

phys. stat. sol. (b) **216**, 117 (1999)

Subject classification: 71.20.Nr; 61.50.Ah; S7.14

## Anomalous Behavior of the Nitride Alloys

ALEX ZUNGER

National Renewable Energy Laboratory, Golden, CO-80401, USA  
e-mail: alex\_zunger@nrel.gov

(Received July 4, 1999)

This paper summarizes the way in which nitride alloys InGaN and GaAsN are anomalous. It predicts wave function localization states inside the band gap, unusual pressure dependence, effects of short-range order and percolation.

### 1. Introduction

Imagine that III–V nitrides had no technological significance. Which *physically-interesting* research questions would we then address? In other words, in what way is the physical behavior of nitrides different from that of phosphides or arsenide compounds? In this paper, I summarize the answers to these questions as provided by my theoretical work, in the context of the *bulk properties* of nitrides. This study does not address surface physics or defect physics.

### 2. Nature’s Selection between Wurtzite and Zincblende Structures

III–V nitrides as well as BeO, ZnO and CdS form in the wurtzite (WZ) crystal structure, whereas all other III–V’s and II–VI’s (except HgS) have the zincblende (ZB) structure. Can one predict *a-priori* which compound will have the ZB and which will have the WZ structure? Can one further predict the chemical trends in the difference in the WZ–ZB *structural* total energies?

This is part of a more general question: predict the distribution of binary octet  $A^N B^{8-N}$  compounds (i.e., their structural preferences) in the NaCl, CsCl, ZB, WZ crystal structures. The general answer for this was provided in 1980 [1], when the concept of angular-momentum dependent “atomic orbital radii” was used to systematize all stable crystal structures of the octet compounds ( $\approx 110$  compounds), as well as the non-octet structures ( $\approx 350$  compounds). The idea is [1, 2] that the classic crystallographic radii (e.g., covalent, atomic, metallic) are metrics which do not contain directional bonding information, and thus could, at best, describe only packing of spherical object, but could not distinguish predictively different crystal structures. On the other hand, the  $r_s$ ,  $r_p$ ,  $r_d$  “orbital radii”, derived from first-principles pseudopotential theory [1], do contain such information. Remarkably, simple linear combinations of these radii for A and B atoms

$$R_{\sigma}^{AB} = (r_p^A + r_s^A) - (r_p^B + r_s^B),$$

$$R_{\pi}^{AB} = |r_p^A - r_s^A| + |r_p^B - r_s^B|$$

provide structural coordinates, in that a  $R_{\sigma}^{\text{AB}}$  versus  $R_{\pi}^{\text{AB}}$  “map” distinguishes predictively all different crystal structures of the binary AB compounds with  $\approx 96\%$  accuracy! Recently, Villars and Calvert [3] have extended this dual coordinate map into a three-coordinate map, thus separating *thousands of compounds*.

A recent development in this area is of interest to nitrides: Yeh et al. [4], calculated very precisely, using first-principles LDA, the difference in total energy between the ZB and WZ crystal structure of C, Si, GaAs, GaP, AlAs, AlP, GaN, AlN, InN, ZnS, ZnSe, and CdS. Remarkably, they found that the energy difference  $E_{\text{WZ}}^{\text{AB}} - E_{\text{ZB}}^{\text{AB}}$  has a linear scaling with the atomic orbital radii! Thus, it is now possible not only to predict which AB compound forms in ZB and which forms in WZ [1, 2], but one can also predict, just by knowing the atomic orbital radii of atom A and atom B (tabulated, e.g., in Ref. [2]), what is the WZ–ZB energy difference for *any* AB compound (even hypothetical materials). This study revealed the tendency to stabilize the ZB structure in the series  $\text{B}^{\text{VI}} = \text{O} \rightarrow \text{S} \rightarrow \text{Se} \rightarrow \text{Te}$  in  $\text{A}^{\text{II}}\text{B}^{\text{VI}}$  and in  $\text{A}^{\text{III}} = \text{Ga} \rightarrow \text{Al} \rightarrow \text{In}$  for  $\text{A}^{\text{III}}\text{B}^{\text{V}}$ s, and proposed new, low temperature structures for CdSe(ZB) and MgTe(NiAs, not WZ).

