

Pressure behavior of the alloy band edge and nitrogen-related centers in GaAs_{0.999}N_{0.001}

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The photoluminescence of a GaAsN alloy with 0.1% nitrogen has been studied under pressures up to 8.5 GPa at 33, 70, and 130 K. At ambient pressure, emissions from both the GaAsN alloy conduction band edge and discrete nitrogen-related bound states are observed. Under applied pressure, these two types of emissions shift with rather different pressure coefficients: about 40 meV/GPa for the nitrogen-related features, and about 80 meV/GPa for the alloy band-edge emission. Beyond 1 GPa, these discrete nitrogen-related peaks broaden and evolve into a broad band. Three new photoluminescence bands emerge on the high-energy side of the broad band, when the pressure is above 2.5, 4.5, and 5.25 GPa, respectively, at 33 K. In view of their relative energy positions and pressure behavior, we have attributed these new emissions to the nitrogen-pair states NN₃ and NN₄, and the isolated nitrogen state N_x. In addition, we have attributed the high-energy component of the broad band formed above 1 GPa to resonant or near-resonant NN₁ and NN₂, and its main body to deeper cluster centers involving more than two nitrogen atoms. This study reveals the persistence of all the paired and isolated nitrogen-related impurity states, previously observed only in the dilute doping limit, into a rather high doping level. Additionally, we find that the responses of different N-related states to varying N-doping levels differ significantly and in a nontrivial manner.

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I. INTRODUCTION

In recent years, heavily nitrogen- (N) doped GaAs and InGaAs, often referred to as the ternary GaAs_{1-x}N_x and quaternary In_yGa_{1-y}As_{1-x}N_x alloy, have received considerable physical and technical interest due to their peculiar N-induced properties and optoelectronic applications. It has been found that the incorporation of a small amount of nitrogen leads to dramatic changes in the electronic band structures, such as a giant band-gap reduction and bowing,¹⁻⁵ the anomalously sublinear pressure dependence of the band gap,^{3,6} heavy electron effective masses,^{7,8} etc. From the technical point of view, the shrinkage of the band gap offers the possibility of covering the whole spectral range from infrared, especially the technologically important wavelength range of 1.3–1.55 μm, to ultraviolet, by one material system.^{9,10} In practice, infrared and 1.3–1.55 μm long-wavelength lasers,¹¹ high-efficiency multijunction solar cells,¹² and heterojunction bipolar transistors¹³ have been fabricated by using InGaAsN.

Besides the general interest in physics, these applications have provided a strong impetus for the effort to understand the evolution of the electronic structure of these unconventional alloys with varying N content in a number of important aspects, for instance, the impurity-impurity interaction,^{8,14} the impurity-host interaction,^{3,15-17} and the effect of external perturbations (e.g., pressure).^{3,15,16,18} With different emphases on these interactions, several physical models, such as the two-band anticrossing (BAC),³ the N-impurity

band formation^{8,14} and the multiband hybridization,^{15,16} have been proposed. The BAC model indicates that the repulsion between the nitrogen impurity level N_x and the GaAs conduction band minimum at the Γ point leads to the formation of the upper energy level E₊ and the lower one E₋, with the lower one being the alloy band edge.³ The empirical pseudopotential supercell calculations show that nitrogen doping results in perturbed host states due to strong Γ-L-X mixing inside the conduction band and the cluster states (CS) in the band gap. According to this intraband hybridization model, the CS energy positions are expected to remain fixed while the perturbed host band-edge state moves down in energy and sweeps the CS one by one with increasing nitrogen concentration.^{15,16} While these two models focus on the impurity-host interaction, the impurity band formation model emphasizes the impurity-impurity interaction. In this model, it is suggested that heavy nitrogen doping results in the overlapping of different nitrogen states and thus the formation of an impurity band within the band gap, leading to a drastic change in the host conduction band.^{8,14} It has now become clearer that all of these three effects must be considered in order to achieve a comprehensive understanding of the electronic structure of GaAs_{1-x}N_x alloy, and each effect manifests itself differently in a specific property of the material.^{17,19} However, a quantitative comparison of the experimental data with the existing models is often found to be either ambiguous or not satisfactory.¹⁹ Therefore, a clear understanding toward the electronic properties of the alloy is still lacking.

Among the issues that have obscured the understanding of the band-structure abnormalities is that the origins of the various N-related transitions observed in GaAsN at different N-doping levels are either unclear or controversial.¹⁴ It is well known that a single isoelectronic N impurity introduces the resonant state N_x 150–180 meV above the GaAs conduction band minimum, which was observed by Wolford *et al.* in the dilute doping limit through the application of hydrostatic pressure.²⁰ When the nitrogen concentration is in the range 10^{16} – 10^{17} cm⁻³, a series of N-related below-band-gap transitions have been observed, signifying the existence of N-related levels within the GaAs forbidden gap at such a doping level.^{21–24} They are controversially attributed to either isolated nitrogen or to nitrogen pairs.^{21–24} Liu *et al.*'s measurements under pressure have shown that the N-related levels in the band gap are due to N pairs, labeled as NN_1 and NN_2 , whereas other N-pair states, NN_i ($i \geq 3$) together with N_x , are resonant above the conduction band edge.^{24,25} This result has been supported by recent theoretical calculations.^{26,27} It is worth mentioning that the host band gap starts to shrink even when $[N]$ is as low as 10^{17} cm⁻³.¹⁷

