



Dilute nitride based III–V alloys for laser and solar cell applications

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Abstract

The dilute nitrogen alloy $\text{GaAs}_{1-x}\text{N}_x$ is of recent technological importance for high efficiency solar cells and vertical cavity surface emitting diode lasers used in fiber optic communications. The giant band gap lowering and the abnormal effective mass phenomena observed in this material have been extensively researched. There exist many inconsistencies between the results of various theoretical models and experimental techniques used to probe the above phenomena. It appears that these arise because $\text{GaAs}_{1-x}\text{N}_x$ should be viewed not as an abnormal alloy but rather as a heavy isoelectronically doped semiconductor. © 2001 Elsevier Science Ltd. All rights reserved.

1. Introduction

The lack of III–V semiconductor materials with band gaps near 1 eV that are lattice matched to GaAs has hampered the development of vertical cavity surface emitting lasers (VCSELs) for use in long haul optical communications [1] as well as the development of very high efficiency solar cells [2]. For fabricating 1.3 or 1.55 μm communications range VCSELs this has necessitated the use of InP substrates, AlAs/GaAs Bragg reflectors and complex fusion bonding steps or the use of Bragg reflectors synthesized from alternate ternary or quaternary alloys which exhibit poorer reflectivity and thermal conductivity [1]. The current state of art for high efficiency solar cells is the 32% efficient triple junction solar cell comprising of GaInP₂, GaAs and Ge absorbers [2]. Enhancing the efficiency of this cell to 40% requires the sequence of band gaps 0.67/1.05/1.42/1.9 eV [2]. GaInP₂, GaAs and Ge are ideally suited lattice matched semiconductors for the top, next to top, and bottom cells, but there exists no III–V semiconductor lattice matched to GaAs with a band gap of 1.05 eV. The novel properties exhibited by $\text{GaAs}_{1-x}\text{N}_x$ where it was observed that [3] the incorporation of just 3% N reduced the band gap by 400 meV bringing it close to 1 eV has thus generated a recent flurry of research activity because of the exciting possibility of fabricating very high efficiency solar cells [2] as well as synthesizing VCSELs for use in fiber optic communications based on a single step growth process on GaAs substrates [4]. It soon

became evident, however, that incorporation of the desired amount of nitrogen into GaAs resulted in severe degradation of its electronic properties. The electron mobility for example gets reduced to $\approx 300 \text{ cm}^2/\text{V/s}$ [5]. There has thus been an intense effort devoted to understanding the reasons for the giant band gap reduction and the poor transport properties of $\text{GaAs}_{1-x}\text{N}_x$.

2. Models for giant band gap lowering

The mechanism for the giant band gap reduction in $\text{GaAs}_{1-x}\text{N}_x$ has become the subject of extensive theoretical and experimental investigations. Using first-principles total energy calculations (density functional theory in the local density approximation (LDA)) Neugebauer et al. [6] observed a strong bowing of the band gap for ordered $\text{GaAs}_{1-x}\text{N}_x$ and very limited solubility of N in this material. Based on a quasiparticle study of the fundamental excitations in ordered $\text{GaAs}_{1-x}\text{N}_x$, Rubio et al. [7] concluded that the strong red shift of the conduction band minimum (CBM) could be explained by effects arising from the 20% lattice mismatch between GaN and GaAs. They observed that for the bottom of the conduction band, the charge density was localized on the N atoms and tended to form atomic like orbitals. Using first-principles supercell calculations (linearly augmented plane wave LDA) for $\text{GaAs}_{1-x}\text{N}_x$, Wei et al. [8] observed a giant and composition dependent bowing coefficient and that the CBM wave functions showed strong localization on the N sublattice. It is important to note that all the above calculations were performed for ordered as opposed to disordered $\text{GaAs}_{1-x}\text{N}_x$ alloys.