### 3. Indirect $\rightarrow$ Direct Band Gap Reversal in ZB $\rightarrow$ WZ Structures of AlN, GaP

While the difference in total energies between the ZB and WZ crystal structures is only  $\leq 10$  meV/atom (consistent with the fact that the two structures are identical for the first two neighbor shells), the difference in *band gap* energy between the ZB and WZ crystal structures can be (e.g., SiC) as large as  $\approx 1000$  meV. This surprising effect was explained by Yeh et al. [5], in terms of direct–indirect band folding. They predicted that while AlN and GaP both have an indirect gap in the ZB structure, in the WZ structure the band gap will become direct. Can GaP be stabilized in the WZ structure? If so, it will have a direct band gap.

### 4. “Normal” versus “Anomalous” Isovalent Alloys

Before we show how “anomalous” the nitride alloys are, let us define what is a “normal” alloy. In a “normal” isovalent  $\text{A}_x\text{B}_{1-x}$  alloy, as one increases the composition  $x$  from zero, the conduction band moves as a whole, the valence band moves as a whole, and no new (defect) levels appear in the band gap. Furthermore, the bowing coefficient  $b$  in

$$E_g(x) = xE_A + (1 - x)E_B - bx(1 - x)$$

is “small” (less than 1 eV), and composition-independent. Also, normal isovalent alloys retain, to a large degree, the translational invariance of the underlying compounds A and B, even though the alloy is random. This behavior can be quantified by “projecting” a calculated random alloy wave function onto the Bloch orbitals of the constituent [6]. If a single wave vector  $\mathbf{k}$  (“majority representation”) dominates the projection, then we can say that the alloy wave function retains the “personality” of the parent components. The existence of a single dominant wave vector  $\mathbf{k}$  in each alloy wave function means that the alloy states are extended and translationally nearly invariant.

“Normal” isovalent alloys are usually made of components whose properties are “similar”, e.g., the band offsets are below 1 eV and the lattice mismatch is below say, 5%. In contrast, the valence band offset between GaAs–GaN is 2.3 eV, and the lattice

constant mismatch is  $\approx 22\%$ . In GaN–InN, the valence band offset is  $\approx 0.5$  eV and the lattice mismatch 10%. We will see that the nitrides are thus “anomalous” since each alloy component poses a large chemical and size perturbation on the other component. Thus, we will encounter localization, loss of translational invariance, deep isovalent gap states, “giant” bowing and  $x$ -dependent bowing.

### 5. InGaN-Hole Localization in the Valence Band

Low-In content ( $x < 0.1$ )  $\text{In}_x\text{Ga}_{1-x}\text{N}$  alloys exhibit experimentally: (i) localized excitons as well as (ii) large ( $b > 3$  eV) and composition-dependent band gap bowing coefficients. The first anomaly was usually explained in terms of the existence of In clustering, while the second was explained in terms of the large Ga–In size mismatch. Both explanations seem problematic: a) indium clustering was initially expected on the basis of calculations by Ho and Stringfellow [7] showing limited *bulk* solubility. However, these authors neglected surface effects. Indeed, more refined calculations [8] 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 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. We showed theoretically [9] 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 [9]. To clarify the underlying physics, we carried 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 [9].

We found 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 ( $\approx 100$  meV range). Thus, the hole state has a *resonant* character. The calculated band gap bowing parameter has a strong composition dependence: it ranges from  $\approx 1.5$  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. Our results agree with the recent experimental investigations finding large (3.8 to 4.4 eV) bowing coefficient in low-In content InGaN alloys.

In summary, we find [9] 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 coefficient  $b$  is large and composition dependent; (ii) these alloys exhibit exciton localization; (iii) the PL intensity is relatively weak, and (iv) the optical properties depend strongly on the microscopic atomic arrangement.

