave function that is an extended Bloch-like state, so  $Q_i(R)$  increases slowly. (iii)  $\underline{\text{GaN}}:\text{In}$  has a state with resonant character, so the behavior of  $Q_i(R)$  is intermediate between the two extremes (i) and (ii), indicating the dual character of the wave function: short-range localization and long-range delocalization. This behavior leads to exciton localization (since the hole is localized) even if there is no *chemical* clustering of In atoms. In conventional alloys such as  $\text{In}_x\text{Ga}_{1-x}\text{As}$  or  $\text{Al}_x\text{Ga}_{1-x}\text{As}$ , a single isovalent impurity does not lead to any wave function localization; one needs clustering of a *few* like atoms to create a ‘‘local quantum well’’ with localized wave function.<sup>14</sup>

*Band gap bowing in InGaN:* Figure 3(a) shows the calculated band-gap bowing coefficient in  $\text{In}_x\text{Ga}_{1-x}\text{N}$  alloy. The bowing parameter has a strong composition dependence: it ranges from  $\sim 1.5$  eV for large In compositions to over 5 eV for small ( $x < 0.1$ ) compositions. The large bowing at small  $x$  is a direct consequence of the resonant wave function inside the valence band described above [Fig. 1(a)]: Fig. 3(b) shows that the VBM eigenvalue has large bowing as a function of composition  $x$  while the conduction band minimum (CBM) exhibits only small bowing. The real-space localization of the VBM states implies that the optical and electronic properties of  $\text{In}_x\text{Ga}_{1-x}\text{N}$  can depend sensitively on atomic

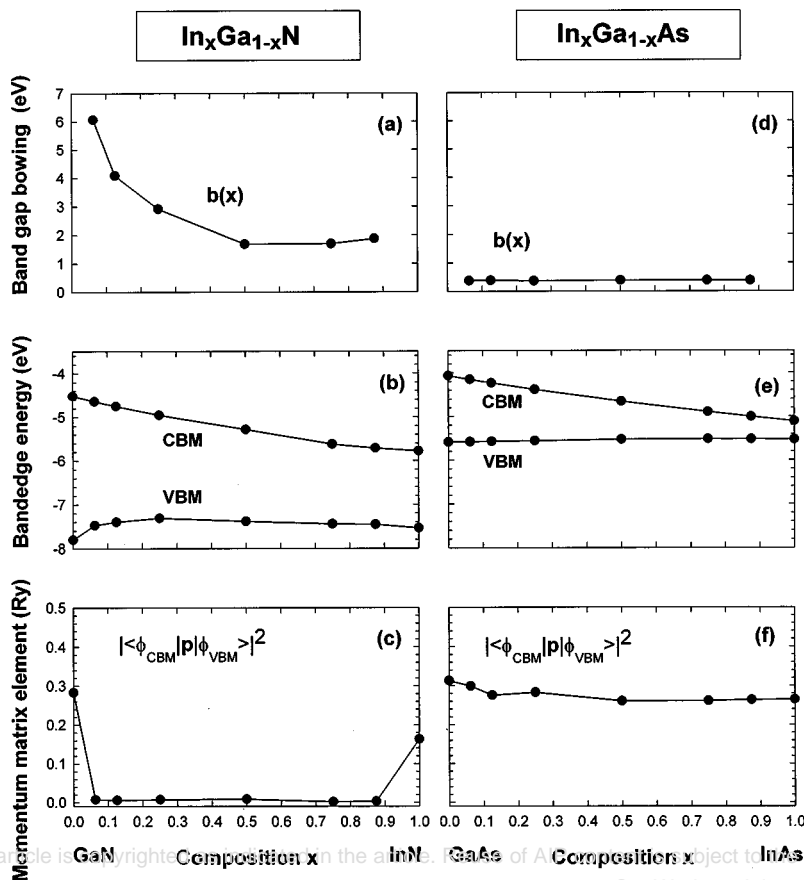


FIG. 3. Optical and electronic properties of  $\text{Ga}_{1-x}\text{In}_x\text{N}$  and  $\text{Ga}_{1-x}\text{In}_x\text{As}$  alloys. (a) and (d) Band gap bowing. (b) and (e) The energies of valence and conduction band edges. (c) and (f) Momentum matrix element  $M_{v,c}$  between the VBM and CBM states.

clustering; we find that the bowing coefficient of  $\text{In}_{0.125}\text{In}_{0.875}\text{N}$  changes more than 30% even if we change only 10% of the first-shell short-range order parameter.<sup>15</sup>

Our results agree with the recent experimental investigations finding large (3.8–4.4 eV) bowing coefficients in low-In content InGaN alloys.<sup>4,5</sup> Our results also agree qualitatively with the recent local density approximation (LDA) calculations.<sup>5</sup> However, our values for  $b(x)$  are even larger than the LDA derived values at small  $x < 0.1$  In compositions. We believe that this difference can be attributed partly to the fact that the LDA calculations have been performed with small supercells. The choice of supercell size and symmetry should not greatly affect the predicted alloy properties if all states are delocalized. Indeed, in a conventional alloy such as InGaAs, we find  $b \sim 0.4$  eV, nearly independent of the supercell size and shape used. If, however, the alloy has some localized states, the choice of the supercell size and shape is crucial, (unless one uses a very large cell). This reflects the fact that, depending on the supercell geometry, different Brillouin zone (BZ) points fold into the  $\bar{\Gamma}$  point.

