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Electronic structure of nitrogen doped GaAs and GaP

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ABSTRACT

The dilute nitrogen alloys $GaAs_{1-x}N_x$ and $GaP_{1-x}N_x$ have recently become technologically important for applications in high efficiency solar cells and vertical cavity surface emitting diode lasers used for fiber optic communications. There exist many inconsistencies between the results of various experimental techniques and theoretical models used to probe the giant band gap lowering observed in. these systems. It appears that these inconsistencies originate because $GaAs_{1-x}N_x$ and $GaP_{1-x}N_x$ should perhaps not be viewed as an abnormal alloys but rather as a heavy isoelectronically doped semiconductors. The similarity and dissimilarity between the two systems will be discussed with respect to: (1) The perturbation of the host band structure caused by nitrogen doping. (2) The evolution of nitrogen bound states with increasing nitrogen doping (3) The dominant contributors to the band edge absorption, and (4) Whether there exists a universal model that explains the anomalous behaviour of $GaAs_{1-x}N_x$ and $GaP_{1-x}N_x$. Key issues such as the relevance of various theoretical band structure calculations to the experimentally measured parameters, and as to how exactly does one define the band gap for these materials will also be examined. Finally, possible solutions for regularizing the abnormal behavior of dilute N alloys will be discussed.

Keywords: isoelectronic impurity, impurity band, band gap bowing, co-doping

1. INTRODUCTION

Large band gap reductions, along with several other modifications to the band structure, have been observed in heavily nitrogen doped GaAs and GaP for almost a decade[1,2]. Two recent reviews[3,4] have discussed the relationship of these phenomena to the field of isoelectronic impurities in semiconductors which has been researched for over thirty-years. For Nitrogen concentrations up to a few percent, $GaAs_{1-x}N_x$ and $GaP_{1-x}N_x$ have frequently been referred to as dilute nitride alloys. Since GaN has a much larger band gap than either of the hosts, the observed large band gap reduction has been portrayed as a "giant" bowing, using the terminology for describing conventional alloys. However, if one notes that the band alignment for GaP/GaN or GaAs/GaN is type II with the conduction band edge of the GaN lower than that of GaP by ~ 560 meV or GaAs by ~ 200 meV, then the large band gap reduction is really not surprising[3]. Nitrogen is one of a very distinct group of isoelectronic impurities in III-V semiconductors. Long before the observation of the large band gap reductions it was known that the impurity states

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associated with an isolated nitrogen and various nitrogen pairs have progressively lower energy levels (see Fig. 1) in GaP[5] and GaAs[6,7]. In fact, this trend already hinted at type II band alignments. If one considers the bowing for each individual band edge instead of the entire band gap, one will find the bowing coefficient to be much smaller than that given in the literature for the band gap of $GaAs_{1-x}N_x$ and $GaP_{1-x}N_x$. However, the microscopic origin for the band gap reduction, i.e., its relationship with the host band structure or the nitrogen impurity states, has been an intensively debated issue in recent years. A phenomenological model, namely the so-called "band anti-crossing" model, suggests that the primary effect of nitrogen doping is to cause a repulsion between the isolated nitrogen level and the conduction band edge[8,9], ignoring the fact that the isolated nitrogen level is above the conduction band edge in GaAs but below the conduction band edge in GaP. Several attempts have been made to shed light on this problem using band structure calculations[10-13] and the following generic argument proposed for explaining the large band gap reductions: nitrogen incorporation breaks the lattice symmetry and causes the bulk states at the Brillouin zone boundaries (e.g., X and L point) to fold to the Γ point. Consequently, the repulsion between the folded states and the state at the Γ point gives rise to the band gap reduction. Such an argument implies that any impurity incorporation should result in a band gap reduction, which is obviously untrue. As has been discussed in Ref. [3], an apparent reason for the large band gap reduction is simply the large type II band offset, but a more fundamental reason is that the 2s valence atomic level of the N atom is much lower than that of As 4s or P 3s. Nevertheless, all these band structure calculations were able to yield a band gap reduction, although the values obtained have a considerable scatter. According to these calculations, the band edge state is always bulk-like[10,11] or more simply, a lowest bulk-like state is defined as the band edge[12,13]. Another suggested mechanism for the band gap reduction is based on the formation of an impurity band from nitrogen bound states[14,15]. In $GaP_{1-x}N_x$, all existing experimental data seem to indicate the weak role of any perturbed host states in the band edge absorption[5,16-18], and instead point to the formation of an impurity band from various nitrogen bound exciton states[15,18]. However, recent theoretical calculations[12,13] claim that the nitrogen impurity states can not interact sufficiently so as to broaden and form an impurity band, and that the band gap reduction is due to the host state "plunging down" as a result of nitrogen perturbation. In $GaAs_xN_{1-x}$, nitrogen induced bound states have also been found to broaden and turn into a continuous spectrum[19,20]. However, it has not been clear as to how the nitrogen bound states and the bulk-like states compete with each other, and which of them is the dominant contributor to the band edge absorption. This will be a major issue that is to be addressed.

Another issue which has rarely been addressed for these so-called dilute nitride alloys is the relevant meaning of a measured bandstructure parameter. Such a parameter can be, for instance, the band gap and the effective mass both of which are well-defined for an ideal crystal and known to be meaningful for conventional alloys. Experimentally, the band gap of $GaAs_{1-x}N_x$ and $GaP_{1-x}N_x$ has been derived in many different ways: photoluminescence (PL), absorption or PL excitation spectroscopy (PLE), and derivative spectroscopy techniques which include electro- or photo-reflectance or absorption. From absorption spectra, one can fit the absorption near the "band edge" to the lineshape function for free carrier absorption, i.e., $(E - E_g)^n$ with $n = ½$ for the direct transition and $n = 2$ for the indirect transition. Ambiguity in the fitting procedure has led to