### 6. GaAs: N-Electron Localization in the Conduction Band

Since the CBM of GaN is *below* that of GaAs [10], addition of GaN to GaAs creates levels near or below the GaAs CBM. In contrast, since the VBM of GaN is (much)

lower than that of GaAs, addition of GaN creates nitrogen states only deep in the GaAs valence band. Indeed, our first principles calculations [11, 12] show a dramatic localization of the wave function of the CBM near the nitrogen atoms. This localization causes a giant ( $\approx 20$  eV) bowing coefficient  $b(x)$  which also depends on composition  $x$  [12]. Our analysis of the wave functions of GaAs:N show that there are a few new states [13].

### 6.1 The conventional $a_1(\text{N})$ state

In the *impurity* limit ( $x \rightarrow 0$ ), nitrogen induces a resonant impurity state  $a_1(\text{N})$  inside the conduction band of GaAs. We find that this state exhibits nitrogen localization: nearly half of the charge of the  $a_1(\text{N})$  state is contained inside the nearest-neighbor shell surrounding the nitrogen atom. This localization in real space is reflected in delocalization in reciprocal space, evidence by the spectral projection (only 15% of the wave function is due to  $\Gamma$ ). In this impurity limit we find this state to be 180 meV above the CBM, in good agreement with the experimental estimate 150 to 180 meV. However, the energy of this  $a_1(\text{N})$  state rises rapidly as the nitrogen composition increases. Thus, in the alloy ( $x \gtrsim 1\%$ )  $a_1(\text{N})$  is too far in energy to be important optically.

### 6.2 The perturbed host states

Substitution of N on As site exerts such a large perturbation that the host crystal states  $\Gamma_{1c}$ ,  $L_{1c}$  and  $X_{1c}$  mix thoroughly, forming new low-energy states. From the point of view of symmetry, substitution at a  $T_d$  symmetry site modifies the  $\Gamma_{1c}$  state  $a_1(\Gamma_{1c})$ , splits the fourfold  $L_{1c}$  valley into  $a_1(L_{1c})$  and  $t_2(L_{1c})$  representations, and splits the threefold  $X_{1c}$  valley into  $a_1(X_{1c})$  and  $e(X_{1c})$ . All  $a_1$ -symmetric levels  $a_1(\text{N})$ ,  $a_1(\Gamma_{1c})$ ,  $a_1(L_{1c})$  and  $a_1(X_{1c})$  can interact under the influence of the nitrogen potential, producing the low-energy states  $E_-$  and  $E_+$ . This model [13], emphasizing  $\Gamma$ -X-L mixing, is thus very different from the model of Shan et al. [14] that couples nitrogen only to the  $\Gamma_{1c}$  state.

### 6.3 The $E_-$ state

The lowest conduction band  $E_-$  is mostly a combination of  $a_1(\Gamma_{1c})$  and  $a_1(L_{1c})$ , with only little contribution from the higher energy  $a_1(X_{1c})$  state. This description of  $E_-$  as significantly perturbed  $\Gamma_{1c}$  state is very different from earlier models [14] which neglected the interaction of  $a_1(\Gamma_{1c})$  with non- $\Gamma$  states. Repulsion from these non- $\Gamma$   $a_1$ -states depresses  $E_-$ , leading to a pronounced red-shift with composition (“optical bowing” [15]). The  $\Gamma_{1c}$ - $L_{1c}$  interaction is strong:  $E_-$  shows a reduced (increased)  $\Gamma_{1c}$ ( $L_{1c}$ ) character as  $x$  increases. Since the  $L_{1c}$  electrons have heavier mass than the  $\Gamma_{1c}$ , we find that nitrogen alloying increases the effective mass of the  $E_-$  state, in agreement with experimental observations. This is in contrast with conventional alloys (e.g., InGaAs) where alloying does not promote significant  $\Gamma$ -L mixing. The  $\Gamma$ -L mixing (delocalization in reciprocal space) indicates localization in real space: unlike conventional CBM states that are delocalized, the  $E_-$  state in  $\text{GaAs}_{1-x}\text{N}_x$  alloy is localized (around the Ga atoms nearest to nitrogen). The localization suggests that electron diffusion lengths must be *intrinsically short* in  $\text{GaAs}_{1-x}\text{N}_x$  alloys.