For example, the  $\bar{\Gamma}$  point of a 16 atom fcc cell contains the  $\Gamma + 4L + 3X$  points, while a 32 atom bcc cell contains the  $\Gamma + 12\Sigma + 3X$  points (note, no  $L$  folding). Since localized wave functions consist of many different  $\mathbf{k}$  points, not all small supercells are adequate for their representation. LDA calculations are restricted to small supercells due to the computational burden. However, with our empirical pseudopotential approach we can use very large cells. We find that one In atom in 32 bcc, 64 sc, and 16 fcc atom GaN supercells produces bowing of 3.3, 4.9 and 5.5 eV, respectively. This correlates with the amount of  $L$  character we find in the alloy VBM: 0%, 8%, and 37%, respectively. Large supercells (4096 atoms) represent well the full BZ, and give  $b > 5$  eV at low  $x$ . Indeed, large supercell calculations also give much stronger localization than small cells.

*Comparison of band gap bowing in InGaN versus InGaAs:* Comparison of Fig. 3(a) with Fig. 3(d) demonstrates that the behavior of the band-gap bowing versus composition of  $\text{In}_x\text{Ga}_{1-x}\text{As}$  differs considerably from the one of  $\text{In}_x\text{Ga}_{1-x}\text{N}$ . The bowing parameter  $b(x)$  of  $\text{In}_x\text{Ga}_{1-x}\text{As}$  is nearly independent of the composition  $x$ . This suggests that the anomalous behavior of  $b$  versus composition in  $\text{In}_x\text{Ga}_{1-x}\text{N}$  is not a consequence of the large lattice mismatch between GaN and InN,<sup>5</sup> but instead is a consequence of the wave function resonance shown above: in InGaN the energy of the VB bows upwards because the VB resonance pushes the VBM up, while in InGaAs, due to lack of resonance, VBM is nearly linear with composition. At the In-rich end of InGaN alloy the CBM and VBM energies [Fig. 3 (c)] also behave linearly, revealing no Ga-induced resonances in InN.

*Transition intensities:* The photoluminescence (PL) intensity is proportional to the momentum  $\mathbf{p}$  matrix element  $M_{v,c} = |\langle \psi_v | \mathbf{p} | \psi_c \rangle|^2$  between the VBM and CBM states. The calculated  $M_{v,c}$  as a function of composition  $x$  is shown in Figs. 3(c) and 3(f) for InGaN and InGaAs, respectively. The momentum matrix element of  $\text{In}_x\text{Ga}_{1-x}\text{N}$  decreases rapidly when  $x$  increases from 0 to 0.0625 (by two orders of magnitude). This dramatic decrease in  $M_{v,c}$  is another consequence of the localization of the VBM states. Projecting

the alloy wave functions on periodic Bloch states<sup>16</sup> shows that for  $x = 0.0625$  in  $\text{In}_x\text{Ga}_{1-x}\text{N}$  the VBM states have only 2% of  $\Gamma$  character. As a consequence,  $M_{v,c}$  is reduced since the probability for a direct transition (in reciprocal space) is reduced.<sup>17</sup> On the other hand, Fig. 3(f) shows that  $M_{v,c}$  of  $\text{In}_x\text{Ga}_{1-x}\text{As}$  has a rather usual behavior: it is large and smoothly composition dependent. In  $\text{In}_x\text{Ga}_{1-x}\text{As}$ , the VBM retains over 90% of  $\Gamma$  character at all compositions which correlates well with the large calculated  $M_{v,c}$ .

In summary, we find that the alloying of GaN with In leads to localization of the hole states in the upper valence band. In contrast with conventional alloys, no chemical clustering of In atoms is needed to induce this localization. We propose that this wave function localization is responsible for four optical anomalies of InGaN alloys: (i) the band-gap bowing coefficient is large and composition dependent, (ii) these alloys exhibit exciton localization, (iii) the PL intensity is small, and (iv) the optical properties depend strongly on the microscopic atomic arrangement.

The authors wish to thank C. Wetzel for very useful discussions. This work is supported by the U.S. Department of Energy, OER-BES-DMS Grant No. DE-AC36-83-CH10093.

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