Discrete and continuous spectrum of nitrogen-induced bound states in heavily doped GaAs$_{1-x}$N$_x$

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We perform a spectroscopic study on GaAs$_{1-x}$N$_x$ samples with N concentrations near an important value of $x=0.1\%$, an intermediate concentration between the impurity limit and the alloy region. We find that near $x\sim0.1\%$, samples exhibiting seemingly different spectra as reported in the literature and observed in our measurements actually have the same underlying electronic structure. Namely, the shallow N-induced bound states have already formed an impurity band and thus led to an observable band-gap reduction, but deeper N-related bound states persist as discrete levels below the newly formed band edge. The role of these discrete states in the formation of the new band edge on further increasing the N doping levels is discussed. We point out that although the nitrogen bound states form an impurity band in heavily N-doped GaAs, the states constituting such a newly formed band continue to retain certain localization characteristics of the impurity in the dilute limit. We observe that the impurity band gives rise to strong resonant Raman scattering, which makes it possible to obtain the resonant Raman profile near the direct band edge of this direct-gap semiconductor.

I. INTRODUCTION

Heavily nitrogen- (N) doped GaAs, often referred to as a dilute GaAs$_{1-x}$N$_x$ alloy, has been intensively studied for the past decade. The incorporation of small amounts of N leads to giant band-structure changes in the host semiconductor GaAs. However, the mechanisms underlying the N-induced band-gap reduction[1] and the appearance of the resonant band[2] remain contentious. Also, the origins of various N-related transitions observed below the GaAs band gap at relatively low N doping levels are either unclear or controversial, which in turn obscures the understanding of the mechanisms underlying the band-structure changes.

From the point of view of isoelectronic doping, the behavior of N impurities in the dilute N limit of GaAs:N is relatively less well understood as compared to the case for GaP:N.[3–8] A better understanding of the behavior of N impurities in the dilute doping limit and the evolution of N-related transitions on increasing the N doping level into the intermediate region between the impurity limit and the alloy region has been shown to be critical for understanding the N-induced band-structure effects in the GaP:N system.[9] In the impurity limit, an isolated N impurity introduces a resonant state (N$_x$) 150–180 meV above the GaAs conduction-band edge, which was first observed by Wolford et al.[10] and later confirmed by Leroux et al.[11] and Liu et al.[12] and qualitatively agrees with the theoretical prediction that the isolated N center generates a resonant state in GaAs.[13,14] A series of N-related below-band-gap transitions (X_1-X_5 and a few phonon sidebands) were observed by Schwabe et al.,[15] Liu et al.,[12] and have recently been reproduced by Makimoto and Kobayashi[16] and Shima et al.[17,18] Liu et al.[12] assigned X_1 and X_2 to recombinations from excitons bound to N pair centers (labeled as NN$_1$ and NN$_2$, respectively),

which is supported by a recent model calculation for GaAs:N.[19] However, other controversial assignments exist in the literature for these bound states.[16–18] Although the N doping levels were not accurately known in the above-mentioned studies,[10–12,15–18] they were presumably below 10^{18} cm^{-3}. For [N]$>10^{18}$ cm^{-3}, Makimoto et al.[20,21] observed a set of new N-related transitions (labeled as NN$_J$, $J=A-F$) and attributed them to different N pairs; Shima et al.[18] reported another series of N-related transitions Y_1-Y_8 and also ascribed them to N pair transitions. In the alloy region of $x>0.1\%$, a typical emission spectrum of GaAs$_{1-x}$N$_x$ shows a broad peak with its energy redshifted from the GaAs band edge proportional to the N doping level.[22] This work will focus on the intermediate region of $x\sim0.1\%$ where not only a significant band-gap reduction is observed but also nitrogen-related impuritylike transitions are seen.

For the region of $x\sim0.1\%$, photoluminescence spectra reported in the literature for similar N doping levels differ drastically from the results of one research group to another,[21,23,24] even changing greatly from one sample to the other with the same average x value but grown under different conditions.[24] Table I summarizes the nitrogen-related transitions reported in the above-mentioned references as well as observed in our measurement. Despite the discrepancy in the literature, a few N-related transitions appear at nearly the same energies in the spectra reported in Refs. 21 and 23, and their energy positions remain stationary with varying N doping level. These states are labeled as NN$_C$, NN$_D$, and NN$_E$ in Ref. 21 and are attributed to N pairs in Ref. 21 and N clusters in Ref. 23. Our recent study of heavily N-doped GaP has revealed the detailed evolution of the transitions related to N pairs and clusters.[9] We found that with increasing N doping in GaP, the N-related transitions first

TABLE I. Peak energies for nitrogen-related transitions in GaAs:N reported in literature and measured in this work (in units of eV). Boldface numbers indicate transitions common to Refs. 20, 23, and this study.