As shown in Fig. 1 N generates a series of isoelectronic

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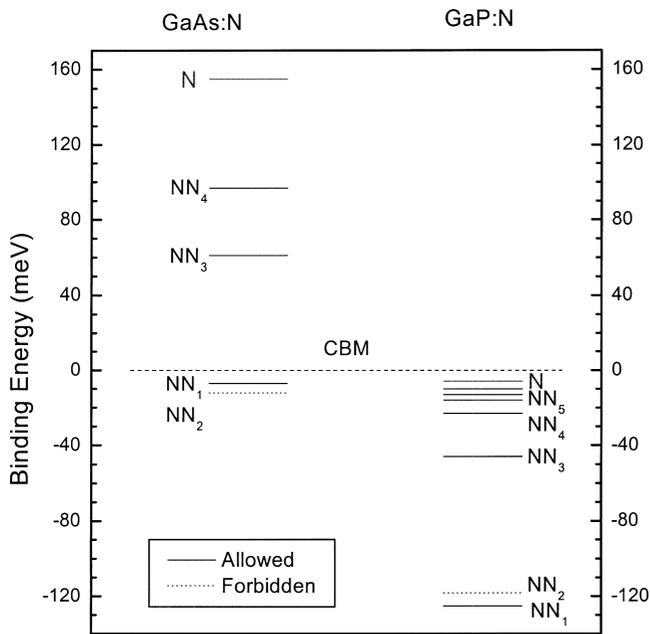


Fig. 1. Energy levels of nitrogen induced bound and resonant states in GaAs:N and GaP:N. CBM stands for conduction band minimum [22,23].

trap states in GaAs. High pressure photoluminescence studies performed at low temperatures indicated that the isolated N impurity generates a resonant state (N_x) \sim 160 meV above the CBM of GaAs followed by the NN_i pair states of which only NN_1 and NN_2 are bound states [9,47,10]. Bellaiche et al. [11,48] using the empirical pseudopotential method observed a resonant N level 250 meV above the conduction band minimum of $\text{GaAs}_{1-x}\text{N}_x$ in the dilute N limit, and intermediate localization of the conduction band wavefunctions on the N atoms. They also studied the effects of clustering by examining the effects of N–N pairs ranging from the first to the fourth fcc neighbor positions. Although they did not observe any bound states for the pairs they noted that the CBM of GaAs with nitrogen pairs was particularly sensitive to the pair separation and symmetry. A resonant state E_+ in the conduction band of $\text{GaAs}_{1-x}\text{N}_x$ whose blue shift correlated with the red shift of the CBM on increasing the N concentration, was directly observed by Perkins et al. [*12] in electroreflectance spectra. Shan et al. [13] inferred the existence of such a state from photorefectance studies and they later also reproduced the observations of Perkins et al. [*12]. Their peculiar observation was that adding N to GaAs induced a much weaker pressure dependence of its band gap at low pressures and a tendency for this dependence to saturate at high pressures. They inferred from this the existence of a narrow resonant band formed by N states which was situated above the CBM and postulated that the pronounced change in the pressure dependence resulted from an anticrossing of these localized N resonant states and the extended states at the CBM. A simple band anti-crossing (BAC) model of two interacting levels: one associated with the extended states of the