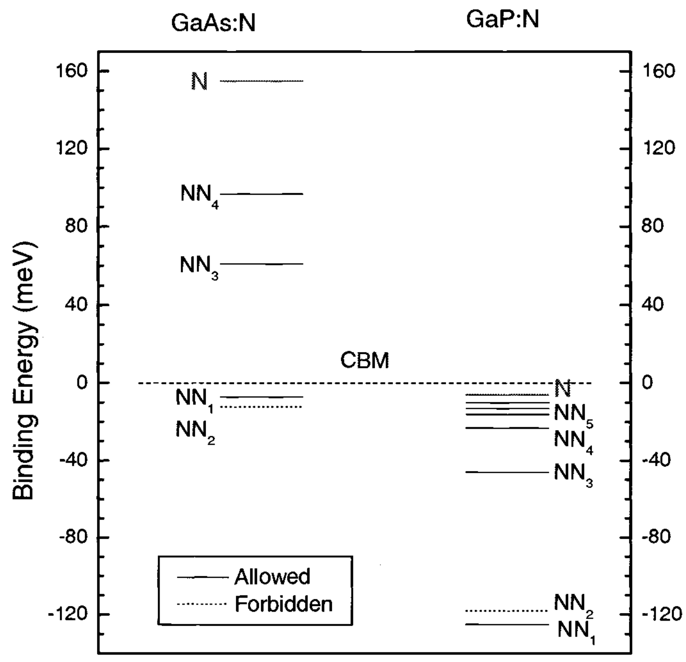

Figure 1: Nitrogen induced trap levels in GaAs and GaP.

contradictory conclusions[4] of the same material being indirect according to one study and direct according to another study. A more fundamental concern is that the inter-band transition in an intrinsic semiconductor should always be excitonic, even if inhomogeneous broadening smears out the measured excitonic feature in some cases. However, depending on whether one takes the excitonic peak (if any) as the band gap or uses the above mentioned fitting procedure, one may obtain a significantly different band gap for a material like $GaAs_{1-x}N_x$ which frequently exhibits a rather slow rising slope in its absorption curve[1]. In the case of $GaP_{1-x}N_x$, since the band edge absorption originates from nitrogen bound states, it is not at all clear what kind of lineshape function can be justifiably used[15]. Regarding the various derivative spectroscopies which are commonly believed to be more accurate than the linear spectroscopies, the band gap can be determined with much less ambiguity (provided a proper lineshape function is used for fitting the experimental curve). However, the physical process that results in the measured derivative lineshape is complex for these strongly perturbed semiconductors. It is also unclear how well the band gaps derived from using these somewhat different criteria agree with one another.

To add to the confusion many attempts have been made for quantitative comparisons between experimental data and theoretical results. In many cases, it was not at all clear what exactly was being compared, although excellent but likely fortuitous agreements between experimental and theoretical results have been claimed[13]. In this review a comprehensive view of the so-called $GaAs_{1-x}N_x$ and $GaP_{1-x}N_x$ alloys will be presented. We will (1) examine differences in the band gap measured by different techniques or using different criteria; (2) investigate how nitrogen doping affects the host band structure and the band edge excitonic absorption; (3) illustrate the evolution of nitrogen bound states on increasing nitrogen doping level; and (4) discuss the relevance of comparisons between the experimental data and theoretical modeling.

2. EXPERIMENTS

$GaAs_{1-x}N_x$ samples discussed below were grown by low pressure metal-organic chemical vapor deposition (MOCVD) on semi-insulating GaAs substrates. A 50 nm AlAs layer was inserted in between for lifting off the epilayer by chemical etching. The nominal epilayer thickness was 1 μm. Transmission was measured on a film that was either van der Waals bonded to a cover glass or free standing, i.e., glued at its edge to a thin metal wire. The film on glass was found to be slightly strained at low temperature, but the "wire mounted" film remained strain-free in the area away from the wire. $GaP_{1-x}N_x$ samples were grown by MBE on GaP substrates, as described in Ref.[15]. Some $GaP_{1-x}N_x$ samples were thinned down to ~ 50 μm by mechanical polishing for the transmission measurement. Transmission measurements were performed using a tungsten lamp, focused and spatially filtered to have a 50-μm spot size. 1.5 K linear absorption spectra were measured using a system with a ISA 270 spectrometer and a CCD detector. Differential absorption spectra were measured using a system with a Triax 320 spectrometer and a Si-detector. A 405 nm diode laser was used as the modulation source. Nitrogen compositions were determined by either SIMS (for $x < 0.1$ %) or x-ray measurements.

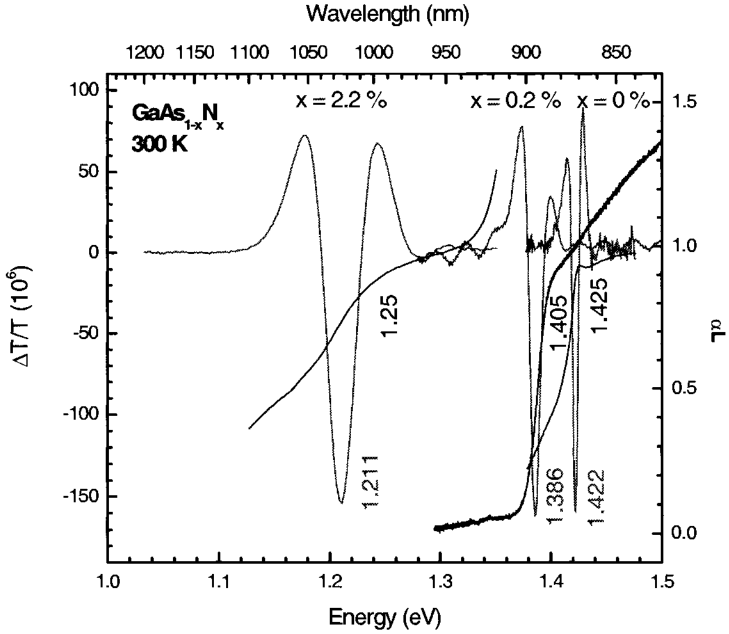

Figure 2. Linear (right) and differential (left) absorption spectra of $GaAs_{1-x}N_x$, measured at 300 K.