As the N concentration is increased to 10^{18} – 10^{19} cm⁻³, the situation becomes more complex. Firstly, more N-related levels emerge in the band gap. The origins of these levels have been assigned more controversially to different N-pair and N-cluster states,^{28–31} the phonon replica of nitrogen-pair and -cluster states,¹⁰ or both.¹⁸ Secondly, the emissions associated with the GaAsN alloy band gap are observed to exhibit a more rapid reduction and approach the N-related levels with increasing N concentration.^{9,10,17,29,31} A very recent study has closely tracked the relative shifts of the alloy band gap, NN_1 , and NN_2 up to a doping level of $\sim 10^{19}$ cm⁻³,¹⁷ which indicates that extra caution needs to be exercised when assigning N-related transitions. As the nitrogen concentration $x > 0.1\%$ (2.2×10^{19} cm⁻³), all the pair/cluster lines broaden severely and then merge into a single broad emission peak.^{9,10,14,18,31} The band-gap reduction of GaAsN and the line broadening of N-related emissions indicate that the doping range 0.01%–0.1% is a very critical N-doping regime wherein the impurity-host interaction has already occurred to a significant degree,^{14,17} and can be monitored and studied with much less ambiguity, compared to higher doping levels.^{3,6,18} It is worth pointing out that none of the existing theoretical calculations can realistically address the impurity-host interaction in this critical doping region. Pressure studies have previously been performed by Klar *et al.* for $0.043\% \leq x \leq 0.21\%$ and Weinstein *et al.* for $x = 0.25\%$ and 0.4% .^{10,18} Their results are detailed in the next paragraph. On further increasing x to near 1% or higher, the behavior of N-related states becomes even less certain. Most measurements under hydrostatic pressure focused on the nonlinear pressure behavior of the GaAsN alloy band edge (E_-) and the E_+ transitions.³ For example, Tsang *et al.*³² have observed the sublinear pressure behavior of the photoluminescence (PL) peak related to the E_- transition in a $\text{GaN}_{0.015}\text{As}_{0.985}/\text{GaAs}$ quantum well as well as the N_x -related features in the GaAs barrier. The obtained pressure dependence has shown clearly the deficiency of the BAC model.³² The once well-accepted association of the E_+ transition with N_x (Ref. 3) has now also been pointed out most likely to be wrong.^{33,34}

It can be seen from the above brief review that the pressure experiments serve either to ascertain the origin of N-related states when $x < 0.01\%$ or to study the anomalous pressure behavior of the GaAsN band edge when $x > 0.1\%$. In the critical intermediate concentration regime, the pressure study is expected to help shed light on both the origin of N-related features and the anomalies of GaAsN alloy band structure. Thus, the pressure measurements in this regime are of vital importance. In fact, Klar *et al.* have measured the PL from GaAsN with $x = 0.043\%$, 0.095% , and 0.21% under pressure.¹⁰ The evolutions of both the below-band-gap N-related features and the GaAsN band edge on pressure were observed in the pressure range of 0–0.91 GPa.¹⁰ However, in such a small pressure range, the resonant N-related states are difficult to observe. Recently, Weinstein *et al.* have performed PL experiments under pressure up to 6.2 GPa on GaAsN/GaAs quantum wells with $x = 0.25\%$ and 0.4% . Their most important discoveries are that two NN_3 -related features, identified as LO phonon replicas of NN_3 , appear in the $x = 0.25\%$ sample at pressures above 2.9 GPa, but not in the $x = 0.4\%$ sample.¹⁸ Based on these discoveries and the multiband hybridization model, they believed that the nitrogen states are selectively delocalized in the order of decreasing energy; i.e., the isolated nitrogen state first, then the nitrogen pair states, and other deeper nitrogen cluster states last.^{18,35} Both Klar *et al.*¹⁰ and Weinstein *et al.*¹⁸ also identified a number of below-band-gap peaks, existing even at ambient pressure, as different orders of phonon replicas of NN_i states,^{10,18} but never observed their zero-phonon lines. Therefore, a few puzzles remain unanswered: (1) Can these NN_i states survive when $x \geq 0.1\%$? (2) If they do, where are they located, since we now know that NN_1 shifts even if x is below 0.1%?¹⁷ (3) Are those previously identified emission peaks really phonon replicas? If so, what happens to their zero phonon lines? (4) If E_+ is not derived from N_x , where is N_x located when $x \geq 0.1\%$? In this paper we attempt to answer these questions by performing the pressure PL study on a GaAsN epilayer sample with $x = 0.1\%$, a typical value for the intermediate concentration regime,^{14,17} under pressures up to 8.5 GPa, at 33, 70, and 130 K. At ambient pressure both the below-band-edge discrete N-related features and the GaAsN alloy band-edge emission are observed. Under pressure, the alloy band-edge emission gets smeared out and the discrete N-related states merge into a broad band above 1 GPa. With increasing pressure, the emissions associated with the resonant N pairs, NN_3 , NN_4 , and NN_i ($i > 4$), and the isolated nitrogen state N_x are observed sequentially at different pressures at 33 K. The N_x level is found to be at approximately the same position as that in the dilute limit, despite the fact that a significant band-gap reduction (~ 40 meV) has been observed in the sample. The high-energy part of the broad band appearing above 1 GPa is shown to be composed of the resonant or near-resonant pair states, NN_1 and NN_2 , respectively. The main body of the band is associated with nitrogen cluster centers formed by more than two nitrogen atoms.

II. SAMPLES AND EXPERIMENTS

The sample studied here was grown by gas-source molecular-beam epitaxy on a semi-insulating (001) GaAs

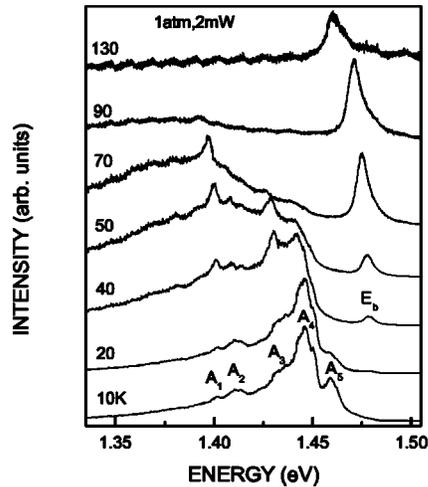


FIG. 1. PL spectra of $\text{GaAs}_{0.999}\text{N}_{0.001}$ at different temperatures at ambient pressure. The spectra have been normalized according to the respective strongest peak and shifted vertically for clarity.