CBM and the other with the N induced resonant states N_x , was used to model this interaction, leading to the conclusion that the interaction between these levels transforms them into new levels E_+ (resonant level) and E_- (CBM) and was thus responsible for the downward repulsion of the conduction band in $\text{GaAs}_{1-x}\text{N}_x$. In contrast to this, first principles LDA based studies by Jones et al. [*14] concluded that the non-linear dependence of the band gap on pressure did not result from localized nitrogen states but rather from a repulsion of the CBM by an X-derived singlet state. Their calculations showed no evidence of any nitrogen induced resonant states located above the CBM but indicated a 100-meV splitting of the conduction band minimum at the L point into a singlet and triplet state with 0.78% N incorporation, and the possibility that it was the singlet state that evolved into the N_x resonant impurity state at even lower concentrations. In an attempt to explain the abnormal pressure-dependence and the giant band gap reduction, Matilla et al. [15] using empirical pseudopotential supercell calculations concluded that substituting N on an As site in GaAs exerted a large perturbation on the Γ_{1c} , L_{1c} and X_{1c} host crystal states causing them to mix thoroughly giving rise to new low-energy host crystal states [15]. Their calculations indicated that the fourfold degenerate L_{1c} valley split into a singlet $a_1(L_{1c})$ and triplet $t_2(L_{1c})$ state and the three fold degenerate X_{1c} valley split into a singlet $a_1(X_{1c})$ and doublet $e_1(X_{1c})$, and that under the influence of the nitrogen potential the a_1 symmetry states all interacted and produced the low energy states E_- and E_+ which correspond to the CBM and the nitrogen-induced resonant state, respectively. A hint of such a splitting was provided by ballistic electron emission microscopy (BEEM) measurements where faint evidence for an additional level situated just below L_{1c} was reported [*16]. There have been several experimental attempts that have probed the E_1 transition originating from the valence to the conduction band at the L point in $\text{GaAs}_{1-x}\text{N}_x$. Room temperature reflectance studies by Grüning et al. [17] determined the E_1 and the split-off transition $E_1 + \Delta_1$ and indicated that these transitions did not shift much but broadened with increasing N content and noted that this broadening was similar to that observed in heavily doped semiconductors [17]. The effects of N concentration on the E_1 and $E_1 + \Delta_1$ transitions was also studied by Leibiger et al. [18] using spectroscopic ellipsometry measurements at room temperature. They observed the expected red shift of the band gap with increasing N concentration but also observed linearly blue shifted E_1 and $E_1 + \Delta_1$ transitions. A similar blue shift of E_1 was also observed by Li et al. [19] and Shan et al. [20] from photorefectance studies. The lack of any observed splitting of the E_1 transition led the authors of the latter group to conclude that the interaction of nitrogen induced resonant impurity levels with the L_{1c} states was minimal indicating minimal coupling between these states in line with their BAC model. The equal but opposite rate of shifts with N concentration they observed

for the E_+ and E_- transitions was viewed as a confirmation of their two level repulsion model. In fact, these rates of shifts are not equal but rather the rate of shift of E_+ is only $\sim 70\%$ of that of E_- [12,21]. In addition Klar et al. [21] observed that their pressure coefficients for E_+ and E_- calculated based on a two-level model to be much lower than their experimental results, which they attributed to as due to the mixing of Γ_{1c} states with L_{1c} and X_{1c} states [21]. The inadequacies of the theoretical approaches and models mentioned above will be discussed further later.

Low temperature photoluminescence (PL) spectra are a powerful probe of the band edge electronic states. From their PL studies on $\text{GaAs}_{1-x}\text{N}_x$ samples with nitrogen contents near 0.1%, Zhang et al. [22] observed that (1) GaAs:N samples with very different PL spectra actually share common features that are intrinsic to this system; and (2) the newly formed band edge of the GaAs:N contains discrete cluster levels of N induced states that are embedded in a continuous spectrum of the N-related bound states. They concluded that the shallow N induced bound states form an impurity band that gave rise to the band gap reduction that was observed, but that the deeper N-related bound states persisted as discrete levels below the newly formed band edge. On increasing the N concentration, the states constituting the newly formed impurity band continued to retain the localization characteristics of the impurity in the dilute limit. The PL transitions from these levels did not red shift but merely broadened in contradiction with expectations of level-repulsion models. The electronic structure near the band edge of $\text{GaAs}_{1-x}\text{N}_x$ shares a great deal of similarity with that of $\text{GaP}_{1-x}\text{N}_x$ (see Fig. 1). For heavily N-doped GaP:N , using PL and absorption studies the formation of a nitrogen related impurity band that comprised of the contributions of a hierarchy of nitrogen impurity related bound states was clearly demonstrated and this was suggested as the reason for the greatly enhanced band-edge absorption in this material as well [23].