As pressure is applied, the  $E_-$  state experiences repulsion from two sources. Initially, the  $\Gamma(L)$  character of  $E_-$  state decreases (increases) due to the anti-crossing with

$a_1(L_{1c})$  and  $a_1(N)$ . At higher pressures, the  $\Gamma$ -L interaction becomes less important and is replaced by repulsion from the  $a_1(X_{1c})$  state, as evidenced by the rapidly increasing X-character of the  $E_-$  state. Since the electron effective mass at  $X_{1c}$  is considerably larger than at  $\Gamma_{1c}$ , the mixing of  $X_{1c}$ -character into  $E_-$  results in a significant increase in  $m^*(E_-)$  as a function of pressure, as seen in experiments. In summary, at zero pressure  $E_-$  is a  $\Gamma$ -L mixed state, while at high pressure it is a  $\Gamma$ -X mixed state. It is never a  $\Gamma$ -like state [14].

#### 6.4 The $E_+$ state

The  $E_+$  state starts out at the nitrogen impurity ( $x \rightarrow 0$ ) limit as an  $a_1(N)$  impurity state, but as the nitrogen concentration increases, it acquires  $a_1(L_{1c})$  character. At the impurity limit ( $x \approx 0.05\%$ ) the coupling between  $a_1(L_{1c})$  and  $a_1(N)$  pushes  $a_1(L_{1c})$  energy above  $t_2(L_{1c})$ , however, this  $t_2$ - $a_1$  splitting remains small (13 meV). When the nitrogen concentration increases, the energy of resonant state  $a_1(N)$  increases rapidly, and its coupling with  $a_1(L_{1c})$  leads to the lowering of the energy of  $a_1(L_{1c})$ . As pressure is applied, both  $a_1(N)$  and  $a_1(L_{1c})$  shift nearly linearly up in energy. The pressure coefficient for their  $\Gamma$ -weighted average  $E_+$  has a small value of 60 meV/GPa at small pressures (similar to  $E_-$ ) but increases to a value  $\approx 100$  meV/GPa at higher pressure.

### 7. Effects of Short-Range Order

We have investigated the effect of atomic short-range order (SRO) on the electronic and optical properties of dilute and concentrated GaAsN, GaInN, and GaInAs alloys [16]. We find that in concentrated alloys, the clustering of like atoms in the first neighbor f.c.c. shell (e.g., N-N in GaAsN alloys), leads to a large decrease of both the band-gap and the valence-to-conduction dipole transition-matrix element in GaAsN and in GaInN. On the other hand, the optical properties of GaInAs depend only weakly on the atomic SRO. The reason that the nitride alloys are affected strongly by SRO while GaInAs is affected to a much lesser extent, is that in the former case there are band-edge wave-function localizations around specific atoms in the random alloys.

### 8. Percolation in GaAsN

Tradition has it that in the absence of structural phase transition, the properties of semiconductor alloys (bond lengths, band gaps, elastic constants, etc.), have simple and smooth (often parabolic) dependence on composition. Indeed, it is believed that in the absence of composition-induced structural phase transitions in alloys, physical properties  $P(x)$  are simple 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, e.g., a linear (Vegard-like) term, plus a small quadratic correction.

