Electronic structure near the band gap of heavily nitrogen doped GaAs and GaP

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ABSTRACT

Isoelectronic impurity nitrogen atoms have been found to generate a series of localized states in GaP and GaAs. These states can be either bound (within the band gap) or resonant (above the band gap) when in the dilute doping limit (roughly $< 10^{19}$ cm$^{-3}$ for GaP and $< 10^{18}$ cm$^{-3}$ for GaAs). With increasing nitrogen doping level, a shift of the absorption edge from the binary band gap has been observed for the so-called GaPN or GaAsN alloy. We discuss the similarity and dissimilarity between the two systems in the following aspects: (1) How does the nitrogen doping perturb the host band structure? (2) How do the nitrogen bound states evolve with increasing nitrogen doping level? (3) What are the dominant contributors to the band edge absorption? And (4) does a universal model exist for GaPN and GaAsN? Other issues that will be discussed are: how does one define the band gap for these materials, and what is the relevance of various theoretical band structure calculations to the experimentally measured parameters.

INTRODUCTION

Large band gap reductions, along with many other modifications to the band structure, have been observed in heavily nitrogen doped GaAs and GaP for nearly a decade [1,2]. Two recent reviews [3,4] have related the newer research activities in this area to a field that is more than thirty-year old, that is, isoelectronic impurities in semiconductors. These materials 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 “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 less surprising [3]. Nitrogen is one of a very distinct group of isoelectronic impurities in III-V semiconductors. Long before the finding of the large band gap reduction it was known that the impurity states associated with an isolated nitrogen and various nitrogen pairs have progressively lower energy levels in GaP [5] and GaAs [6,7]. This trend had actually already hinted at the type II band alignment between GaP or GaAs and GaN. Considering the bowing for each individual band edge instead of the entire band gap, one will find the bowing coefficient to be rather different from that given in the literature for the band gap of GaAsN or GaPN. 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, 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 $\Gamma$ conduction band edge [8,9], disregarding that the isolated nitrogen level is higher in GaAs and lower in GaP than the $\Gamma$ point. Attempts to provide an answer using band structure calculations have been made [10-13]. A generic argument has been proposed for explaining the band gap.
reduction: the 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 $\Gamma$ point, consequently, the repulsion between the folded states and the $\Gamma$ 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 N atom is much lower than that of As 4s or P 3s. Also, a recent calculation [14] indicates that the first order perturbation of the nitrogen impurity potential, which does not involve the inter-valley coupling, already results in a considerable band gap reduction for GaAsN. Although all these band structure calculations were able to yield a band gap reduction, the values scatter considerably. According to these calculations, the band edge state is 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 the impurity band formation of the nitrogen bound states [15,16]. In GaPN, all existing experimental data seem to indicate the weak role of any perturbed host states in the band edge absorption [17-19], and instead point to the formation of an impurity band from various nitrogen bound exciton states [16,19]. However, recent theoretical calculations [12,13] claimed that the nitrogen impurity states can not interact sufficiently so as to broaden and form an impurity band, and the band gap reduction was due to the host state “plunging down” as a result of nitrogen perturbation. In GaAsN, nitrogen induced bound states have also been found to broaden and turn into a continuous spectrum [20,21]. However, it has not been clear as to how 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 to be addressed in this work.

Another issue which has rarely been addressed for these so-called dilute nitride alloys is the relevant meaning of a measured parameter. Such a parameter can be, for instance, band gap and effective mass which are well-defined for an ideal crystal and meaningful for a conventional alloy. Experimentally, the band gap of GaAsN and GaPN has been derived in many different ways: photoluminescence (PL), absorption or PL excitation (PLE), derivative spectroscopy techniques which include electro- or photo-reflectance or absorption. From absorption, one can fit the absorption near the “band edge” to the lineshape function for free carrier absorption, i.e., $(E - E_g)^n$ with $n = \frac{1}{2}$ for the direct transition and $n = 2$ for the indirect transition. Ambiguity in the fitting procedure has led to 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, taking the excitonic peak (if any) as the band gap versus the above mentioned fitting may give a significantly different band gap for a material like GaAsN which frequently exhibits a rather slow rising slope in its absorption curve [1]. For GaPN, 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 [16]. 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 not trivial for these strongly perturbed semiconductors. It is also unclear how well the band gaps derived from using these somewhat different criteria agree with each other.
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 agreements between experimental and theoretical results have been claimed [13].

In this work, we intend to present a comprehensive view of the so-called GaAsN and GaPN alloys. We will (1) examine the difference for 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) reveal 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.