3. RESULTS

3.1 New "Band gap" of $GaAs_{1-x}N_x$

Fig. 2 shows a comparison of the linear and differential absorption spectra for $GaAs_{1-x}N_x$ with x = 0, 0.2 % and 2.2 %. The two samples with x = 0 or 0.2 % were measured on cover glass, and the 2.2 % sample was measured on the substrate. For the x = 0 sample, the peak of the $\Delta T/T$ signal is shown to be very close to the excitonic absorption peak. However, the excitonic absorption peak smears out for the other two nitrogen-doped samples. Obviously, the main peak of the $\Delta T/T$ signal does not occur at the absorption "threshold" which itself is not well-defined. Thus, Fig.2 illustrates the fact that using the absorption "threshold" of the linear absorption spectrum may give rise to a rather different band gap from that determined by the differential absorption. However, there are no fundamental arguments that favor one result over the other. Fig.3 shows 1.5 K absorption spectra for a set of relatively low nitrogen concentration samples with x < 0.5 %. These films were "wire mounted", thus, being nearly strain free, whereas films on cover glass show typically ~ 2 meV splitting and shifts of the absorption peaks at this temperature.

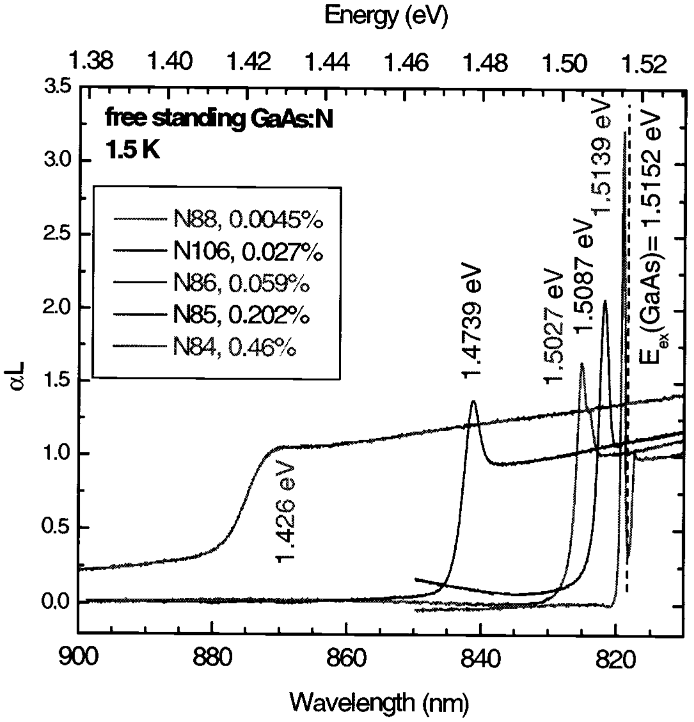

Figure 3. Linear absorption spectra of $GaAs_{1-x}N_x$ with low nitrogen concentrations, measured at 1.5 K. The absorption peak shifts monotonically with increasing nitrogen concentration.

The GaAs-like excitonic absorption peak is found to shift down in energy continuously with increasing nitrogen concentration. A small band gap reduction of ~ 1 meV has been observed for a sample with nitrogen concentration as low as 1 x 10^{18} cm^{-3} or x = 0.0045 %. When x approaches 0.5 %, the absorption peak has broadened drastically, indicating

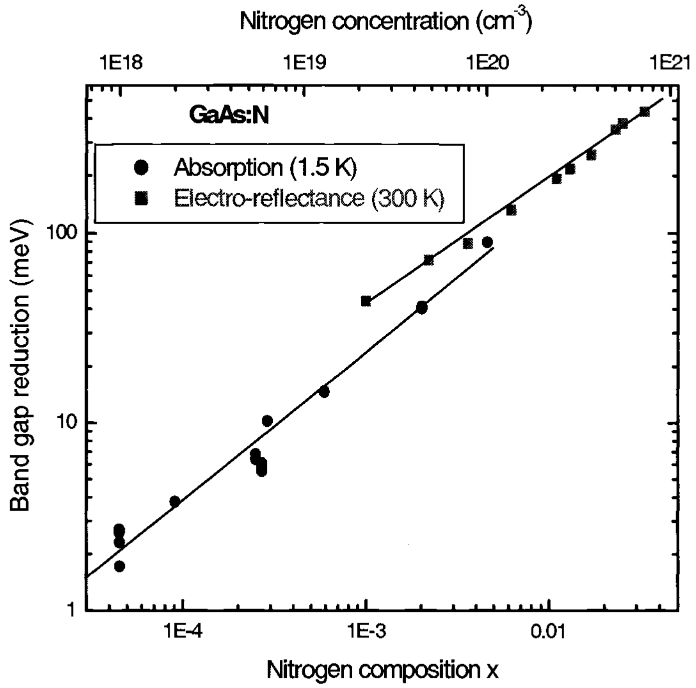

Figure 4. Band gap reduction of $GaAs_{1-x}N_x$ vs. N composition, determined by the excitonic absorption peak at 1.5 K and electroreflectance lineshape fitting at 300 K.

a strong interaction between the bulk-like states and the nitrogen bound states associated with nitrogen pairs or clusters. Fig. 4 summarizes results for the band gap reduction measured by the excitonic absorption peak as a function of nitrogen composition for the low x region, together with the results for the high x region obtained from electro-reflectance measurements[21]. There is indeed a deviation between the band gaps determined by the two techniques.

To better understand the character of the electronic states that contribute to the absorption, for an x = 0.1 % sample, we have measured the PL spectra with excitation energies above and below the $GaAs_{1-x}N_x$ band gap[19,20]. Fig. 5 shows a PLE spectrum that is reconstructed from the selective excitation PL spectra, together with a few such PL spectra at representative excitation energies. As one can see, the PLE spectrum has a peak at 1.475 eV which agrees within a few meV with the band gap determined by the electroreflectance[20]. It is important to point out that with each excitation energy near but below the band gap, we observed a sharp zero-phonon line at ~ 1 meV below the excitation energy plus a TA phonon sideband and enhanced LO_Γ and TO_Γ resonant Raman peaks, which indicates that these states behave like typical localized states[15]. Apparently, these impurity-like states exist in a spectral range at least 100 meV below the "band gap". Thus, the existence of an impurity band is an indisputable fact, although the impurity-like states may not be the dominant contributors to the absorption near the "band gap".