3. Conduction band effective mass

Further light on the nature of the Γ_{1c} band-edge states is shed by probing the conduction band effective mass. The very short carrier lifetimes in $\text{GaAs}_{1-x}\text{N}_x$ make it difficult to use conventional methods like cyclotron resonance for this purpose and thus other techniques have been employed. Zhang et al. [24] used electroreflectance to study the blue shift of sub-bands in $\text{GaAs}/\text{GaAs}_{1-x}\text{N}_x$ quantum wells as a function of x and well width to estimate the conduction band effective mass m_c^* . Their data suggest that the band offset between the wells and barriers is type I, in agreement with other theoretical calculations [11,15,25], but they surprisingly obtained an abnormally high value of $m_c^* \sim 0.56$ at 0.9% N which gradually

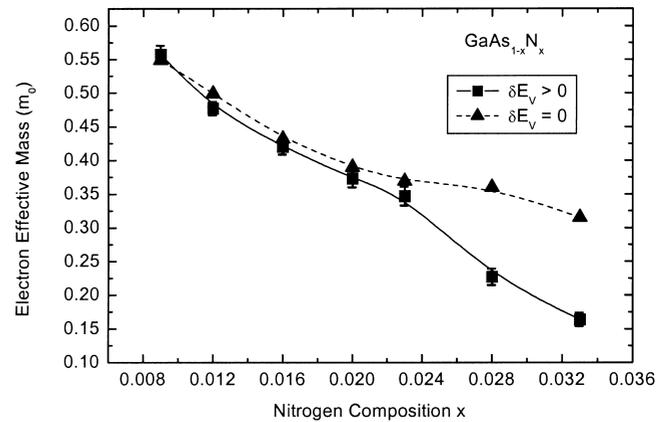


Fig. 2. Electron effective mass as a function of nitrogen composition [24].

decreased to a value $m_c^* = 0.16$ at 3.3% N as shown in Fig. 2. They concluded that the increase in curvature of the impurity band with increased N doping caused the effective mass to decrease from its abnormally high value in the flat impurity band that is characteristic of low N doping concentrations, and that is reminiscent of hopping transport between impurity levels that overlap only weakly. These results thus supported their claim that impurity bands which evolve from the NN trap levels, broaden with heavy Nitrogen doping and merge with the bottom of the conduction band, giving rise to the giant band gap lowering phenomenon [22].

The electron effective mass in $\text{GaAs}_{1-x}\text{N}_x$ and $\text{Ga}_{1-y}\text{In}_y\text{As}_{1-x}\text{N}_x$ has been derived by a few other measurements: infrared reflectivity [26], magneto-photoluminescence (from either the energy shift or linewidth) [27,28] and microwave induced optically detected cyclotron resonance (ODCR) [29]. For the infrared reflectivity measurement of Skierbiszewski et al. [26], the effective mass was derived from the plasma edge with the use of heavily n-type doped samples. Although the results of this study were explained using the two-level model with the inclusion of the conduction band dispersion, other than the effective mass being heavier than that in GaAs, no clearly trend was established due to the fact that the samples parameters were not changed in any systematic ways. In fact, the BAC model would predict that the effective masses for $x = 1$ and 3.3% would be ‘practically the same’ for low n-type doping levels [26]. However, for higher n-type doping levels, the data appeared to have showed the same trend observed in Ref. [24], but the result was explained as the Fermi level effect. The analysis of their magneto-photoluminescence data by Jones et al. [28] yielded $m_c^* = 0.15 m_0$ for $\text{Ga}_{0.93}\text{In}_{0.07}\text{As}_{0.978}\text{N}_{0.022}$ from analysis of the diamagnetic shift [27], and $m_c^* = 0.1 m_0$ for $\text{Ga}_{0.97}\text{In}_{0.03}\text{As}_{0.99}\text{N}_{0.01}$ and $m_c^* = 0.15 m_0$ for $\text{Ga}_{0.94}\text{In}_{0.06}\text{As}_{0.98}\text{N}_{0.02}$ from their luminescence linewidth analysis [28]. Although there were only two data points, the results of Ref. [28] showed that the effective mass