Ref. 15	X_1	X_2	X_3	X_4	X_5					
	1.5082	1.4960	1.4935	1.4515	1.4432					
Ref. 18	Y_1	Y_2	Y_3	Y_4	Y_5	Y_6	Y_7	Y_8		
	1.491	1.489	1.486	1.485	1.478	1.466	1.458	1.449		
Ref. 24	C_{10}	C_6	C_3	C_1						
	1.4773	1.457	1.4438	1.4365						
Ref. 20	NN_F	NN_A	NN_C	NN_E	NN_D	NN_B				
	1.4886	**1.4760**	**1.4623**	**1.4583**	**1.4493**	**1.4284**				
Ref. 23			N cluster	N cluster	N cluster					
			1.461	**1.457**	**1.447**					
XT2658	Y						NC			
	1.4392	**1.473**				**1.4286**	1.441	1.412	1.408	1.400
MB365	Y						NC			
	1.4392		**1.461**	**1.4571**	**1.4484**	**1.4286**	1.441			

broaden due to intercenter coupling and subsequently red-shift due to the carrier relaxation toward the lower-lying states of the impurity band, and that the relative intensity amongst different centers changes greatly. This process occurs sequentially with increasing binding energy and N doping levels. Because of the band-structure difference, the distribution of nitrogen-induced impurity levels with respect to the conduction-band edge is very different for GaAs:N and GaP:N.[19] The implication of this difference on the similarity or dissimilarity in the electronic structure of GaAs:N and GaP:N near the band edge has not yet been well understood in previous studies.

As regards the formation mechanism of the new band edge, there exist quite a few different models. In GaP:N, Yaguchi *et al.*[25] suggested that the band-gap reduction resulted from the formation of an impurity band arising from isolated N centers. In GaAs:N, Güning *et al.*[23] described the new band as a result of N-cluster states merging with the perturbed GaAs band gap. Zhang *et al.*[26] demonstrated a key effect of impurity band formation from N-induced bound states in GaAs:N, which is that an electron in the N impurity band initially had a very heavy mass that subsequently decreased on further increasing the N doping level. The study of Zhang *et al.*[9] for GaP:N showed that the new impurity band consisted of not only a continuous spectrum of perturbed pair states but also of discrete cluster states. Even though all these states form a continuous spectrum in the density of states, they are localized in nature. A distinctly different model was proposed by Shan *et al.*[27,28] In their model, the band-gap reduction was the result of a two-level repulsion between the GaAs band edge and the resonant N_x state.

There have been a number of theoretical calculations for the band structure of the $GaAs_{1-x}N_x$ alloy.[29–36] Ordered structures in one form or the other were used in these calculations. With almost no exception, the paring or clustering effects of N were excluded. Thus, for the energy spectrum near the band edge, these calculations are not expected to give an adequate description of reality (which is that nitrogen is randomly distributed in GaAs).

The aim of this study is to investigate the electronic structure of heavily N doped GaAs in the intermediate doping region so as to clarify the origin of a few N-related transitions below the GaAs band gap and the role of these states in the formation of the N-related impurity band in this system. We will show that (1) GaAs:N samples with very different photoluminescence spectra actually share common features that are intrinsic to this system; (2) the new band edge of the GaAs:N contains discrete N cluster levels that are embedded in a continuous spectrum of the N-related bound states; (3) these N-related bound states give rise to strong resonant Raman scattering; and (4) the electronic structure near the band edge of the $GaAs_{1-x}N_x$ alloy shares a great similarity with that of the $GaP_{1-x}N_x$ alloy. Our results lead to the conclusion that even though heavy N doping generates a continuous spectrum of bound states below the GaAs band gap, which effectively gives rise to a new band edge, these impurity states are still localized in nature.