substrate. The GaAsN epilayer thickness was nominally 400 nm, with a 200 nm undoped buffer (but without any cap layer). The nitrogen concentration was determined to be 0.10% by the high-resolution x-ray rocking curve measurement and theoretical dynamical simulation. The detailed growth process has been described elsewhere.^{14,30}

For the hydrostatic pressure experiments the sample was mechanically thinned to a total thickness of 20 μm , and then cut into pieces of $100 \times 100 \mu\text{m}^2$ in size. A piece of the sample was then loaded in a diamond-anvil cell (DAC) used to generate pressures up to 8.5 GPa. Condensed argon was used as the pressure-transmission medium. The pressure was determined from the shift of the ruby R_1 fluorescence line and was always changed at room temperature so as to ensure the best possible hydrostatic conditions. The DAC was mounted in a He closed-cycle cryogenic refrigeration system for the pressure PL measurements at several temperatures. In the same system, the evolutions of the PL spectra of the sample and ruby with temperature were measured at ambient pressure. The obtained variation of the intensity ratio of the R_2 line to the R_1 line of ruby (I_{R2}/I_{R1}) with temperature was then used to determine the actual temperature of the sample inside the DAC.

The PL spectra were measured in a Jobin-Yvon T64000 micro-Raman system working in the single spectrograph mode and backscattering geometry. The signal was dispersed by the third stage monochromator and detected by a multi-channel charge coupled device cooled by liquid nitrogen. The PL excitation was provided by the 514.5 nm line of an Ar^+ laser, focused into a 30 μm spot on the sample. The excitation power was, typically, 0.15 mW on the sample in the pressure experiments.

III. EXPERIMENTAL RESULTS

Figure 1 shows the PL spectra of the GaAsN sample outside the DAC at different temperatures under an excitation power of about 2 mW. These spectra are similar to those

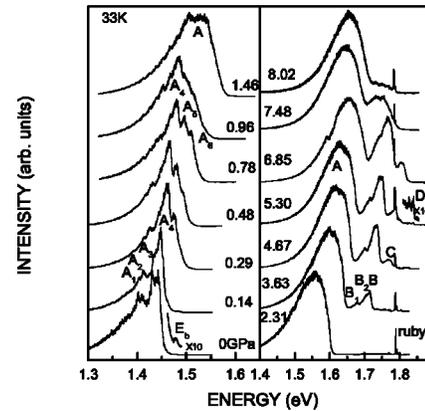


FIG. 2. PL spectra of $\text{GaAs}_{0.999}\text{N}_{0.001}$ under different hydrostatic pressures at 33 K. The number beside a spectrum is the value of the pressure at which it is measured. The spectra have been normalized according to the respective strongest peak and shifted vertically for clarity.

obtained by Luo *et al.* under an excitation power of 10 mW with a Ti:sapphire laser.³⁰ At 10 K, five distinct features, labeled as A_i ($i=1-5$), can be observed. Their peak energies are 1.402, 1.412, 1.434, 1.446, and 1.459 eV, respectively. A_2 seems to be a double-peak feature, and A_4 has a high-energy shoulder at 1.45 eV. These features have been previously reported and assigned to different nitrogen pair/cluster states or their optical phonon replicas.^{9,10,14,18,21,28-31} With increasing temperature, the relative intensities of the nitrogen-related peaks change significantly. A_1 (A_3) is weaker than A_2 (A_4) at temperatures lower than 40 K, which is reversed at higher temperatures. A_3 and A_4 are much stronger than A_1 and A_2 , respectively, below 40 K, but quench with increasing temperature, and A_1 becomes dominant at 70 K. A_5 also quenches with increasing temperature and disappears at about 40 K. All the above variations are due to thermally induced exciton transfers among different nitrogen-related states. Furthermore, a broad band with a very long tail underlying these discrete features becomes evident above 40 K, and its center shifts to the lower-energy side with increasing temperature. At temperatures higher than 20 K, a new peak labeled E_b appears at around 1.48 eV. Luo *et al.* have attributed this feature to the edge transition of the GaAsN alloy.³⁰ At 130 K, only E_b can be seen in the spectra due to an overwhelming thermal occupation of carriers. The assignment and pressure behavior of E_b are discussed in the next section.

The PL spectra under different pressures at about 33 K are shown in Fig. 2. At ambient pressure A_1-A_4 can be seen clearly, while A_5 and E_b are very weak. With increasing pressure, A_1-A_4 exhibit a blueshift. When the pressure is higher than 0.29 GPa, E_b becomes undetectable, while A_5 and a new feature, A_6 , become distinctly observable. As pressure is further increased to above 1 GPa, A_1-A_6 continue the blueshift but gradually merge into a broad band, labeled as A. The center of A continues the blueshift with pressure. Above 2.5 GPa, a new band comprising a series of features, labeled as B, B_1 , and B_2 , appear on the higher-energy side of the A band. B_1 and B_2 can be viewed as phonon replicas of B with

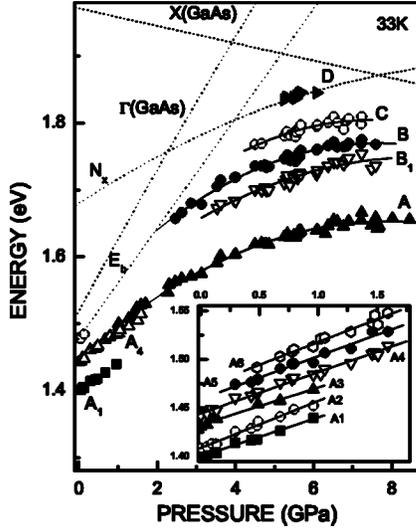


FIG. 3. Pressure dependence of the PL peak energies of $\text{GaAs}_{0.999}\text{N}_{0.001}$ at 33 K. The solid lines represent the results of least-squares fits to the experimental data. The dotted lines are the pressure dependence of the Γ and X gaps of GaAs, the expected pressure dependence of the alloy band gap and the result of N_x obtained from the literature (Refs. 20 and 32). The inset detailed the pressure dependence and corresponding fits of A_1 – A_6 energy positions.

