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

provide structural coordinates, in that a R_s^{AB} versus R_p^{AB} "map" distinguishes predictively all different crystal structures of the binary AB compounds with 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 $E_{WZ}^{AB} - E_{ZB}^{AB}$ 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 $B^{VI} = O \rightarrow S \rightarrow Se \rightarrow Te$ in $A^{II}B^{VI}$ and in $A^{III} = Ga \rightarrow Al \rightarrow In$ for $A^{III}B^{V}$s, and proposed new, low temperature structures for CdSe(ZB) and MgTe(NiAs, not WZ).

3. Indirect → Direct Band Gap Reversal in ZB → WZ Structures of AlN, GaP

While the difference in total energies between the ZB and WZ crystal structures is only 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 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 A_xB_{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 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 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

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 (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(N) state

In the impurity limit …x ! 0), nitrogen induces a resonant impurity state a_1(N) inside the conduction band of GaAs. We find that this state exhibits nitrogen localization: nearly half of the charge of the a_1(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 G). 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(N) state rises rapidly as the nitrogen composition increases. Thus, in the alloy …x & 1%) a_1(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 G_{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 G_{1c} state a_1…G_{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(N), a_1…G_{1c}†, a_1…L_{1c}† and a_1…X_{1c}† can interact under the influence of the nitrogen potential, producing the low-energy states $E_ÿ$ and $E_‡$. This model [13], emphasizing G±X±L mixing, is thus very different from the model of Shan et al. [14] that couples nitrogen only to the G_{1c} state.

6.3 The $E_±$ state

The lowest conduction band $E_ÿ$ is mostly a combination of a_1(G_{1c}) and a_1(L_{1c}), with only little contribution from the higher energy a_1(X_{1c}) state. This description of $E_ÿ$ as significantly perturbed G_{1c} state is very different from earlier models [14] whict7y392.372 284.372

$a_1(L_{1c})$

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 $GaAs_{1-x}N_x$ 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. Ga<u>N</u> : P and Ga<u>N</u> : As – Deep Gap Isoelectronic Levels

In contrast with the conventional isovalent III–V systems, Ga<u>N</u> : P and Ga<u>N</u> : As are shown to exhibit deep gap levels. The calculated [18] donor energies are $e(+/0) = e_v + 0.22$ and $e_v + 0.41$ eV, respectively, and the double donor energies are $e(++/+) = e_v + 0.09$ and $e_v + 0.24$ eV, respectively. The p-like gap wave function is found to be strongly localized on the impurity site. Outward atomic relaxations of 13% and 15% are calculated for the nearest-neighbor Ga atoms surrounding neutral Ga<u>N</u> : P^0 and Ga<u>N</u> : As^0, respectively. The relaxation increases by 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 Ga<u>N</u> : P and Ga<u>N</u> : 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 n 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 ($n \to$ 1) impurities indicates pairing tendency for $n = 1$ and 2 whil

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

4. InGaN exhibits localizatiaon 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 : 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 G±X±L mixing and level anticrossing.

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 $GaAs_{1ÿx}N_x$ reaches the (unfortunately impractical) percolation value of x 19%, we predict a transition in bond lengths and bulk modules, resulting from the formation of an uninterupted, 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. G-2.446 D(As)o4owledg0u5p4j1.436 0 gTD(serihe)Tj1.755 0 TD(ba