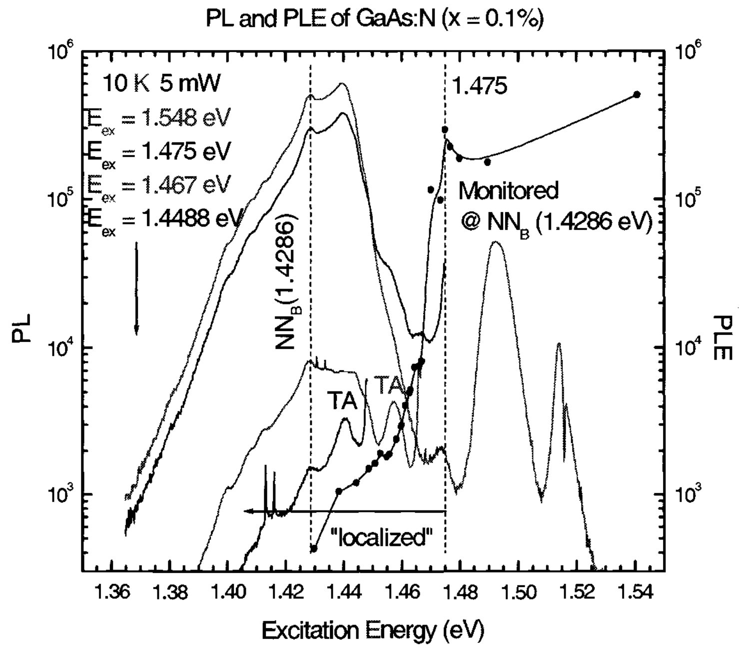

Figure 5. (left) Selective excitation PL spectra and (right) PLE spectrum reconstructed from PL intensities at the energy of NN$_B$ peak for a GaAs$_{1-x}$N$_x$ sample with x = 0.1 %.

3.2 New "Band gap" of GaP$_{1-x}$N$_x$

For GaP$_{1-x}$N$_x$, early studies[5,17] have shown that nitrogen doping indeed perturbs the host band structure, making the forbidden indirect band gap transition A$_x$ partially allowed. However, the absorption at the direct band gap was found to be only ~ 1/150 of the A line (the isolated nitrogen state) absorption (only ~ 1/450 if the contribution of the A line acoustic phonon sideband is subtracted)[17]. More recent PLE measurements for nitrogen compositions up to 2 % showed absorption features near A$_x$ as well as near the direct gap energy, but no sign of any absorption feature at the L indirect gap energy[18]. Thus, it is highly unlikely that in GaP$_{1-x}$N$_x$ any perturbed bulk states could make comparable contributions to that from the band edge absorption of the nitrogen bound states. Fig. 6 shows PL spectra[15] for a set of GaP$_{1-x}$N$_x$ samples with x varying 0.004 % to 0.6 %. The spectrum of the most dilute sample shows the emission lines of nearly all the nitrogen induced bound states in GaP$_{1-x}$N$_x$[5]. However, on increasing the nitrogen concentration, the sharp lines due to nitrogen pairs at the higher energy side broaden and quench sequentially in the order of increasing binding energy. Simultaneously, a broad emission band appears at the lower energy side of the NN$_1$ line.

Selective excitation of PL is used to reveal the nature of the states that give rise to the broad emission band, while absorption measurements are used to monitor the evolution of the nitrogen pair states. The results are shown in Fig. 7. To the left, the PL spectra obtained under selective excitation are found to always consist of a sharp zero phonon line NN$_1'$ together with various phonon sidebands, typical of the spectrum for a nitrogen pair like NN$_1$. This indicates that the states in the broad band are nothing but nitrogen bound exciton states with different local environments. To the right, an absorption spectrum shows that the peak positions of nitrogen pair states barely move with respect to

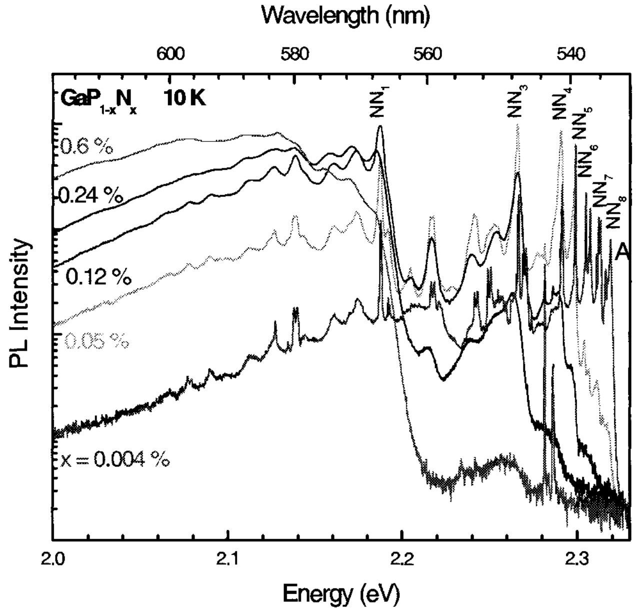

Figure 6. PL spectra of $GaP_{1-x}N_x$ with different N compositions, measured at 10 K with an excitation energy of 2.33 eV.

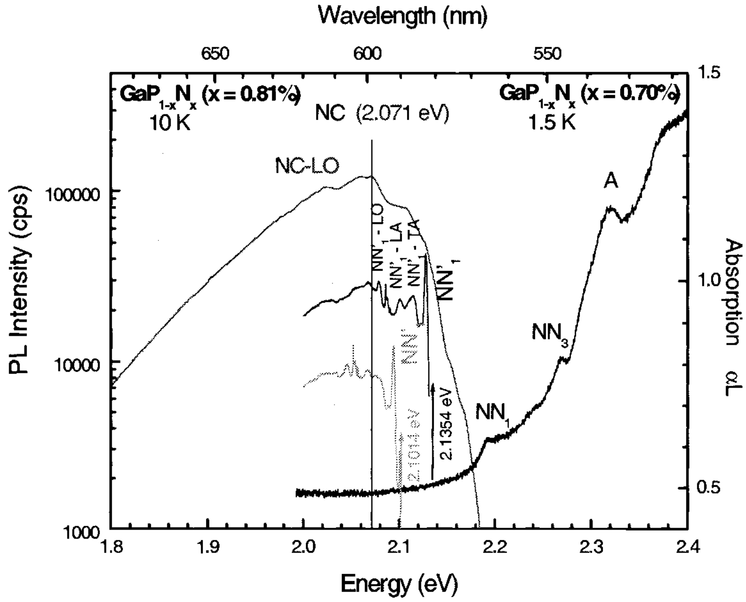

Figure 7. Left: selective excitation PL spectra for a $GaP_{1-x}N_x$ sample of x = 0.81 %, with excitation energies of 2.3306, 2.1354, and 2.1014 eV. Right: an absorption spectrum for a 750 nm thick $GaP_{1-x}N_x$ sample with x = 0.70 %.