increased on increasing nitrogen doping. By fitting the ODCR curve, Hai et al. [29] found $m_c^* = 0.12 m_0$ and $0.19 m_0$, respectively, for two GaAs_{1-x}N_x/GaAs QW samples with $x = 1.2$ and 2.0% . Thus a trend opposite to that of Ref. [24] was observed for these samples. Although the authors of Ref. [29] claim their ODCR measurement is a direct measurement as compared to the other studies, in our opinion, this is unjustified. One can discuss the differences in results for all the techniques used, in terms of the degree of the complexity involved in each of the fitting procedures used. None of them is more ‘direct’ than the other. In all cases, assumptions and equations which have only been tested for conventional semiconductors have been made or applied in the data analysis without much rigorous justification. For the quantum confinement technique [24,27,30], the validity of the envelope function approximation is of concern regarding the accuracy of this approach. For the plasma frequency measurement, it supposedly yielded the effective mass at the Fermi level and not at the band-edge, assuming everything else worked just like in GaAs. The fact is that the heavy doping by donors has modified the material in an unknown manner. Questions such as how does a donor behave in GaAs_{1-x}N_x or where precisely is the donor level located are interesting subjects to be studied on their own. In fact, experimental data seems to suggest that the donor level could become resonant above the GaAs_{1-x}N_x band edge [31]. It will not be a surprise if this speculation turns out to be true, since the donor binding energy is frequently found to be smaller than that of nitrogen pair bound states in either GaAs:N or GaP:N. For the magneto-photoluminescence measurement, not only is the applicability of the relevant equations to the current problem questionable but also their applicability to conventional alloys [32–34]. As regards the ODCR measurement [29], due to the use of microwaves, this technique has been known to measure the effects of hot carriers or lattice heating [35]. Thus, there was no guarantee in the measurement of Ref. [29] that the resonance occurred at the energy level of the ‘band edge’ and not at other higher energy states. In fact, it frequently happens that CR modifies the emission signal associated with various types of localized states but has nothing to do with the effective mass of those localized states (since it is not even appropriate to talk about the effective mass of an impurity state). Instead, the CR may give the mass of the band from which the carriers are captured to the localized states (numerous examples can be found in Ref. [35]). Theoretically, the experimentally observed heavy electron mass was explained as a consequence of the Γ -X mixing [14] or Γ -L mixing [15], which to some extent parallels the expectations of the BAC model, i.e. that the effective mass increases on increasing nitrogen doping level. Finally, a tight-binding calculation [25] also predicts that the electron mass increases with nitrogen doping level. The reason for many of the inconsistencies with respect to m_c^* described above will be discussed below.

4. Abnormal alloys versus heavy isoelectronically doped GaAs

When two semiconductors AC and BC are mixed, this typically results in the formation of a disordered alloy A_xB_{1-x}C if the physical properties of A and B do not differ greatly from each other, and in that case the properties of the alloy change smoothly from those of BC to those of AC as x is changed from 0 to 1. Such is the case for Al_xGa_{1-x}As and In_xGa_{1-x}As for example. The semiconductors AC and BC must of course be miscible for a range of x , which is mostly true when the properties of A and B do not differ greatly. This contrasts with the n or p-type charge doping of semiconductors, where the solubility of the donor or acceptor in the host is limited (as for e.g. GaAs:Si and GaAs:Zn). In some situations the differences between alloys and doped semiconductors is not so clear. Heavy n-type doping of the order of 10^{19} (or 0.1% dopant concentration) causes a nearly 200 meV band gap reduction in GaAs which results from impurity band formation [36], whereas, a 0.1% N doping in GaAs results in a band gap reduction of less than 50 meV [12]. However, one does not speak of GaAs:Si as an alloy and so the question arises as to why is GaAs:N being referred to as a GaAs_{1-x}N_x alloy? The reason for this is that N is an isoelectronic impurity in III-V alloys and thus does not result in charge doping. There are two types of isoelectronic impurities: those that do not give rise to bound states (such as GaAs:Al or GaAs:In) and those that do give rise to bound states in the host. If the isoelectronic impurity generates bound states located in the band gap (either through isolated centers or pairs) such as is the case for GaAs:N and GaP:N, then with heavy doping the impurity levels associated with these bound states evolve into impurity bands that broaden and merge with the conduction band edge, and this merger gets manifested as a giant band gap ‘bowing’. The formation of an impurity band in heavily n or p-type doped semiconductors has been well studied together with its associated Mott metal–insulator transition [37,38]. Although the formation of impurity bands in heavily isoelectronically doped alloys like GaAs:N and GaP:N is relatively new, the phenomenon was actually observed in the CdS_{1-x}Te_x system for concentrations $x > 10^{-4}$ almost 35 years ago [39]. More insight into the common physical relationships between alloys, heavily charge doped semiconductors and heavy isoelectronically doped semiconductors is provided by a scaling rule recently observed by Zhang et al. [40]. As shown in Fig. 3, the band gap reduction in a doped semiconductor is observed to follow a scaling rule, $\delta E_g(x) = \beta x^\alpha$, where x is the mole fraction of the dopant. For alloys like In_xGa_{1-x}As, the scaling exponent α is very close to 1. For heavily doped p-type semiconductors $\alpha \approx 1/3$. The physics underlying the $x^{1/3}$ scaling rule is simply that the bandwidth of the impurity band or the band gap reduction is proportional to the electron–electron interaction, and this