II. SAMPLES AND EXPERIMENTS

$GaAs_{1-x}N_x$ samples grown by two different techniques, atmospheric-pressure metal-organic chemical vapor deposition (MOCVD) and gas-source molecular beam epitaxy (MBE), were investigated by low-temperature photoluminescence (PL) with above-band-gap and selective excitation. We will particularly focus on a comparative study of two samples with approximately the same N doping level of $x \sim 0.1\%$ ($\sim 2.2 \times 10^{19}$ cm^{-3}) grown, respectively, by MOCVD (MB365) and MBE (XT2658). MB365 was grown on a Zn-doped (001) GaAs substrate miscut 2° toward (111)B at 650 °C and a growth rate of 7 μm/h without a buffer, using dimethylhydrazine as the nitrogen source. The epilayer thickness is 7 μm. The N concentration was measured by secondary-ion mass spectroscopy (SIMS) to be 2.2×10^{19} cm^{-3} (or 0.1%) and by double-crystal x-ray diffraction to be 0.16%. An undoped GaAs sample, MB364, was used as a reference. The growth conditions for MB364 were the same as those for MB365. XT2658 was grown on semi-insulating (001) GaAs at 420 °C and a growth rate of 0.8 μm/h with a 2000-Å GaAs buffer, using a rf nitrogen
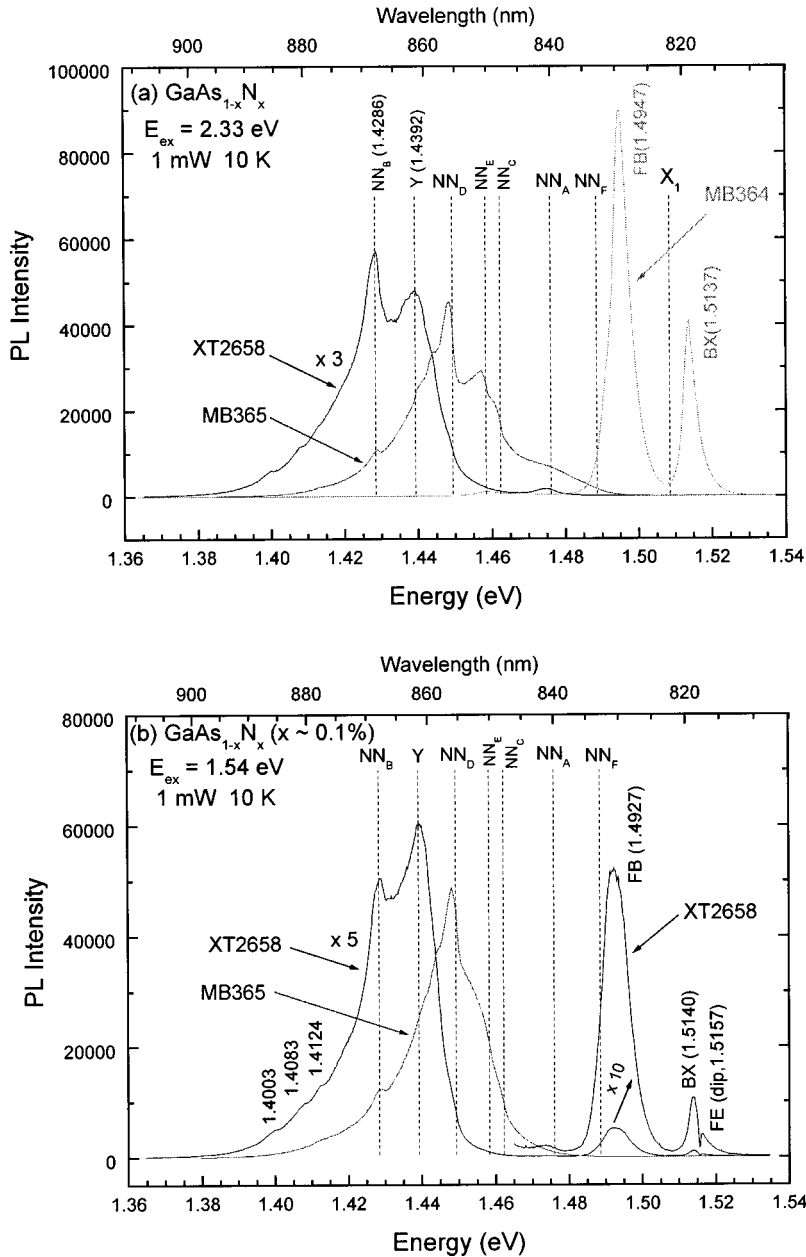
FIG. 1. PL spectra for three GaAs:N samples with excitation energy (a) far above and (b) near the GaAs band gap. NN_A-NN_F indicate the energy positions for the N-related transitions reported in Refs. 20 and 21. BX and FB stand for bound exciton and free-to-bound transitions in GaAs.

radical beam source with a mixture of N_2 and Ar in a ratio of 1:9. The epilayer thickness is nominally 4000 Å. The N concentration was determined by high-resolution x-ray rocking curve (XRC) measurement and theoretical dynamical simulation to be 0.1%. Photoluminescence (PL) was measured with samples in a closed cycle cryostat at ~10 K. The detection system included a SPEX1403 double-grating spectrometer and a cooled RCA C31034 GaAs photomultiplier tube. A 532-nm laser was used for above-band-gap excitation, and a Ti: sapphire laser was used for selective excitation. The typical power used was 1–5 mW focused by a conventional lens. The spectral resolution was ~0.2 meV.