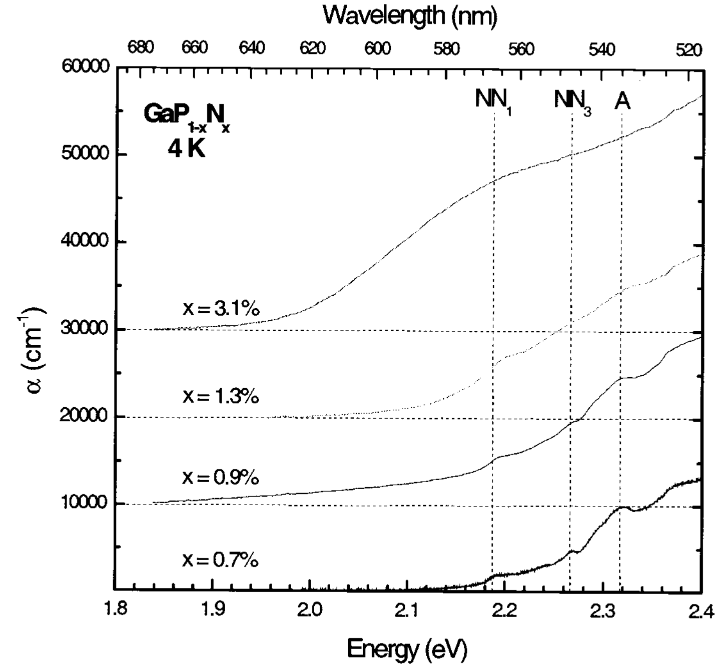

Figure 8. Absorption spectra for GaP$_{1-x}$N$_x$ with x = 0.70, 0. 90, 1.3, and 3.1 %, measured at 4 K (except for the x = 0.70 % at 1.5 K). The curves are shifted for clarity.

the dilute limit, but they strongly broaden and merge with each other with higher N doping. In fact, the absorption peak at NN$_1$ very much resembles an excitonic absorption peak in a conventional semiconductor. The results of Fig. 6 and Fig. 7 clearly reveal that for $x > 0.1$ %, nitrogen bound states in GaP$_{1-x}$N$_x$ rapidly broaden into a continuous spectrum that is more than 300 meV wide. Fig.8 shows a set of absorption spectra for different nitrogen compositions. It is clear that the positions of nitrogen bound states remain more or less stationary until they all merge together at high nitrogen concentrations, which unambiguously disproves the N - Γ repulsion suggested by the "band anti-crossing" model[9].

4. DISCUSSIONS

4.1 Validity of the "band anti-crossing" model

The "band anti-crossing (BAC)" model suggests that the band gap reduction is simply due to mutual repulsion between the isolated nitrogen state and the Γ conduction band edge[8,9], irrespective of the whether or not the isolated nitrogen level is higher or lower than the conduction band edge and ignoring the possible role of bulk states belonging to other valleys (namely the X and L valleys) or nitrogen pair states. Although this model has been successfully used for fitting various experimental data, a number of serious internal inconsistencies have been pointed out[4], due to the over simplified nature of this model. An equal but opposite shift of the band edge and the isolated nitrogen state is expected by the BAC model. However, in GaAs$_{1-x}$N$_x$, this has been disproved experimentally[22,23], with one exception comprising data [24] from the authors of the model. Also, there exists an inconsistency in the coupling matrix element, V_{MN}, between what was derived from the band gap pressure dependence and from the composition dependence[8,24]. An extended version of this model with the k-space dispersion included is also problematic[25]. First, it is conceptually wrong to view the nitrogen level as a dispersionless band in k-space. Second, it is not clear for what range in k-space the k-independent V_{MN} model is applicable. If one simply applies the model to the entire Brillouin zone, one will obtain large splittings at both the L and X point (e.g., 540 meV at the L point and 600 meV at the X point for x = 1 % with V_{MN} = 0.27 eV), which is exactly opposite to the suggestion that the BAC model would not yield a significant splitting at the L point[24]. Although there is no reason to believe that the interaction between the nitrogen state and any bulk states is uniform, it is unreasonable to believe that the nitrogen state does not interact with the states with which it is in resonance or with the nearby L point. For $GaP_{1-x}N_x$, the experimental data of Fig. 7 and Fig. 8 show clearly that the A line is not repelled down by any bulk states, as suggested in Ref. [9]. Whether or not the Γ band edge shifts up with increasing nitrogen doping[9,18] is a different issue deserving further investigation. In fact, in contradiction to their own claim that the A line starts to be repelled down beginning at concentrations x > 0 % in Ref. [9], the authors on a different occasion admitted[24] that the A line energy was independent of nitrogen concentration up to x ~ 0.5 %.