phonon energies of 10 and 37 meV, respectively. Another new band, labeled as C , appears at pressures higher than 4.5 GPa. It lies energetically near the ruby lines, but exhibits distinctly different line shape and pressure dependence. Near 5.25 GPa, more new features, although rather weak, can be observed on the higher-energy side of C and the ruby lines. Among them, D is the highest in energy. On further increasing pressure, D , C , and B disappear successively at about 6.1, 7.2, and 8.0 GPa, respectively. The band A , however, remains visible up to 8.5 GPa. This sequential quenching of D , C , and B is due to the fact that they sequentially approach the X valley of the conduction band. As for the peak intensity, A is always dominant, B is stronger than C , and D is the weakest.

The pressure dependences of the peak energies for the features in Fig. 2 are depicted in Fig. 3. The energy positions of sharp features, such as A_1 – A_6 , are obtained at their peak positions, and the position of the A band is taken roughly at its center. In the inset of Fig. 3, the data for A_1 – A_6 are shown in detail. The solid curves running through the data points are the results of the least-square fits to the experimental data using quadratic (for A , B , B_1 , and C) or linear relations (for A_1 – A_6). The corresponding first- and second-order coefficients are listed in Table I. We do not fit the data for D and E_b due to insufficient data points. The dotted lines represent the pressure dependences of the Γ and X band gaps of GaAs, the expected pressure dependence of the alloy band gap obtained by using the energy positions of E_b measured at 33 K and the pressure coefficient obtained at 70 K, and the dependence of isolated nitrogen center (N_x) obtained from the literature in the dilute limit (the pressure dependence is $1.68 + 0.038 \times P - 0.0017 \times P^2$ eV).^{20,32} As can be seen from Fig. 3 and Table I, A_1 – A_6 have similar pressure coefficients,

TABLE I. Coefficients describing the dependence on pressure of the PL peaks of $\text{GaAs}_{0.999}\text{N}_{0.001}$ obtained from least-squares fits to the experimental data at different temperatures by using $E(p) = E_0 + S_1 \times p$ or $E(p) = E_0 + S_1 \times p + S_2 \times p^2$.

Temperature (K)	Peak	E_0 (eV)	S_1 (meV/GPa)	S_2 (meV/GPa ²)
33	A_1	1.400(1)	40(2)	
	A_2	1.409(1)	48(2)	
	A_3	1.433(1)	38(2)	
	A_4	1.444(1)	42(1)	
	A_5	1.459(2)	44(2)	
	A_6	1.471(3)	47(3)	
	A	1.449(3)	52(2)	–3.3(2)
	B_1	1.526(23)	51(8)	–3.0(7)
	B	1.531(9)	63(4)	–4.1(4)
	C	1.561(61)	65(21)	–4.0(2)
70	A_1	1.394(2)	46(4)	
	A'	1.471(3)	39(2)	
	E_b	1.473(3)	82(9)	
130	A'	1.498(5)	31(3)	
	E_b	1.471(8)	71(17)	

about 40 meV/GPa, which are comparable to the results reported in the earlier works.^{10,24} Similar to N_x , A , B , and C shift nonlinearly with pressure. Their slopes decrease continuously with increasing pressure, showing close similarity with Liu *et al.*'s results for various N -pair states.²⁴ Although only a few data are obtained for D , it can be seen clearly that they almost exactly fall on the curve of N_x .

The evolution of the spectra with pressure at 70 and 130 K is shown in Figs. 4 and 5, respectively. At 70 K, A_1 dominates the spectra and A_2 – A_4 can also be observed under low pressures. The underlying broad band A is more pronounced at this temperature even at ambient pressure. Above 1 GPa, A_1 – A_4 have smeared out and become undis-

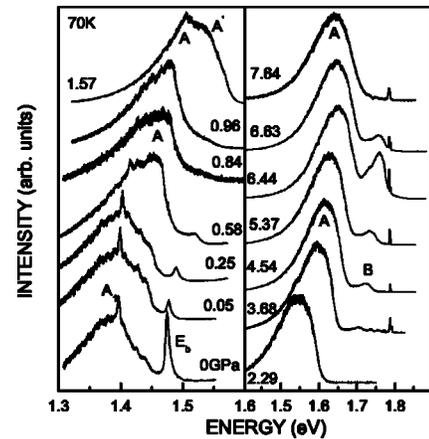


FIG. 4. PL spectra of $\text{GaAs}_{0.999}\text{N}_{0.001}$ under different hydrostatic pressures at 70 K.

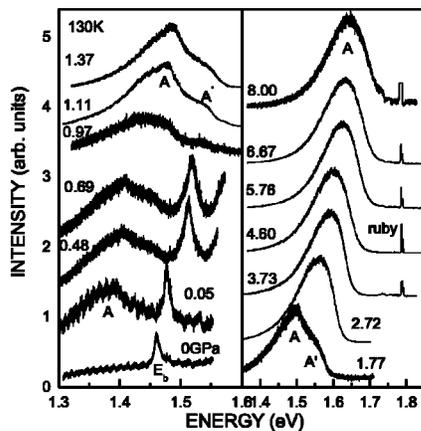


FIG. 5. PL spectra of $\text{GaAs}_{0.999}\text{N}_{0.001}$ under different hydrostatic pressures at 130 K.

tinguishable from the A band. With increasing pressure, the higher energy portion of A becomes dominant, and a shoulder appears, labeled as A' , which could be related to A_5 and A_6 , in the pressure range of 1–2 GPa. On further increasing pressure, A' and A merge into one band, also labeled as A . The center of A exhibits a blueshift with increasing pressure. B can be observed when the pressure is above 3.5 GPa, whereas C and D remain unobservable in the entire measured pressure range. At ambient pressure, the GaAsN band-edge feature E_b can be clearly seen. As the pressure is applied, it shifts rapidly to higher energy position, while its intensity decreases rapidly as well. When pressure is greater than 0.8 GPa, E_b becomes undetectable. At 130 K, only E_b is observed at ambient pressure. Its intensity changes little with pressure at first, but it disappears abruptly at 0.97 GPa. In addition, the higher-energy shoulder A' emerges at around 1.1 GPa and then merges into A . The center of the A band blueshifts with increasing pressure, as it does at lower temperatures. At 130 K, none of B , C , and D is observed.