III. EXPERIMENTAL RESULTS

Figure 1 shows PL spectra of three samples (MB364, MB365, and XT2658) with excitation energies far above the

GaAs band gap [Fig. 1(a)] and near the GaAs band gap [Fig. 1(b)]. Energy positions of the N-related transitions that have been reported in the literature are also shown in the figures. For the two MOCVD and MBE samples with approximately the same N doping level of $x=0.1\%$, their spectra look quite different from each other and from those in Refs. 23 and 24 for samples with the same given doping level, but the peaks positions appear to be either in agreement with each other or with those reported in Refs. 20 and 21. Especially, the peak at 1.4286 eV appears in the spectra of both samples and at exactly the same position of NN_B.[20,21] Thus, these transitions are genuinely N related. Perhaps due to the higher concentration, a few higher energy peaks (i.e., NN_A, NN_C, NN_E, and NN_D) in our samples shift to slightly lower energies relative to those in Ref. 20, an effect similar to the concentration effect observed for GaP:N [as shown in Fig. 2(c)].[9] The discrepancy between the two samples and be-
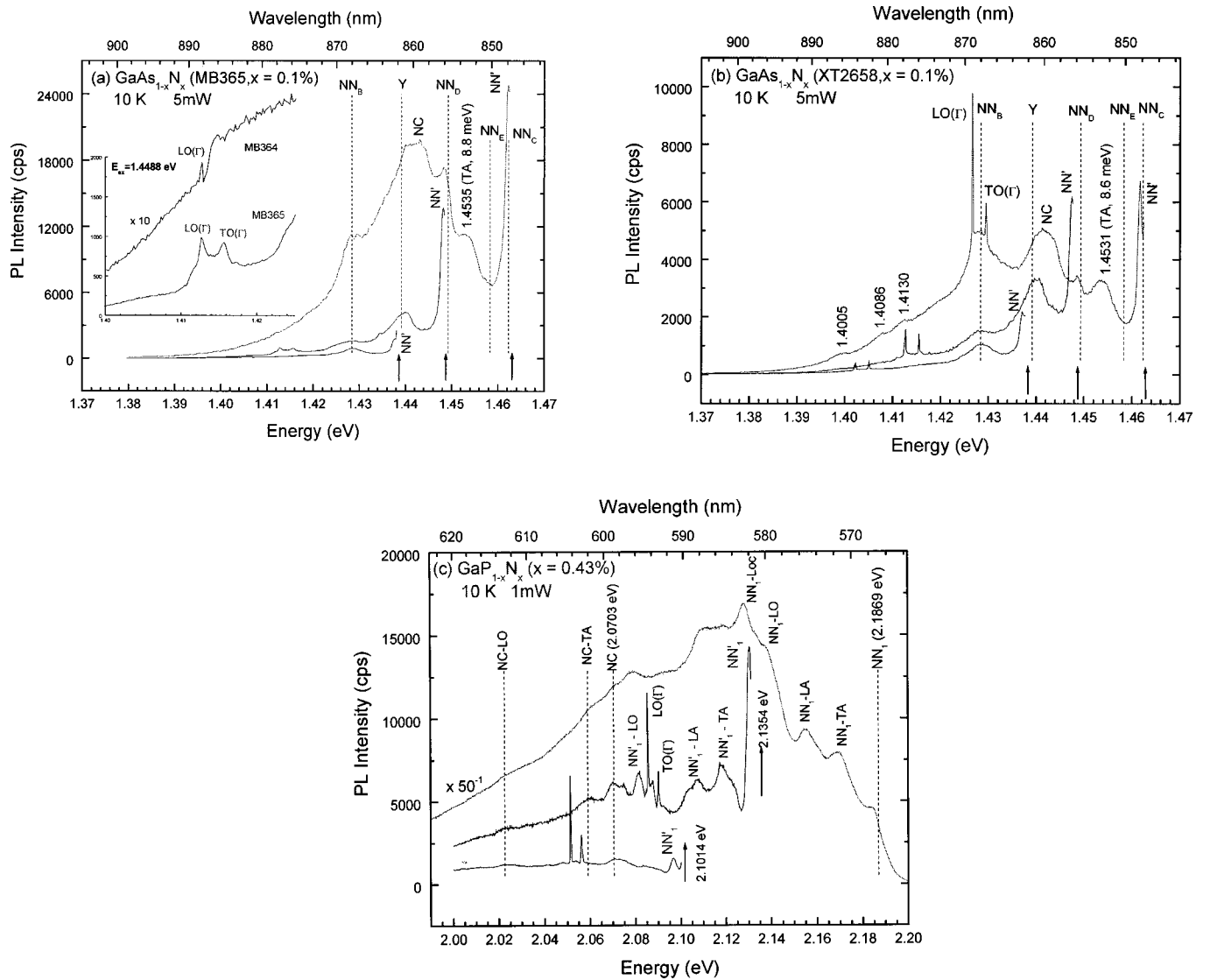
FIG. 2. PL spectra with different selective excitations for (a) the MOCVD sample and (b) the MBE sample. Excitation energies are indicated by arrows: 1.4628, 1.4488, and 1.4384 eV. NN′ represents the exciton bound to perturbed nitrogen pairs. LO(Γ) and TO(Γ) indicate two Raman lines, TA indicates the TA-phonon sideband of the NN′ transition. The inset of (a) compares MB365 ($x=0.1\%$) with MB364 ($x=0\%$) for the Raman features. (c) shows PL spectra for a GaP$_{1-x}$N$_x$ sample under above-band-gap excitation (2.33 eV) and selective excitations. Note that the peak position of NN$_1$ is slightly redshifted due to the high concentration.