4.2 Relevance of the comparison between experiment and theory.

The discussions above suggest that making quantitative comparisons between the experimental data and the results of theoretical calculations is a delicate issue. Besides the ambiguity in defining the band gap experimentally, it is not at all clear as to what is the exact meaning of the calculated band gap. The observed large band gap reduction in $GaAs_{1-x}N_x$ can be qualitatively understood by calculating the band structure of ordered nitrogen arrays in GaAs[10,11,26,27]. However, not only do the calculated results vary significantly from one method to the other, but also neither of them agrees quantitatively with experimental results[21]. Obviously, a randomly nitrogen doped structure is expected to differ electronically from the ordered structure[15,19,21], which has been well demonstrated even for a conventional alloy like $Ga_xIn_{1-x}P$[29]. It has also been indicated by recent calculations[13] that the mere existence of nitrogen pair states could change the band gap of the ordered structure. Attempts to model the random structure have to contend with the issue of how does one define the band gap[12,13,29]. Ref.[30] defined the band gap by averaging the lowest states (most likely being nitrogen localized states) over different randomly generated configurations. Refs.[12,13] instead tried to identify the lowest bulk-like state as the new band edge. Theoretically, one could choose different definitions for the band gap, but the relevance of the calculated band gap to the experimentally determined band gap would need further clarification. Thus, any claimed excellent agreement with experimental data could only be fortuitous, without an actual calculation of the specific quantity that was measured. For heavily nitrogen doped GaAs or GaP, the band gap is not a well defined parameter as it is for undoped GaAs or GaP. However, for a given nitrogen composition and an assumed random distribution, there will be a statistically well defined absorption profile or a distribution of impurity-like and bulk-like states. Any measurement (e.g., PL, absorption, differential absorption or electro-reflectance) will be merely probing the collective behavior of these states which are expected to respond to the different probing techniques distinctly. One could define, for example, a band gap based on the technique used and a certain set of criteria. Thus, the state at the "band edge" could be either impurity-like or bulk-like.

4.3 Possibility of impurity band formation in $GaAs_{1-x}N_x$ and $GaP_{1-x}N_x$.

Impurity band formation of the nitrogen bound states has been suggested as the primary mechanism for the band gap reduction[14,15]. To refute this model, Refs.[12,13] claimed that the nitrogen impurity states could not interact sufficiently so as to broaden and form an impurity band. The experimental results, as summarized in the previous sections, indicate that whether or not an impurity band is formed is really not the issue. Rather, if one defines the band gap through, e.g., an absorption measurement, the key issue becomes which of the impurity-like states or bulk-like states are the dominant contributors to the absorption profile. Since GaAs is a direct gap but GaP is an indirect gap semiconductor, the relative absorption strength of the impurity-like and bulk-like states is expected to be very much different. The absorption cross section for a nitrogen bound state in GaP is known[31] to be $\int \sigma d\nu = 9.5x10^{-15} cm$, and in GaAs this is estimated to be $\int \sigma d\nu = 2.1x10^{-13} cm$ (based on the experimental data of Ref.[7] and following the detailed balance analysis of Ref.[32]). Fig. 9 shows estimated peak absorption coefficients for the A line, A_x line, and NN_1 in $GaP_{1-x}N_x$, and for the X_1 line in $GaAs_{1-x}N_x$, using their absorption cross sections obtained in the dilute limit and assuming no broadening. Without broadening, the peak absorption of the A line in GaP could reach 98,000 cm^{-1} at x = 0.1 %, which is about the magnitude of the GaAs band edge excitonic absorption[33]. Similarly, for the NN_1 state at x = 0.1 %, the peak absorption is estimated to be ~ 1,100 cm^{-1} in GaP and 14,000 cm^{-1} in GaAs. Indeed, the absorption of the nitrogen pair bound state in GaAs should be capable of reaching a value comparable to the GaAs band edge excitonic absorption at such a composition, if the state remained bound and unbroadened. However, because of the fast decrease of the GaAs band edge on increasing nitrogen doping, as shown in Fig. 3, a strong interaction between the

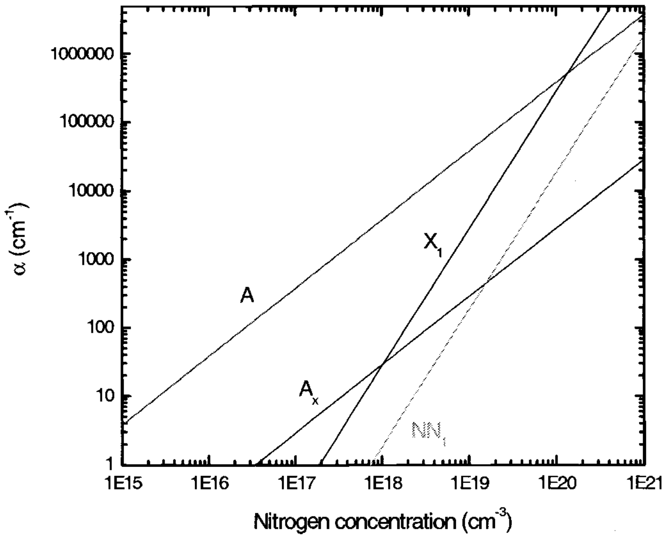

Figure 9. Estimated peak absorption coefficients for A, A_x, and NN_1 transition in GaP:N, and for X_1 in GaAs:N, using the absorption cross sections in the dilute limit and assuming no broadening.

shallow nitrogen pair bound states and the bulk-like states is expected. It is yet unclear how the interaction transforms the GaAs band edge and the nitrogen pair bound state from either the theoretical or experimental point of view. The recent theoretical calculation[12,13] suggests that the nitrogen states would remain more or less stationary, whereas the bulk band edge moved lower down surpassing them. Since the calculations yielded[12,13] an electron binding energy of ~ 100 meV for nitrogen pairs in $GaAs_{1-x}N_x$, it would imply that for $x > 0.5$ %, the nitrogen pair states should remain bound according to the data of Fig. 3, which is obviously contradictory to the experimental fact [19].

To uderstand why the theoretical calculation[12,13] resulted in the conclusion that there is no impurity band formation in GaAsN and GaPN, in contrast to the experimental results, both the intrinsic limitations and the technical inadequacy of the theory need to be examined. As summarized in Ref.[20], there are several channels for the nitrogen bound states to interact. In addition to the difficult coupling considered in Refs.[12,13,14], i.e., the coupling of the highly localized bare electron bound states, there are two other channels. One is through the excitonic states which are ultimately relevant in the experimental measurement, but not taken into account in the theoretical modeling. The other is the randomness-induced inhomogeneous broadening which can also effectively give rise to a continuous spectrum. A serious effort has been made in Refs.[12,13] to model the random structure by using a large supercell with up to 14,000 atoms. However, such a size is still not adequate for realistically simulating the random structure in the composition range of interest. For instance, for $x = 0.1$ %, the average pair separation is ~ 200 Å, and a 200 Å size supercell would have ~ 333,000 atoms. Even for $x \sim 0.4$ %, in order to statistically obtain just 10 pairs of the same configuration appearing in a supercell so as to observe their interaction, the supercell size should be ~ 160 Å with ~ 180,000 atoms[4]. Thus, the supercell used in Refs.[12,13] was not sufficiently large enough to generate an adequate number of nitrogen bound states with different local configurations that would be capable of forming a quasi continuous spectrum. In addition, the calculations[12,13] yielded an electron binding energy of ~ 100 meV for nitrogen pairs in GaAsN and ~ 30 meV for the isolated nitrogen in $GaP_{1-x}N_x$, whereas the experimental values for both cases are known to be < 10 meV[3,5,7,19]. At least to some extent, the insufficient accuracy for the impurity potential could affect the description of the impurity-impurity and the impurity-host interaction.