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  $P(x)$  might have been previously overlooked or "smoothed over." Likewise, theoretical calculations of alloy properties are often based on small supercells, restricting explorations to only sparsely spaced discrete compositions. Possible irregular behavior of  $P(x)$  in a narrow composition range could have been easily overlooked. We addressed the general question of the possibility of irregu-

lar behavior of  $P(x)$  versus  $x$  in alloys lacking structural, topological, or electronic direct-to-indirect transitions. We find that there is a significant *structural* anomaly at those compositions where a continuous wall-to-wall chain of bonds form in an alloy medium, e.g., Ga–N–Ga–N... or Ga–As–Ga–As... in the  $\text{GaAs}_{1-x}\text{N}_x$  alloy. This occurs at the impurity percolation threshold  $x_p = 0.19$  for the f.c.c. lattice [17]. We predicted that alloy bond lengths and elastic behavior can change at the percolation composition.

### 9. GaN:P and GaN:As – Deep Gap Isoelectronic Levels

In contrast with the conventional isovalent III–V systems, GaN:P and GaN:As are shown to exhibit *deep* gap levels. The calculated [18] donor energies are  $\varepsilon(+/0) = \varepsilon_v + 0.22$  and  $\varepsilon_v + 0.41$  eV, respectively, and the double donor energies are  $\varepsilon(++/+ ) = \varepsilon_v + 0.09$  and  $\varepsilon_v + 0.24$  eV, respectively. The p-like gap wave function is found to be strongly localized on the impurity site. Outward atomic relaxations of  $\approx 13\%$  and  $\approx 15\%$  are calculated for the nearest-neighbor Ga atoms surrounding neutral GaN:P<sup>0</sup> and GaN:As<sup>0</sup>, respectively. The relaxation increases by  $\approx 1\%$  for the positively charged impurities. The impurity-bound exciton binding energy is calculated at  $E_b = 0.22$  and  $E_b = 0.41$  eV for GaN:P and GaN:As. The former is in good agreement with the experimental data ( $E_b = 0.232$  eV) whereas the latter is offered as a prediction. We next turned to impurity *pairs* [19], i.e., P–P or As–As in GaN.

The electronic and atomic structure of substitutional  $n$ -th neighbor ( $1 \leq n \leq 6$ ) P–P and As–As impurity pairs in zincblende GaN is investigated. A single impurity introduces a deep  $t_2$  gap level. We showed [19] that the interaction between the  $t_2$  defect orbitals of the impurity pairs leads to an interesting pattern of single-particle level splitting, being largest for the first ( $n = 1$ ) and fourth ( $n = 4$ ) neighbor pairs, both exhibiting a  $C_{2v}$  symmetry. The total energy of the  $n$ -th order pair  $\Delta E^{(n)}$  relative to isolated ( $n \rightarrow \infty$ ) impurities indicates pairing tendency for  $n = 1$  and 2 while  $n = 4$  pairs are unstable. We explain this behavior of  $\Delta E^{(n)}$  versus  $n$  as a consequence of the interplay between two effects: 1. an “elastic contribution” representing the interaction between the elastic strain fields of the two impurities; and, 2. an “electronic contribution” describing the interaction of the defect orbitals of the two impurity atoms. The binding energies of the impurity-pair bound excitons are calculated for the  $n = 1$  As–As and P–P pairs (1.27 and 0.85 eV, respectively), and are found to be significantly larger than for the corresponding isolated impurities. The probabilities for electronic transitions between the defect levels and conduction band are calculated. The results predict the existence of a rich series of spectroscopic features distinct from single impurities.

### 10. Summary

We have surveyed the way that bulk nitrides and their alloys are physically different than conventional (e.g., phosphide or arsenide) alloys:

1. The nitrides have the wurtzite crystal structure, not the zincblende. This structural preference is explained via the “orbital radii” concept.
2. AlN and GaP have an indirect band gap in the zincblende structure, but a direct gap in the wurtzite structure. This is explained by band folding.

3. InGaN does not exhibit vanishing solubility, as expected from bulk-thermodynamic models. The surface-induced solubility is rather high.

4. InGaN exhibits localization of the hole wave functions. This could explain exciton localization even without atomic clustering. This leads to large (1 to 5 eV) and composition-dependent bowing coefficient.