Figure 6 shows the variations of the peak energies with pressure at 70 and 130 K. The fitting results for E_b , A_1 , and A' , represented by the solid lines in Figs. 6(a) and 6(b), are listed in Table I. The pressure coefficients of E_b are 82 ± 9 and 71 ± 17 meV/GPa. The dotted lines represent the pressure dependence of the Γ and X band gap of GaAs and that of A and B measured at 33 K, respectively. The curves have been vertically shifted to fit the data at 70 and 130 K. It can be seen that at 70 and 130 K, the A band exhibits a more rapid shift in the pressure range below 2.5 GPa since the intensity of the high-energy portion of band A increases more rapidly in the low-pressure range.

IV. DISCUSSION

A. Assignment and pressure behavior of E_b

Luo *et al.* have previously observed an emission, named E_b , at the proximity of the expected band gap of the GaAsN alloy from the same sample investigated here under a pulse-wave excitation with a power of 40 mW at 14 K.³⁰ It was found that E_b had a lifetime comparable to that of the GaAs emission and accordingly was identified as a band-edge tran-

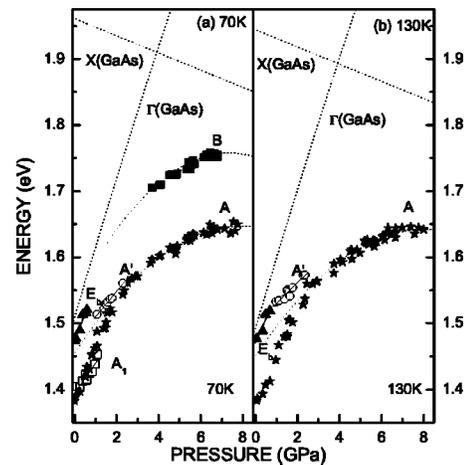


FIG. 6. Pressure dependence of the PL peak energies of $\text{GaAs}_{0.999}\text{N}_{0.001}$ at (a) 70 K and (b) 130 K. The solid lines represent the results of least-squares fits to the experimental data. The dotted lines are the pressure dependence of the Γ and X band gaps of GaAs and that of A and B measured at 33 K, respectively.

sition in the GaAsN alloy. This feature, however, was not detected on the same sample under a cw excitation of 1 mW at 10 K,¹⁴ which could be due to the low excitation intensity. The band gap determined by modulation and PL excitation spectroscopy^{19,36} and our pressure experiments support Luo *et al.*'s assignment. The pressure coefficient of E_b measured here is about 80 meV/GPa at either 70 or 130 K. This value is in good agreement with that of E_- obtained by Klar *et al.*,¹⁰ confirming that E_b is a GaAsN alloy band-edge-related emission rather than a nitrogen-related one. Since it is well known that the pressure coefficient of the GaAs band edge is 108 meV/GPa, the band edge of the GaAsN alloy with $x = 0.1\%$ exhibits a significantly smaller pressure coefficient than that of bulk GaAs, indicating a dramatic change of the conduction band edge due to the incorporation of nitrogen. It has been theoretically calculated that the band edge of GaAsN contains some L and X character due to the nitrogen-mediated coupling of the host states.^{15,16,37} The significant decrease of the pressure coefficient of the GaAsN band edge observed here qualitatively agrees with the expected consequence of such a coupling, since the pressure coefficients of L and X valleys of GaAs are much smaller than 80 meV/GPa, although no numerical value can be found to make a quantitative comparison.

B. Assignment and pressure behavior of B , C , and D

As described above, the experimental data of D fit rather well with the pressure dependence of N_x , the isoelectronic trap state of isolated nitrogen in GaAs:N.^{20,32} Furthermore, the linewidth (full width at half-maximum) of D , measured to be about 3.5 meV, is much smaller than that of B and C (10 meV or so) and comparable to that of N_x measured before (~ 5 meV).³² It is, therefore, reasonable to ascribe D to the emission from the isolated nitrogen center in the alloy. The fact that the intensity of D is the weakest among A , B , C , and D suggests an efficient energy relaxation from isolated N

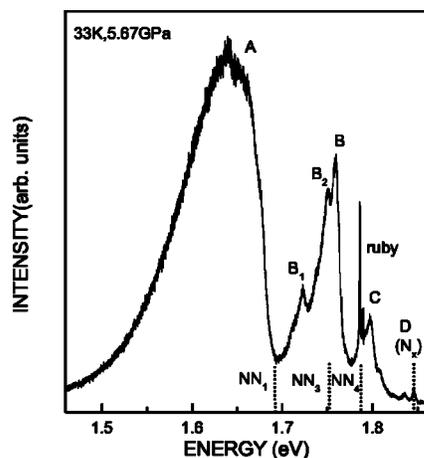


FIG. 7. PL spectrum of $\text{GaAs}_{0.999}\text{N}_{0.001}$ measured at 33 K and 5.67 GPa. The vertical dotted lines represent the energy positions of N_x , NN_4 , NN_3 , and NN_1 , obtained from Liu *et al.* (Ref. 24).