5. FUTURE DIRECTIONS

5.1 Irregular Alloys

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 *eg*. 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[35], whereas, a 0.1% N doping in GaAs results in a band gap reduction of less than 20 meV[34]. 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. 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[36]. 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 thirty five years ago[37]. More insight into the common physical relationships between alloys, heavily charge doped semiconductors and heavily isoelectronically doped semiconductors is provided by a scaling rule recently observed by Zhang *et al*[21]. As shown in Fig. 10, the band gap reduction in a doped semiconductor is observed to follow a scaling rule:

$$\delta E_g(x) = \beta x^{\alpha} \qquad (1)$$

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 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 influenced by 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 as will be discussed below.

5.2 Physics of isoelectronic traps

Because of the difference in valence between the dopant atom and the host atom that it replaces, a non iso-electronic donor (acceptor) atom donates an electron (hole) to the conduction (valence) band of the host crystal. The Coulomb potential of the resulting ionized donor (acceptor) atom varies with distance as r^{-1} and generates a shallow donor (acceptor) bound state. In contrast, for isoelectronic traps that are generated by isoelectronic impurities such as N in GaAs or GaP, it is the difference in electronegativity, size, and pseudopotential between the isoelectronic impurity and the host atom it replaces that generates the trap state[38]. Such traps are characterized by a potential that varies with distance much faster[39] than r^{-1}. The potential well created by the isoelectronic trap is therefore much steeper than that created by the non-isoelectronic donor (acceptor) and because of this an electron (hole) trapped around the isoelectronic impurity atom is localized much more tightly around it. This spatial localization of electrons (holes) by isoelectronic traps smears out the electronic eigenstates in k-space causing them to be delocalized in the Brillouin zone. This proves advantageous in allowing radiative transitions from these states to the band edges, thus enabling light emission from indirect gap semiconductors like GaP. As discussed above, heavy N doping in GaP and GaAs leads to impurity band formation, red-shifts in the photoluminescence, and the giant band gap "bowing" phenomenon. However, the spatial localization around the isoelectronic traps that generate the impurity bands is precisely what disadvantageously affects the carrier mobility. This is the caveat with heavily isoelectronically doped semiconductors wherein the properties of the resulting alloy are irregular. Evidently, the very success in incorporating large amounts of insoluble isoelectronic dopants using non-equilibrium growth techniques is what leads to "irregular alloy" behavior.

5.3 Physics of co-doping

It is of considerable practical importance to inquire whether there exists a solution to the above problem. Having established the analogies between isoelectronic doping and charge (n or p-type) doping, the simplest approach to providing an answer is to seek a solution in a manner that parallels the analogous problem that exists for charge doping. Here, it is well known that the solubility of an acceptor (donor) impurity can be significantly increased by co-doping with a donor (acceptor). Using this approach, it has been possible to increase the doping concentrations of As donors and Ga acceptors in Si by almost 3 orders of magnitude[40]. Recent theoretical predictions indicated that co-doping of ZnO with Ga donors and N acceptors would overcome the difficulties in obtaining low resistivity p-type ZnO and this has been experimentally verified[41,42]. The enhancement in solubility to a level well above the solubility limit was explained in terms of the formation of ion-pairs between donors and acceptor ions and a consequent reduction in the Madelung energy[41]. In GaN, Ploog and Brandt observed a significant enhancement in the solubility of Be acceptors when co-doped with O donors, and that this was accompanied by an improvement of one to two orders of magnitude in the carrier mobilities despite the high doping concentrations[43]. The enhancement in mobility resulted because pairs of oppositely charged long-range Coulomb scatterers combine to behave as single short-range dipole scatterers. The above mentioned successes motivate the use of a similar strategy for overcoming the limitations of isoelectronic doping.

5.4. Physics of isoelectronic co-doping

In GaP:N up to ten N pairs along with the isolated N center have been found to generate trap states below the conduction band edge[5]. Because of the short-range impurity potential associated with the N isoelectronic traps, they can capture an electron and result in the formation of a long-range screened Coulomb potential[44]. Thus the Nitrogen isoelectronic traps in GaP behave as deep acceptors (levels near the conduction band edge). In contrast to N, Bi is known to form isoelectronic trap levels just above the valence band edge in GaP and the isolated Bi and Bi pair levels are known to behave as hole traps[45]. Because these traps can capture holes and result in the formation of a long-range Coulomb potential, the Bi isoelectronic traps behave as deep donors in GaP[46]. Isoelectronic co-doping GaP with N and Bi should therefore yield advantages analogous to those obtained in the charge co-doping of semiconductors. The solubility of the isoelectronic dopants as well as the carrier mobility should be enhanced leading to a more "regular alloy" like behavior with a concomitant improvement in photoluminescence efficiency and carrier lifetime. In fact, evidence for the enhanced solubility of N and Bi co-dopants in GaP already exists in the literature[47]. In contrast to GaP, the behavior of Bi in GaAs has only rarely been studied and it is not known whether Bi generates hole traps in GaAs. $GaAs_{1-x}Bi_x$ has recently been grown and its band gap shows a large "bowing"[48]. However, the observed temperature insensitivity of its band gap[48] may have less to do with the explanations relating to the semimetallic behavior of GaBi[48,49] but more to do with the fact that the valence band edge evolves out of a Bi impurity band, and that since Bi traps behave as deep donors, the temperature variation of these levels does not follow that of the band edge, which is a characteristic of deep levels. Thus one of the benefits