tween ours and others indicates that the uncertainty in the doping-level measurement is quite significant and that the spectral shape is very sensitive to the doping level in this range of the doping levels. Note that in the spectrum of the MBE sample (XT2658) with near-band-gap excitation shown in Fig. 1(b), we observe two extra peaks, labeled as FB (for free-to-bound transitions) and BX (for bound excitons) that do not appear in the spectrum of Fig. 1(a) with far above band-gap excitation. It is reasonable to assume that these two new peaks originate from the GaAs buffer layer or substrate. An interesting observation is that a dip appears at the energy of the GaAs band gap. The explanation for this is that the emission from the buffer or substrate at the GaAs band-gap energy gets absorbed by the N-doped epilayer. Thus, even though the band gap for this N-doped sample has been reduced by ~45 meV as determined by

electroreflectance,[2] a vestige of the undoped GaAs band-edge state persists within the new band, which is consistent with the fact that the PLE spectra of N-doped samples show a peak near the GaAs band edge.[21,23] Three additional transitions at 1.412, 1.408, and 1.400 eV shown in Fig. 1(b), are also likely to be N related. In Fig. 1 an additional peak (labeled *Y*) appears at 1.4392 eV for the MBE sample, and it appears as a shoulder for the MOCVD sample, but not in the spectra of Refs. 21 and 23. The origin of this peak is unclear, though it could be related to other impurities (e.g., an acceptor-related transition[21]).

We next measured PL under selective excitation to explore the underlying electronic structure that gives the broadened PL spectra of Fig. 1. Selective excitation has been used in GaAs$_{1-x}$P$_x$:N to resolve phonon sidebands (PS's) in a PL spectrum of the isolated N center that was inhomogeneously
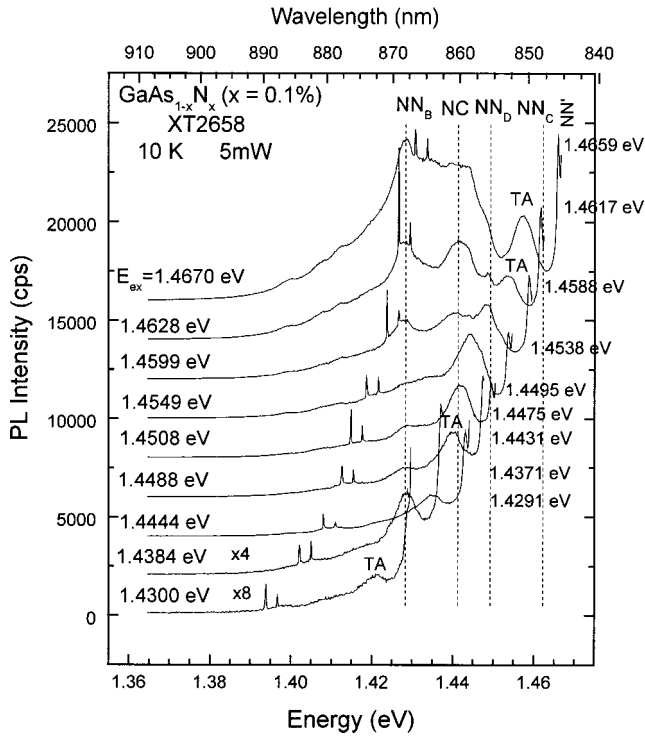
FIG. 3. Selective excitation PL spectra of the MBE sample with a series of excitation energies. Excitation energies are shown on the left, peak energies for the NN′ transition are shown on the right. Spectra are vertically shifted for clarity.