centers to deeper pair or cluster centers, as is known for GaP:N.^{38–40} However, we do need to rule out the possibility that D could originate from the N_x state in the buffer layer, which might have been unintentionally doped with N, due to the existence of the carriers either directly excited in or diffused into the buffer. Indeed, the N_x transition in N-contaminated GaAs barriers was observed in a GaAsN/GaAs quantum well samples by some of us previously.³² In that case, however, because the thickness of the $\text{GaAs}_{0.985}\text{N}_{0.015}$ quantum well was only 15 nm, the N_x transition was excited by the direct excitation in the GaAs barrier layers. In contrast, because the sample studied in this work has a 400 nm thick GaAsN epilayer without any GaAs cap layer, the 514.5 nm excitation light with a light penetration depth of about 150 nm is unlikely to directly generate a meaningful number of carriers in the GaAs buffer layer. The other possibility left is the diffusion of the carriers, generated in the epilayer, into the buffer layer. By noticing the fact that the band gap of the GaAsN epilayer is about 30 meV lower than that of the GaAs buffer layer, the diffusion is also difficult, especially at low temperature. In fact, we did not observe any GaAs-related emissions from the buffer at ambient pressure. In addition, the emission from N_x in the dilute limit becomes observable at 2–3 GPa,^{20,24,25,32} while D is observed only when the pressure is up to 5.25 GPa, which in fact reflects the band-structure change in the epilayer due to the heavy N doping (as discussed further below).

Liu *et al.* have shown schematically the energy levels of NN_i ($1 \leq i \leq 10$) relative to N_x in GaAs:N with the nitrogen concentration $[\text{N}] \sim 5 \times 10^{17} \text{ cm}^{-3}$ at ambient pressure.²⁴ In addition, Weinstein *et al.* have observed PL features similar to A and B found here, but with somewhat different energies, at 1 atm and 2.9 GPa, in GaAsN/GaAs quantum wells with a nitrogen concentration of 0.25%. They attributed the A -like and B -like features to the phonon replicas of NN_1 and NN_3 , respectively.¹⁸ Comparing with previous results, a spectrum of our sample measured at 33 K and 5.67 GPa in which all the four features, A , B , C , and D , are observed simultaneously as shown in Fig. 7. The vertical dotted lines in Fig. 7 indicate the energy positions of N_x and NN_i ($i=1,3,4$)

given by Liu *et al.* We have in the above paragraph attributed D to the N_x state of GaAsN. In fact, D does have the same energy value as N_x 's obtained by Wolford *et al.* at 5.67 GPa.²⁰ Thus it is natural to locate D and N_x at the same energy position. Since the relative energy sequence and non-linear pressure dependence of B , C , and D are similar to those of NN_3 , NN_4 , and N_x , respectively, given by Liu *et al.*, we attribute B to NN_3 , with its TA phonon replica at B_2 (10 meV below B) and LO phonon replica at B_1 (37 meV below B), and ascribe C mainly to NN_4 , possibly with some contributions from NN_5 . The weak features between C and D could be related to other NN_i ($i \geq 5$) and the phonon replica of N_x , although reliable assignments are difficult due to their low intensities.

It is worth noting that the energy positions of B and C are not exactly the same as those of NN_3 and NN_4 given by Liu *et al.* for the dilute sample. Extrapolated to zero pressure, the energy positions of N_x , NN_4 , and NN_3 are 1.68, 1.622, and 1.586 eV, respectively,^{24,25} but those of D , C , and B are 1.68, 1.561 and 1.531 eV, respectively. It seems that N_x remains stationary, while NN_3 and NN_4 have redshifted by ~ 55 and ~ 61 meV, respectively from their dilute limits. The shifts for these resonant N-pair states are similar to those recently reported for the bound pair states,¹⁷ which reflect the response of the impurity states to the host band-structure changes and the effect of impurity-impurity interaction with varying the N-doping level. At 5.67 GPa, however, the centers of B and C are located on the higher-energy side of NN_3 and NN_4 , as can be seen in Fig. 7. This is because the pressure coefficients of B and C , 63 and 65 meV/GPa, respectively, are larger than that of D (38 meV/GPa).

Our results reveal the persistence of all the paired and isolated resonant nitrogen states, previously only observed in the dilute doping limit, into the rather high doping level of 0.1%. In addition, we have found that N_x has been very little affected by the host band-structure change, which further confirms that N_x cannot be responsible for the E_+ transition, as pointed out before.^{33,34} Instead, some N-pair states, such as NN_3 and NN_4 , which are expected to be more localized than N_x , are in fact more affected than N_x , as can be seen from their enhanced pressure coefficients and lowered energy positions. Our findings seem to be in disagreement with the notion of selective delocalization starting from N_x to paired states in the order of decreasing energy.^{18,35} Such a finding indicates that the impurity-host interaction occurs in a more sophisticated manner than that has been described by the existing theory.^{15,16,27} In conjunction with the experimental data of Ref. 17, it appears that those N-impurity states closer to the conduction band edge (e.g., NN_1 – NN_4) are more easily affected by the host band-structure change than those relatively farther away (e.g., N_x). Therefore, issues remaining to be studied may include, for instance, the reason for the disparity in their responses to the impurity-host interaction for different N states, what happens to a N-related bound state when the band gap drops below it, and how the pressure dependence of a N-related state varies with N-doping level. Qualitatively, it is not difficult to comprehend that at a sufficiently high N-doping level, the impurity and host states should be strongly hybridized, and eventually it becomes difficult or meaningless to distinguish the per-

turbed host states and affected impurity states.