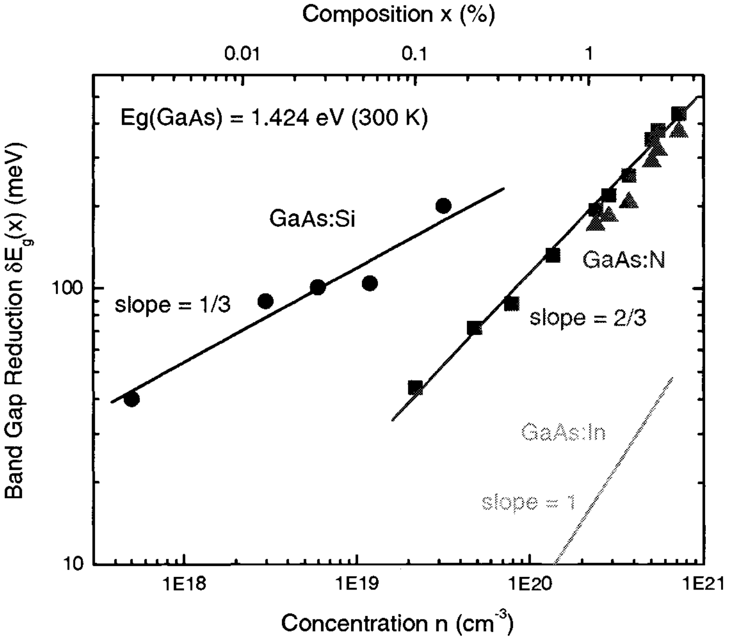

Fig. 10. Comparison of band gap reduction as a function of impurity concentration for three typical systems. Data for a) GaAs:Si (n-type doping) are from Ref. 35, b) GaAs:In (regular alloy) are from J.P Laurenti *et al*, Phys. Rev. B 37, 4155 (1998), and c) GaAs:N are from Ref. 21.

of using isoelectronic co-doping for the active regions of lasers will be the inherent temperature insensitivity of the devices. Bi should also prove beneficial in tuning the valence band offset for holes in the multiple quantum well active regions of lasers independently of the conduction band offset which is mainly determined by N in GaAs:N:Bi.

The ability to enhance the solubility of N and Bi in GaAs should lead to stronger overlap between the wavefunctions of neighboring N dopant atoms and similarly of neighbouring Bi dopant atoms and thus to more regular transport properties as opposed to hopping-like transport properties. The small size of N substituting for As (P) on the group-V sub-lattice can be balanced by the large size of Bi substituting on the same sub-lattice in GaAs (GaP), facilitating coherent epitaxial growth of the isoelectronically co-doped alloy on GaAs (GaP) substrates. In the case of GaP, the direct band gap characteristics of the heavily isoelectronically co-doped material combined with the ability to grow GaP:N:Bi epitaxially on Si substrates would introduce exciting possibilities for use of this material for fabricating photonic devices such as solar cells, LED's and lasers. In fact, the VCSEL, solar cell and LED examples cited earlier would all benefit greatly. N and Bi co-doping could be used beneficially in InP and InGaAs$_2$ as well. Finally, Isoelectronic co-doping could also be used advantageously in II-VI alloy systems, like for example ZnSe which could be isoelectronically co-doped with O deep acceptor like traps and Te deep donor like traps.

6. CONCLUSIONS

The band gap is not as clearly defined in the so-called dilute nitride alloys like $GaAs_{1-x}N_x$ and $GaP_{1-x}N_x$ as it is in binary semiconductors or conventional alloys. Depending on the criteria and techniques used, different band gaps may be derived. It is found that the band gaps defined in various theoretical calculations do not clearly relate to the experimentally determined band gap. Thus, any claimed excellent agreement between experiment and theory is likely to be fortuitous.No sufficient attention has been paid in the past to recognize the difference between the host materials GaAs and GaP, one being direct gap and the other being indirect gap. Because of this major difference, the role of nitrogen impurity states and their perturbation to the host are qualitatively different in many aspects. Thus, it is unwise to attempt to find a universal model or description for these two systems.

In both $GaP_{1-x}N_x$ and $GaAs_{1-x}N_x$, nitrogen bound states quickly form an impurity band on increasing the nitrogen doping level from the dilute limit. The perturbed bulk states in $GaP_{1-x}N_x$ are found to be incapable of making a dominant contribution to the band edge absorption. It is the absorption from nitrogen bound states of isolated centers, pairs, triplets etc. that gives rise to the new band edge below the indirect band edge of the host. Whether or not the bulk-like states actually plunge down into the band gap, as predicted theoretically, is unclear and undetectable at this time. The perturbed bulk states in $GaAs_{1-x}N_x$, however, remain as the dominant contributors to the band edge absorption. A well-defined, but gradually broadened, GaAs-like band edge excitonic absorption peak has been observed for nitrogen composition up to nearly 0.5 %. The interaction between the bulk-like states and the nitrogen bound states transforms the band structure near the new band edge into a mixture of localized and delocalized states. The incorporation of nitrogen into GaAs and GaP generates a series of impurity-like states which co-exists with perturbed bulk states in a wide spectral range. Their collective behavior responds to different experimental measurements differently. Thus, arguments over which technique is more direct or accurate than the other is not always meaningful, especially, given the fact that one usually does not know the detailed mechanisms of the collective response being measured.

The "irregular or abnormal alloy" behavior in $GaAs_{1-x}N_x$ and $GaP_{1-x}N_x$ has been discussed and it has been argued that these materials are better described as heavily doped semiconductors rather than as alloys. Isoelectronic co-doping has been proposed as a method for obtaining "regular alloy" behavior in these systems where it leads to enhancements in 1) the solubility of isoelectronic dopants, and 2) Carrier mobilities. The arguments presented in this article indicate that the use of isoelectronic co-doping should make it possible in several situations to overcome the limitations imposed by semiconductor alloy constraints on the design of some technological important devices such as such as solar cells, lasers and LED's. Use of the technique could expand the repertoire of available choices for semiconductor compounds and alloys having band gap/lattice constant paired values suited for epitaxial growth of device structures that implement design principles closest to the ideal.

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