EXPERIMENTS

GaAs:N samples 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 is 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. GaPN samples were grown by MBE on GaP substrates, as described in Ref.[16]. Some GaPN 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 Spex270 spectrometer and a CCD detector. Differential absorption spectra were measured using a system with a Spex 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.

NEW “BAND GAP” OF GaAsN

Fig.1 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.1 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 which favor one result over the other.

Fig.2 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 a ~ 2 meV splitting and shift of the absorption peaks at this temperature. 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 $1 \times 10^{18} \text{ cm}^{-3}$ or x = 0.0045 %. When x approaches 0.5 %, the absorption peak has broadened drastically, indicating a strong interaction between the bulk-like states and the nitrogen bound states associated with nitrogen pairs or clusters. Fig.3 summarizes the band gap reduction measured by the excitonic absorption peak at 1.5 K as a function of nitrogen composition for the low x region, together with the results for the high x region obtained from electro-reflectance at 300 K [22]. There is indeed a deviation between the band gaps determined by the two techniques. Note that this deviation is not due to the temperature dependence of the band gap. There have been a few reports which suggest a significant difference for the temperature dependence of the band gap between GaAsN and GaAs (for instance, from absorption measurements [23]). However, we have found that the difference is negligible, if any, using the electro-reflectance technique.

![Figure 2. 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.](image)

To better understand the character of the electronic states that contribute to the absorption, for an x = 0.1 % sample, we have measured its PL spectra with excitation energies above and below the GaAsN band gap [20,21]. Fig.4 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 that agrees within a few meV with the band gap determined by the electroreflectance [21]. 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 and TO phonon sidebands.
resonant Raman peaks, which indicates that these states behave like typical localized states [16]. 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 a fact, although the impurity-like states may not be the dominant contributors to the absorption near the “band gap”.

NEW “BAND EDGE” OF GaPN

For GaP:N, early studies [17,18] have indeed shown that nitrogen doping 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) [18]. More recent PLE measurements for nitrogen compositions up to 2% showed absorption features near $A_x$ as well as the direct gap energy, but no sign of any absorption feature at the L indirect gap energy [19]. Thus, it is highly unlikely that in GaPN any perturbed bulk states could make comparable contributions to the band edge absorption of the nitrogen bound states. Fig.5 shows PL spectra for a set of GaP$_{1-x}$N$_x$ samples with $x$ varying 0.004% to 0.6% [16]. The spectrum of the most dilute sample shows the emission lines of nearly all the nitrogen induced bound states in GaPN [5]. However, on increasing nitrogen concentration,
those sharp lines due to nitrogen pairs at the higher energy side broaden and quench sequentially in the order of increasing binding energy. At the same time a broad emission band rises at the lower energy side of the NN₁ line.

Selective excitation PL is used to reveal the nature of the states that give rise to the broad emission band, while absorption measurement is used to monitor the evolution of nitrogen pair states. The results are shown in Fig.6. To the left, the PL spectra obtained under selective excitation are found to always consist of a sharp zero phonon line NN₁′ together with various phonon sidebands, typical of the spectrum for a nitrogen pair like NN₁. 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 the dilute limit, but they strongly broaden and merge with each other. In fact, the absorption peak at NN₁ very much resembles an excitonic absorption peak in a conventional semiconductor. The results of Fig.5 and Fig.6 unambiguously show that for x > 0.1%, nitrogen bound states in GaPN rapidly broaden into a continuous spectrum more than 300 meV wide. Fig.7 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].

Figure 5. PL spectra of GaP₁₋ₓNx with different N compositions, measured at 10 K with excitation energy of 2.33 eV.

Figure 6. Left: selective excitation PL spectra for a GaP₁₋ₓNx 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 GaP₁₋ₓNx sample of x = 0.70%.
DISCUSSIONS

How valid is the “band anti-crossing” model?

The “band anti-crossing (BAC)” model suggests that the band gap reduction is simply due to the isolated nitrogen state and the $\Gamma$ conduction band edge repelling each other [8,9], whether or not the isolated nitrogen level is higher or lower than the $\Gamma$ point 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 gap and $E^+$ is expected by the BAC model. However, in GaAsN, this has been disproved experimentally [24,25], with one exception of the data [26] from the model’s authors. Also, there exists an inconsistency in the coupling matrix element, $V_{MN}$, between what was derived from the band gap pressure dependence and from composition dependence [8,26]. An extended version of this model with the k-space dispersion included is also problematic [27]. 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 whole Brillouin zone, one will have large splittings at both L and X point (e.g., 540 meV at L point and 600 meV at 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 [26]. 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 GaPN, the experimental data of Fig.6 and Fig.7 have shown clearly enough that the A line is not repelled down by any bulk states, as suggested in Ref. [9]. Whether or not the $\Gamma$ band edge shifts up with increasing nitrogen doping [9,19] is a different issue deserving further investigation. In fact, contradicting their own claim of the A line being repelled down starting at $x > 0\%$ in Ref.[9], the authors on a different occasion admitted that the A line energy was independent of nitrogen concentration up to $x \sim 0.5\%$ [26].
Is it possible to make quantitative comparison between experiment and theory?