In analogy to the observations of Liu *et al.* and Weinstein *et al.*, the threshold pressures under which different nitrogen-pair states and N_x -related features emerge as bound states are different from each other. In our experiments, B , C , and D appear at 2.5, 4.5, and 5.25 GPa, respectively. Liu *et al.* observed NN_3 , NN_4 , and N_x at 0.95 GPa, 1.6 GPa, and 2.55 GPa, respectively, while Weinstein *et al.* detected the believed NN_3 phonon replica at 2.9 GPa. Obviously, our results lie in between theirs, as does the N composition of our sample. The reason that the threshold pressure increases with N concentration is that, on the one hand, the pressure coefficient of E_b is about 80 meV/GPa, much smaller than that of the GaAs band gap, and on the other hand, the pressure coefficients of the N-pair states increases. Using the slope obtained at 70 K and the peak energy of E_b measured at ambient pressure at 33 K, we compute the pressure dependence of E_b at 33 K, as shown by the dotted line in Fig. 3. It can be seen clearly that the pressure for the initial appearance of B is very close to the crossing point of the two curves describing the pressure dependence of B and E_b . C and D , however, are farther away from the expected crossing points. This is possibly because the pressure dependence of E_b might not remain linear or become sublinear in the high-pressure region. In addition, only at sufficiently high pressures, the C and D states can become localized enough (or with large enough binding energies) so that their radiative recombination rates can compete with the energy relaxation to the lower bound states. With this consideration in mind, the disappearing of the emission from an impurity center might not necessarily lead to the conclusion that the impurity state has become delocalized.¹⁸

C. Assignment and temperature and pressure behavior of A_i and the A band

When the temperature is below 40 K at ambient pressure and the pressure is lower than 1.5 GPa at 33 K, the fine features A_i in the A band can be clearly resolved, as shown in Figs. 1 and 2. Several groups have reported similar features previously. Their assignments of A_i differ drastically from each other. Some have ascribed A_i to different nitrogen-pair or -cluster states,^{9,14,21,28-31} and others related them to different phonon replicas of certain nitrogen pair or cluster emissions.^{10,18,29} Based on the analysis of the changes of the spectra with temperature and pressure, we are inclined to believe that the main elements of A_i are the zero-phonon lines of different nitrogen-pair or -cluster states rather than their high-order phonon replicas. It appears that (A_1, A_2) is a phonon replica of (A_3, A_4) , since the change of relative intensity of A_2 versus A_1 with temperature resembles that of A_4 versus A_3 , and in addition, the energy separation between (A_3, A_4) and (A_1, A_2) approximates the energy of a GaAs LO phonon.^{10,20} However, the intensity of (A_3, A_4) is stronger than that of (A_1, A_2) below 40 K, but becomes reversed above 40 K. At 10 K, A_4 is dominant; but at 70 K, A_1 is much stronger than A_3 and A_4 . It is well known that the Huang-Rhys factor, which is equal to the intensity ratio of the first phonon replica to the zero-phonon line, is a

temperature-independent parameter.^{24,41} The observed changes in the relative intensities between A_i do not support the phonon replica assignments, but suggest them to be the zero-phonon line of the emissions from different nitrogen-cluster centers.

By studying the spectra for the GaAs:N sample with a nitrogen concentration of $5 \times 10^{17} \text{ cm}^{-3}$ under pressure, Liu *et al.* found that the zero-phonon line of NN_1 is about 6 meV (1.508 eV) below the GaAs donor-bound exciton state.²⁴ Recently, Zhang *et al.* have studied the evolutions of two N-related emissions X_1 (NN_1) and X_2 (NN_2) with N concentration in the $[N]$ range of $10^{15} - 10^{19} \text{ cm}^{-3}$. With increasing $[N]$, X_1 exhibits a significant redshift and X_2 shifts a little. They become nearly resonant with the host band edge when $[N] \sim 10^{19} \text{ cm}^{-3}$. Our work seems to support this result. The increase in the bandwidth of A with increasing pressure indicates that more N-related states become involved in the A band at high pressures. If the entire A band at high pressures is extrapolated to 0 GPa, considering its typical width at high pressures being ~ 100 meV and its band center at zero pressure is 1.449 eV (see Table I), its high-energy side will exceed 1.499 eV, higher than E_b (1.48 meV), the alloy band edge. Moreover, A' appears at the high-energy side of A at 70 and 130 K, and when extrapolated to 0 GPa, its band centers at the two temperatures are 1.471 and 1.498 eV, respectively, which are also near and above the host band edge. Therefore, at the doping level of 0.1%, X_1 (NN_1) and X_2 (NN_2) should be resonant or near-resonant in the host conduction band, and they appear in the high-energy part of A and/or A' when pressed into the forbidden gap above 1 GPa.

In GaAsN samples with nitrogen concentrations lower than 0.04%, the nitrogen-pair-related or cluster-related features are considerably more discrete and sharper without much perceptible background.³¹ When the nitrogen concentrations increase up to 0.1%, these features appear to be superimposed onto a continuous and broad background, as observed here and reported elsewhere in the literature.^{9,14,29,30} As the temperature is raised over 40 K, or the pressure raised higher than 1 GPa, this broad background continuum becomes more prominent, as can be seen in Figs. 1, 2, and 4. Moreover, the discrete nitrogen-related features are hardly resolved when the pressure is higher than 1.5 GPa, and the broad band evolving from the background dominates the spectrum. Zhang *et al.* have attributed the broad background in GaAsN or GaPN to perturbed nitrogen-pair states based on their selective excitation PL spectra results.^{14,39} They pointed out that other relatively remote nitrogen centers could perturb the nitrogen pair states under consideration. Sufficiently nearby fluctuations of the so-called (As, N) or (P, N) configuration are expected to form discrete deeper centers, such as the nitrogen-cluster states labeled as NC. The statistical distributions of the (As, N) or (P, N) configurations away from a nitrogen-pair center lead to the peak broadening of the emission related to the nitrogen pair with increasing nitrogen concentration and then the formation of the broad impurity band.³⁹ The appearances of the discrete features (A_i) and the broad background band (A) observed here seem to support this viewpoint and the existence of the impurity band. On increasing the temperature and pressure, the dis-

crete center-related emissions A_i broaden, then overlap and finally merge into the background continuum. Thus, the impurity band, i.e., the A band, becomes more and more dominant with increasing pressure and temperature.