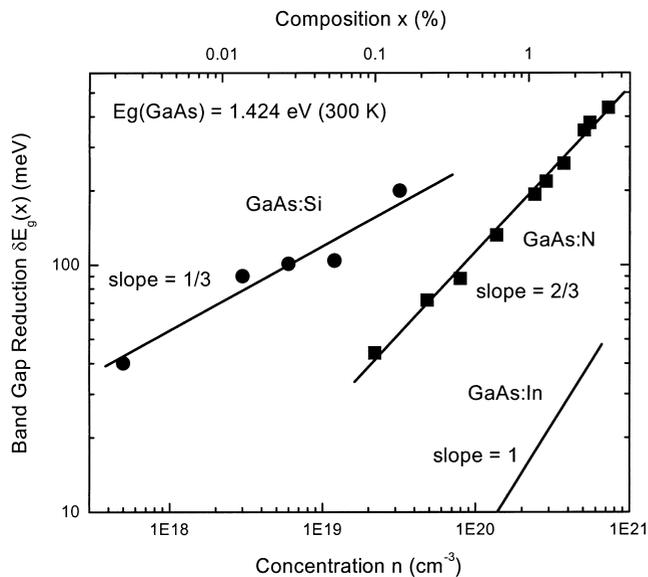


Fig. 3. Comparison of band gap reduction as a function of impurity concentration for three typical systems. Data for (a) GaAs:Si (n-type doping) are from Ref. [36], (b) GaAs:In (regular alloy) are from Ref. [46], and (c) GaAs:N are from Ref. [40].

interaction is proportional to the average impurity separation. For isoelectronically doped GaAs:N the scaling exponent $\alpha \approx 2/3$. The significance of the scaling exponent α being close to $2/3$ lies in that it confirms that the band gap reduction in heavily doped GaAs:N is primarily due to the formation of an impurity band associated with nitrogen pair bound states. This is the primary reason for the irregular or abnormal behavior of these alloys.

5. Inadequacies of models and calculations

The band structure calculations discussed earlier were all capable of yielding a significant band gap reduction for $\text{GaAs}_{1-x}\text{N}_x$ but none of them realistically simulated the real nitrogen distribution in the samples. The so-called ‘supercell’ approach has typically been used implying that a few nitrogen atoms are included in a large supercell, and calculations then performed for an ordered structure comprising the periodic spatial repetition of such a unit cell. Thus the existence of nitrogen pairs, triplets and larger clusters which occur in real samples were excluded. An alternative approach employed was the use of a large unit cell with up to 512 atoms [11,41] in which N was added randomly in proportion to the value of x and configurational averaging used in determining the band gaps, assuming that this would mimic the actual situation in $\text{GaAs}_{1-x}\text{N}_x$. These attempts are still inadequate for modeling the real structure because: firstly, the supercell was far too small to reasonably simulate the random structure for values of x up to a few percent that are most relevant for the experimental data. For instance, for the 512 atom supercell