broadened due to the alloy effect,[37] and in GaP:N to resolve overlapped N pair PS spectra of different NN_i centers.[38]

Firstly, as shown in Figs. 2(a) and 2(b), we find that under selective excitation the spectra for the MBE and MOCVD samples share a great similarity, despite the fact that under above-band-gap excitation their spectra appear quite different. For instance, the transition NN_B which is rather weak for sample MB365 in Fig. 1(a), is now resolved equally well for both samples under resonant excitation; the unresolved transition NN_D for sample XT2658 in Fig. 1(a) is now resolved with the 1.4628-eV excitation; and a new peak at 1.441 eV ($\sim$2 meV above the transition Y, labeled as NC), which is unresolved in Fig. 1(a) for the two samples, is now resolved with the 1.4628-eV excitation. Such a similarity indicates that the underlying electronic structures are similar for these two samples, and the difference in appearance under the above-band-gap excitation is largely due to the difference of the actual N doping levels. The variation in doping levels causes a strong difference for the transition associated with the impurity band but not for the discrete levels.

Secondly, as shown in Fig. 3 as well as in Figs. 2(a) and 2(b), we find that a sharp transition, labeled as NN′, appears for all transition energies with its peak energy very close to but shifting with the excitation energy, accompanied by a TA phonon sideband at 8.6-meV below the sharp line NN′. We attribute this peak to N pair states under the perturbation of other relatively remote but randomly distributed N centers or loosely packed N clusters, based on the similarity of these results with those for GaP:N shown in Fig. 2(c).[9] The redshift between the excitation energy and NN′ can be ex-

plained as follows: the excitons created at the excitation energy tend to transfer to nearby trapping centers with lower energies within their radiative lifetime.[39] The redshift is found to be larger for the MBE sample (1.1–1.3 meV) than that for the MOCVD sample (0.5–0.7 meV), because of a somewhat higher N doping level for the former. However, the peak position of NN_B remains stationary on varying the excitation energy. The above-mentioned new peak NC also remains at nearly the same energy on varying the excitation energy, but it overlaps with the TA PS of NN′. We attribute both NN_B and NC to N clusters, since it would be rather difficult for any N pair transition to survive at this doping level, based on a comparison with the results for GaP:N. A similar N cluster-related transition has been observed in GaP:N at 116 meV below the NN_1.[9] In fact, the spectra shown in Figs. 2(a), 2(b), and 3 share a close similarity with the spectra obtained for $GaP_{1-x}N_x$ samples. As an example, Fig. 2(c) shows PL spectra of a $GaP_{1-x}N_x$ sample with $x = 0.43\%$ under above-band-gap and selective excitations. The similarity lies in three major aspects: Fig. 2(c) shows (1) a sharp peak labeled as NN′₁ that appears at 4.8 meV below the excitation energy when the excitation energy falls anywhere within the continuous spectrum below the NN_1 transition, which is attributed to excitons bound to perturbed NN_1 centers; (2) a peak labeled as NC remains at the same energy position with varying excitation (as well as N composition), which is attributed to the exciton bound to nitrogen clusters; (3) a series of phonon sidebands associated with NN′₁, which resembles the PS spectrum of unperturbed NN_1. The redshift of NN′₁ with respect to the excitation energy has been found to increase monotonically with increasing N concentration, which supports the fact that the actual N concentration is higher for sample XT2658 than for the sample MB365. These observations lead to the conclusion that although the N-induced states form a continuous spectrum energetically, they retain a certain degree of spatial localization, which is precisely the characteristic of an impurity band.[40]