It is therefore a delicate issue to make a quantitative comparison between the experimental data and the results of theoretical calculations. Along with the ambiguity of 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 [10,11,28,29]. However, not only the calculated results vary significantly from one method to the other, but also neither of them agrees quantitatively with experimental results [22]. Obviously, a randomly nitrogen doped structure is expected to differ electronically from the ordered structure [16,20-22,30], which has been well demonstrated even for a conventional alloy like Ga$_x$In$_{1-x}$P [31]. It has also been indicated by recent calculations [13] that merely the 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 to define the band gap [12,13,30,32]. Refs.[30,32] 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 as to how the calculated band gap is relevant to the experimentally determined band gap would need further clarification. Thus, any claimed excellent agreements with experimental data could only be fortuitous, without actually calculating the specific quantity that is 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 just probing the collective behavior of these states, and these states are expected to respond to the different probes accordingly. 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.

Can an impurity band form in GaAsN and GaPN?

Impurity band formation of the nitrogen bound states has been suggested as the primary mechanism for the band gap reduction [15,16]. To disapprove 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 the impurity band is formed or not is not really 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 to be $\int \sigma d\nu = 9.5 \times 10^{-15} \text{ cm}$ [33], and in GaAs this is estimated to be $\int \sigma d\nu = 2.1 \times 10^{-13} \text{ cm}$ (based on the experimental data of Ref.[7] and following the detailed balance analysis of Ref.[34]). Fig.8 shows estimated peak absorption coefficients for the A line, A$_k$ line, and NN$_1$ in GaPN, and for X$_1$ line in GaAsN, using their absorption cross sections obtained at 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 [35]. Similarly, for the NN\(_1\) state at \(x = 0.1\%\), the peak absorption is estimated to be \(\sim 1,100\) cm\(^{-1}\) in GaP and 14,000 cm\(^{-1}\) in GaAs. Indeed, the absorption of the nitrogen pair bound state in GaAs would be able to reach 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.2, a strong interaction between the 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] suggested that the nitrogen states would remain more or less stationary, whereas the bulk band edge moved down and surpassed them. Since the calculations [12,13] yielded an electron binding energy of \(\sim 100\) meV for nitrogen pairs in GaAsN, it would mean that for \(x > 0.5\%\), the nitrogen pair states should remain bound according to the data of Fig.2, which is obviously contradictory to the experimental fact [20].

How did the theoretical calculation [12,13] conclude, in contrast to the experimental results, that there is no impurity band formation in GaAsN and GaPN? To answer this question, both the intrinsic limitations and the technical inadequacy of the theory need to be examined. As summarized in Ref.[21], there are several channels for the nitrogen bound states to interact. In addition to the difficult coupling considered in Refs.[12,13,15], 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 sincere 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 \(\sim 200\) Å, and a 200 Å size supercell will have \(\sim 333,000\) atoms. Even for \(x \sim 0.4\%\), to statistically have just 10 pairs of the same configuration appear in a supercell in order to observe their interaction, the supercell size should be \(\sim 160\) Å with \(\sim 180,000\) atoms [4]. Thus, the supercell used in Refs.[12,13] was not sufficiently large to generate enough nitrogen bound states with different local configurations to form a quasi continuous spectrum. In addition, the calculations [12,13] yielded an electron binding energy of \(\sim 100\) meV for nitrogen pairs in GaAsN and of \(\sim 30\) meV for the isolated nitrogen in GaPN, while experimental values for both cases are known to be \(< 10\)
meV [3,7,17,20]. 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. In fact, in a recent 1,000 atom supercell calculation with improved pseudopotentials for GaAs$_{1-x-y}$P$_x$N$_y$ [36], even the bare electron bound states were found to be able to form an impurity band for $x > 0.3$.

CONCLUSIONS

A band gap is not as clearly defined in the so-called dilute nitride alloys like GaAs$_1$N$_x$ and GaP$_1$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 GaPN and GaAsN, nitrogen bound states quickly form an impurity band on increasing nitrogen doping level from the dilute limit. The perturbed bulk states in GaPN are found to be unable to make a major contribution to the band edge absorption. It is the absorption of 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 non-detectable at this time. The perturbed bulk states in GaAsN, 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 accurate or direct 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.

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