($\sim 23 \text{ \AA}$ in size for GaAs), the lowest concentration that can be modeled is $x \sim 0.4\%$ or $9 \times 10^{21} \text{ cm}^{-3}$ using one nitrogen per supercell. Thus, this is a structure without any randomness. If it were to be a random structure, one would expect to have $\sim 2 \times 10^{18} \text{ cm}^{-3}$ of nitrogen pairs for each possible pair configuration [42]. If there are two nitrogen atoms in each unit cell, and they are placed nearby to each other, they form a pair with a concentration $\sim 9 \times 10^{21} \text{ cm}^{-3}$, which far exceeds the expected concentration of $\sim 8 \times 10^{18} \text{ cm}^{-3}$ for a random structure; when they are separated as far as possible, they behave practically like isolated centers. Secondly, the configurational average is not a sensible way of dealing with random fluctuations in this type of situation, since the energy difference between an isolated nitrogen center and a nitrogen pair or triplet can be as large as $\sim 200 \text{ meV}$ [23]. One can estimate the supercell size that is needed for a realistic description of a random structure. For $x \sim 0.4\%$, in order to have just about ten nitrogen pairs corresponding to a given pair separation present in a supercell, the supercell size should be $\sim 170 \text{ \AA}$ (there are $\sim 200,000$ atoms in such a supercell). The scaling exponent α derived from the theoretical calculations of Bellaiche et al. [11,41], Mattila et al. [15] and Wang [43] when compared with the experimental data, as shown in Fig. 4 are always found to be significantly larger than the experimental value $\alpha \approx 2/3$, irrespective of whether the absolute value of the calculated band gap lowering ΔE_g obtained is larger or smaller than that obtained from the experimental results. Note that very significantly different ΔE_g values were obtained by the same research group using the same technique [11,15] in different publications, indicating the large uncertainty of

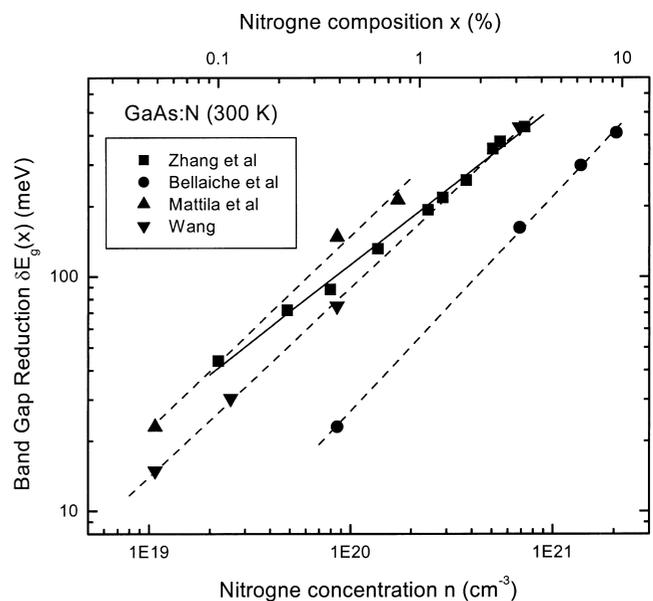


Fig. 4. Comparing the experimental data for the band gap reduction of Zhang et al. [40] with the theoretically calculated values of Bellaiche et al. [11], Mattila et al. [15] and Wang [43].

these calculations. Finally, a four-level interaction model has recently been suggested by Gil [44] to including the coupling with all three valleys: Γ , X and L, whilst considering the localization nature of the impurity potential. However, a number of experimental studies, including selective photoluminescence measurements near the band edge in both GaP_{1-x}N_x [23] and GaAs_{1-x}N_x [22] and resonant Raman studies [45], have indicated that the electronic structure either near the conduction band edge or the E₊ transition are far more complex than what is described by such simple models and is more consistent with the impurity band model proposed by Zhang et al. [40].

6. Conclusions

The poor transport properties of GaAs_{1-x}N_x limit its potential for use in solar cell and laser devices and the reasons for this are related to abnormalities of its conduction band. There exist several inconsistencies amongst the experimentally obtained results for the conduction band effective mass variation with nitrogen content and amongst the various theoretical models proposed for the giant band gap lowering. For further progress in this field it is necessary that a very basic question be answered, namely, should GaAs_{1-x}N_x be viewed as an abnormal alloy or as a heavy isoelectronically doped semiconductor?

Acknowledgements

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