Thirdly, we observe a strong enhancement in the Raman scattering from LO(Γ) and TO(Γ) phonons due to the resonant Raman effect, when compared to that for the undoped sample MB364 [see the inset of Fig. 2(a)]. The Raman intensity for the MOCVD sample is somewhat weaker than that for the MBE sample, which is largely due to the doping-level difference. For instance, with the excitation energy at 1.4488 eV, comparing the enhancement of the LO(Γ) phonon for MB365 with MB364 yields about a factor of 23, and for XT2658 with MB364 a factor of about 37. Even though Raman scattering in this geometry (i.e., the back scattering geometry) from the TO(Γ) phonon is nominally forbidden for a zinc-blend semiconductor, the scattering intensity for this phonon becomes comparable to that for the LO(Γ) phonon in these N-doped samples. In fact, such a N-induced resonant enhancement has been observed in GaP:N,[41] and $GaAs_xP_{1-x}$:N,[42] and recently in GaAs:N near the N_x level.[43] Figure 4 shows the resonant Raman profiles for sample XT2658. (Note that in Fig. 4 the system response has been accounted for.) For the LO(Γ) phonon, a peak occurs near the expected band gap (room-temperature electroreflectance
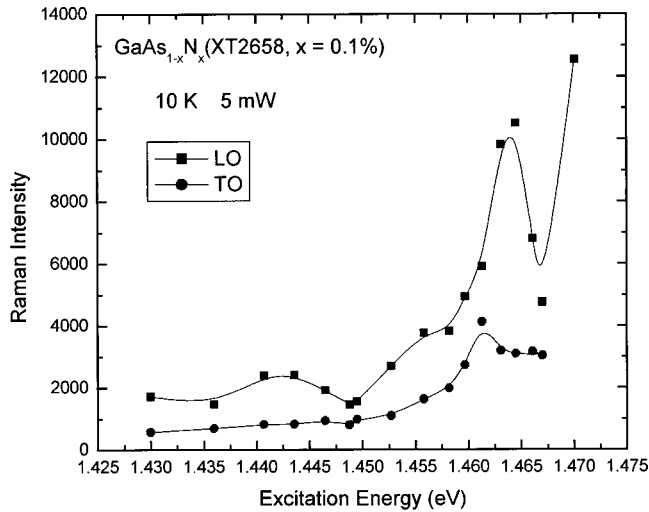
FIG. 4. Resonant Raman profiles of LO(Γ) and TO(Γ) phonons for the MBE sample. Lines through the data points are guides to the eyes.

gives an ~ 45-meV band-gap reduction for this sample.) There might be a second resonance at higher energy. However, due to the interference from strong luminescence, it is not possible to determine the Raman intensity reliably or even see the Raman features for energies higher than the range covered in Fig. 4. For the TO(Γ) phonon, a weaker resonance is found at an energy slightly lower than that for the LO(Γ) phonon. Sharp resonances in resonant Raman profiles associated with isolated N centers[44] and paired N centers[41] in dilute N-doped GaP have been observed previously. Since the enhancement of the Raman scattering from the TO(Γ) phonon is a signature of N-related localized states in these N-doped semiconductors,[41–43] the resonant Raman profile for the TO(Γ) phonon shown in Fig. 4 provides further corroboration of the localized nature of states near the band edge of the N impurity band, although they are partially delocalized due to the impurity band formation. The above observations indicate that it is feasible to obtain resonant Raman profiles near the direct band edge of direct-gap materials like GaAsN. This has hitherto not been possible owing to the fact that the Raman intensities are overwhelmed by the band-edge PL background in GaAs undoped with N.

IV. DISCUSSIONS

There exist a few different models for the mechanism of the band-gap reduction in GaAs:N and GaP:N. Some models appear to be quite different from each other, but actually share a great deal of similarity. In the band-structure calculations for GaAs$_{1-x}$N$_x$ alloys using different techniques,[31–36] N atoms were frequently assumed to be regularly distributed in the GaAs matrix, i.e., the band structure of GaAs:N was mimicked by a superlattice with one N atom in each supercell. Since an isolated N center generates a resonant state above the conduction-band edge,[10–14] one might expect that this type of calculation actually deals with the effect of the interaction of isolated N centers or the formation of the impurity band from the resonant state on varying the N doping

level, and simultaneously on the perturbation of N atoms to the bulk states. Configuration averages (the so-called quasi-random approximation) were performed in some of these calculations;[32,34] however, this does not properly mimic the effect of the random distribution in which the energy levels of N pairs or N clusters may be very different from that of the isolated N center. Similarly, Yaguchi et al.[25] proposed that in GaP:N the band-gap reduction was due to impurity band formation from the isolated N center. However, in GaP:N, since the isolated N center generates a bound state, the perturbed bulk states are not directly relevant to the band-gap reduction. A seemingly different model was the so-called ''two-level repulsion'' model[27,28] in which the band-gap reduction was described as the result of the interaction between the N$_x$ level and the GaAs band-edge state. In fact, the sophisticated pseudopotential supercell calculation of Ref. 36 shares a great deal of commonality with the simple ''two-level'' model. They both suggest that the band-edge state becomes localized in real space, and that the electron effective mass in N-doped GaAs becomes heavier than that in undoped GaAs.[28,36] While Ref. 36 explained these effects as resulting from N-induced mixing of different k states and the repulsion between the Γ state and the folded states, this explanation does not distinguish itself from the ''two-level'' model qualitatively, since the N$_x$ state is in itself a mixed state of different k point states because of its localized nature. In these repulsion models, the predicted dependence of the electron effective mass on the doping level is exactly the opposite of the experimental results of Ref. 26. In our opinion, a major shortcoming of these models is that they are oblivious to the observed bound states of N pairs or clusters that are the genesis of the band-gap reduction.