5. GaAs<sub>1-x</sub>N exhibits localization of its electron wave function, giant (up to 20 eV) bowing coefficients, flattening of the band-gap pressure coefficient, increase of the electron effective-mass with pressure. This is explained by a  $\Gamma$ -X-L mixing and level anti-crossing.

6. Atomic short-range order changes the band gap of GaAsN and GaInN much more strongly than in conventional GaAsP and GaInAs alloys. This is explained by wave function localization.

7. As the alloy composition in GaAs<sub>1-x</sub>N<sub>x</sub> reaches the (unfortunately impractical) percolation value of  $x \approx 19\%$ , we predict a transition in bond lengths and bulk modules, resulting from the formation of an uninterrupted, wall-to-wall chain of Ga-N bonds.

8. P and As form deep isovalent gap levels in GaN.

9. P-P pairs and As-As pairs fill the band gap of GaN by a large number of levels forming a spectroscopic series.

**Acknowledgements** This work has been done in collaboration with L. Bellaiche, T. Mattila, C. Yeh and S. Wei, and was supported by US DOE through SC-BES-DMS.

## References

- [1] A. ZUNGER, Phys. Rev. Lett. **44**, 582 (1980).
- [2] A. ZUNGER, in: Structure and Bonding in Crystals, Eds. M. O'KEEFE and A. NAVROTSKY, Academic Press, New York 1981 (p. 73).
- [3] P. VILLARS and L. D. CALVERT, Pearson's Handbook of Crystallographic Data and Intermetallic Phases, American Society for Metals, 1985, and references therein.
- [4] C. Y. YEH, Z. W. LU, S. FROYEN, and A. ZUNGER, Phys. Rev. B (rapid commun.) **45**, 12130 (1992).  
C. Y. YEH, Z. W. LU, S. FROYEN, and A. ZUNGER, Phys. Rev. B **46**, 10086 (1992).
- [5] C. YEH, S.-H. WEI, and A. ZUNGER, Phys. Rev. B (rapid commun.) **50**, 2715 (1994).
- [6] L. W. WANG, L. BELLAICHE, S. H. WEI, and A. ZUNGER, Phys. Rev. Lett. **80**, 4725 (1998).
- [7] J. HO and G. STRINGFELLOW, MRS Symp. Proc. **449**, 871 (1997).
- [8] S. B. ZHANG and A. ZUNGER, Appl. Phys. Lett. **71**, 677 (1997).
- [9] L. BELLAICHE, T. MATTILA, L. W. WANG, S. H. WEI, and A. ZUNGER, Appl. Phys. Lett. **74**, 1942 (1999).
- [10] S. H. WEI and A. ZUNGER, Appl. Phys. Lett. **69**, 2719 (1996).
- [11] L. BELLAICHE, S. H. WEI, and A. ZUNGER, Phys. Rev. B **56**, 10233 (1997).
- [12] S. H. WEI and A. ZUNGER, Phys. Rev. Lett. **76**, 664 (1996).
- [13] T. MATTILA, S. H. WEI, and A. ZUNGER, Phys. Rev. B (rapid commun.) Oct. (1999).
- [14] W. SHAN, W. WALUKIEWICZ, J. A. AGER, E. HALLER, J. F. GEISZ, D. FRIEDMAN, J. OLSON, and S. KURTZ, Phys. Rev. Lett. **82**, 1221 (1999).
- [15] L. BELLAICHE, S. H. WEI, and A. ZUNGER, Appl. Phys. Lett. **70**, 3558 (1997).
- [16] L. BELLAICHE and A. ZUNGER, Phys. Rev. B **57**, 4425 (1998).
- [17] L. BELLAICHE, S. H. WEI, and A. ZUNGER, Phys. Rev. B **54**, 17568 (1996).
- [18] T. MATTILA and A. ZUNGER, Phys. Rev. B **58**, 1367 (1998).
- [19] T. MATTILA and A. ZUNGER, Phys. Rev. B **59**, 9943 (1999).