Since all the nitrogen-pair states NN_i ($i \geq 1$) are resonant or nearly resonant in the host conduction band, the discrete nitrogen-related features A_i ($i=1-6$), and the main body of the band A (not including the high-energy part) are composed of the emissions mainly from deeper cluster states involving more than two nitrogen atoms. Among these cluster states, NN_1N_α ($\alpha \geq 1$), the triplet center formed by the first two nitrogen atoms in a NN_1 state and a relative remote third nitrogen atom, is fairly probable in our opinion. The subscript α indicates various distances between the third atom and the NN_1 pair, just similar to “ i ” in NN_i . The similar triplet centers $NN_\beta N_\alpha$ have been mentioned previously in the literature.^{39,40} Due to the perturbation of the third nitrogen atom, the NN_1 pair state is energetically lowered and a new deeper triplet center forms. It is known that the emission energy of NN_i converges to that of isolated nitrogen, i.e., N_x with increasing index “ i .”⁴² Similarly, the energy of NN_1N_α converges to NN_1 with increasing index “ α .” Thus, as can be seen in Fig. 7, the energy position of NN_1 given by Liu is near the higher-energy side of A . When the third nitrogen atom occupies a lattice point with a higher degeneracy, the emission from the corresponding NN_1N_α triplet center exhibits a stronger intensity and then leads to a discrete and resolved feature in the spectrum, such as A_i ($i=1-6$). Other emissions from the less degenerate NN_1N_α triplet states and other higher-order nitrogen clusters and their phonon sidebands overlap and constitute the broad and continuous background band A and its long tail. The detailed assignments of the band A as well as its component A_i require more accurate calculations for the energy levels of the N-cluster states than the existing ones,^{15,16} which is a challenging task for a future theoretical study.

Like the isolated nitrogen and nitrogen-pair states in GaP:N (Ref. 40) and GaAsP:N,⁴³ the nitrogen-cluster states, exhibit a thermally activated exciton transfer effect. That is, the exciton can thermally transfer from a shallow impurity center to deeper ones. Hence, with increasing temperature, higher-energy features among A_i quench, while low-energy ones become stronger, and the center of A moves to the lower-energy side, as can be seen in Fig. 1. Meanwhile, because electrons are also thermally excited to the alloy conduction band, the intensity of E_b is enhanced as temperature increases. When the temperature is above 130 K, the latter effect is overwhelming and only E_b remains visible in the PL spectra.

Considering that the pressure coefficient of the GaAsN alloy band edge is larger than those of nitrogen-related states, the binding energies of the A/A_i related states are enhanced, and so are the carrier capture rates for these states,²⁵ with increasing pressure. This effect results in the appearance and enhancement of A_5 and A_6 on the higher-energy side of A_4 at 33 K and the attenuation of E_b at 33 and 70 K, with increasing pressure. The more rapid increase of the center energy of A in the pressure range of 0~2.5 GPa at 70 and 130 K is also due to the pressure-enhanced carrier transfer.

V. SUMMARY

We have studied the photoluminescence of GaAs_{0.999}N_{0.001} under pressures up to 8.5 GPa at different temperatures. At ambient pressure, the N-cluster-related discrete features A_i are observed below the band gap at 10 K. When the temperature is above 20 K, an emission from the GaAsN alloy band edge (E_b) appears. Up to 130 K only E_b could be observed in the PL spectra. Under pressure, both E_b and A_i shift to higher energy. The pressure coefficients of A_i are found to be around 40 meV/GPa, similar to that of NN_1 reported for the dilute N sample, while that of E_b is about 80 meV/GPa, significantly lower than that of GaAs. On increasing pressure to above 1 GPa, the discrete features smear out and merge with the continuous background emission into a broad band, the A band. On further increasing pressure at 33 K, a series of new bands, B , C , and D , appear on the higher-energy side of the A band beyond 2.5, 4.5, and 5.25 GPa, respectively. Considering their relative energy positions and the sublinear pressure dependence, we attribute B , C , and D to the nitrogen-pair states NN_3 and NN_4 , and to the isolated nitrogen state N_x , respectively. NN_3 , NN_4 , and N_x have the similar energy-pressure dependence as in the dilute limit. NN_3 and NN_4 have redshifted from their dilute limits, while N_x remains stationary in energy. At 70 and 130 K, an additional feature A' emerges on the higher-energy side of A in the pressure range of 1~2 GPa. Based on recent experimental results, we attribute the high-energy portion of A and A' emerging above 1 GPa to resonant or nearly resonant X_1 (NN_1) and X_2 (NN_2) states that are severely perturbed and broadened by the impurity-host interaction. The discrete peaks A_i are tentatively attributed to N-cluster states involving more than two nitrogen atoms, such as the highly degenerate N triplets NN_1N_α . The main body of the background band A is related to the emissions from less degenerate triplet states and other nitrogen-cluster states formed by more nitrogen atoms as well as their phonon sidebands.

Based on these observations, the questions raised in Sec. I can be answered as follows. (1) The N-pair states, especially the resonant ones, can survive even when $x \geq 0.1\%$. (2) The resonant N-pair states, especially those near the band edge, have redshifted energetically from the dilute limit positions. (3) Most sharp emission peaks observed inside the band gap under low pressure are zero-phonon lines of N-cluster states (related to more than two nitrogen atoms) rather than phonon replicas. (4) When $x=0.1\%$, the isolated nitrogen state N_x remains practically at the same energy position as that in the dilute limit, which further confirms that E_+ is not derived from the N_x state, and thus the very basic assumption of the BAC model is invalid. Contrasting with the suggestion of “selective delocalization,”^{18,35} we have observed that the NN-pair states close to the host conduction band edge are more sensitive to the change of the host conduction band than the distant N-related states. These observations indicate the inadequacy of the existing theories for quantitative descriptions of the electronic structure of the GaAsN alloy in general, and the impurity-host and impurity-impurity interaction in particular.

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