The impurity band-formation effect occurs at different N doping levels for the different bound states. Although there is not a well-defined N concentration at which GaAs$_{1-x}$N$_x$ alloy formation or band-gap reduction begins, the apparent band-gap reduction should be observed roughly when the shallowest bound state (X_1 or NN$_1$) forms a band. We can give a simple estimate for such a critical doping level (x_0) using the formula $2r_0 = n^{-1/3}$, where n is the concentration of the centers considered and r_0 is the ''radius'' of the impurity wave function. As an estimate, one can use $r_0 = (2mE_b/\hbar^2)^{-1/2}$, where E_b is the binding energy and m is the effective mass. For X_1, using $E_b = 7$ meV,[15] we have $r_0 = 63$ Å, which yields a critical doping level $x_0 = 0.2\%$. Experimentally, the band-gap reduction has been observed to begin at $x = 0.1\%$ or lower.[2,21,23] However, if one takes into account the excitonic effect, the intercenter coupling may start at a lower concentration. As a weakly bound exciton for the X_1 state, the exciton radius is likely to be close to that of the free exciton in GaAs (~ 100 Å). For $r_0 = 100$ Å, x_0 would be 0.1%, which is closer to the experimental results. We should point out that in the vicinity of $x = 0.1\%$ even though modulated reflectance (e.g., electroreflectance or photoreflectance) and PLE spectroscopy have yielded a band-gap reduction of a few tens of meV,[2,21,23] the N-induced deeper bound states (e.g., NN$_B$–NN$_E$) persist as discrete levels below the new band gap. In addition, there is a continuous spectrum of bound states that constitute the tail of the

new band edge. On further increasing the N doping level, these below gap states form their own impurity band and thus define a newer band edge, as shown by the PLE results of Refs. 21 and 23.

In light of the above discussions, a consistent picture has been obtained for the electronic structure of heavily N-doped GaAs samples with $x \sim 0.1\%$ investigated in Refs. 21 and 23 and this study. One can assume that such samples exhibit properties that are characteristic of the GaAs:N system, which is a situation similar to that for GaP:N, where despite the fact that the spectral shape changes greatly on varying the N-doping level, the energy levels of all the N-induced bound states remain well-defined and stationary up to a certain doping level. However, the disagreements that exist amongst the results of Refs. 18, 24, and this study seems to suggest that the distribution of N in GaAs might vary significantly with varying growth conditions. A question, which relates to the distribution of N atoms in GaP and GaAs, has remained unanswered for a long time. If the N atoms are randomly distributed, as usually assumed, why then are far less NN pairs observed compared to what should be expected by simple geometric considerations?[45,8] The absence of certain pairs could be indicative of a nonrandom distribution due to formation energy considerations. Or it could be due to a band-structure effect related to a destructive interaction between the two N atoms for certain pairs.[45] As regards the origin of the observed transitions in GaAs:N, this study seems to indicate that those transitions labeled as $NN_A - NN_E$ are associated with N clusters (with more than two N atoms) and that the X_i series originates from N pairs. Certainly, a set of samples with a continuous variation of N doping level is highly desirable for further clarifying this issue, as has been done for GaP:N.[9] However, the detailed nature of exact configurations for these transitions is not direct relevant to this study and does not affect our conclusions about the electronic properties near the conduction-band edge for the samples we have studied.

V. SUMMARY AND CONCLUSIONS

We have performed a spectroscopic study of GaAs$_{1-x}$N$_x$ samples with N concentrations near $x = 0.1\%$. This is an intermediate concentration at which the shallow N-induced bound states form an impurity band and thus yield an observable band-gap reduction, but at which the deeper N-related bound states persist as discrete levels below the newly formed band edge. We have shown that near the band edge, there exists a continuous spectrum, plus a set of discrete levels, of N-induced localized states, which shares a great similarity with GaP$_{1-x}$N$_x$ samples. The role of these states in the formation of the new band edge on further increasing N doping levels has been discussed. We have observed that these localized states give rise to strong resonant Raman scattering, providing a unique situation where a resonant Raman profile can be measured near a direct gap of a direct-gap material. Finally, even though the band structures of GaAs and GaP are very different, a unified picture has now been obtained for the electronic structure near the conduction-band edge for heavy nitrogen doping in these two systems.

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