Evidence for selective delocalization of N-pair states in dilute $GaAs_{1-x}N_x$

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We report high-pressure photoluminescence (PL) experiments (to $P=62$ kbar at 9 K) on $GaAs_{1-x}N_x$/GaAs quantum wells (QWs) having N compositions ($x=0.0025,0.004$) in the dilute regime where the $GaAs_{1-x}N_x$ alloy conduction band (CB) evolves rapidly via delocalization of N-pair (cluster) states. Under increasing applied pressure, we observe low-energy broadening of the emission spectra, an increase in the Stokes shift of PL peaks relative to the QW absorption edge, and several new N-pair PL features that derive from CB-resonant states at 1 atm. Two of the latter features (assigned to NN_3 replica) appear strongly in the $x=0.0025$ sample at energies below the QW absorption edge for $P\geqslant 29$ kbar, but are completely *absent* in the $x=0.004$ sample—an effect that has not been seen previously in $GaAs_{1-x}N_x$ alloys to our best knowledge. The trends for broadening and increase in Stokes shift under pressure are accounted for using a model of the recombination kinetics that considers competing fluctuation and N-pair states. The absence of the NN_3 features in the $x=0.004$ sample provides evidence that N-pair states incorporate into the CB continuum *via* an *energy*- and/or *state-selective* delocalization process. The observed selectivity in the narrow composition range $0.0025\leqslant x \leqslant 0.004$, while bound states and other resonant states closer to the CB edge remain unaffected, offers an important test for band-structure calculations in $GaAs_{1-x}N_x$ dilute alloys. Selective delocalization of *resonant* N-pair states is difficult to explain within an impurity-band model, but it is qualitatively consistent with recent theoretical studies of CB formation in $GaAs_{1-x}N_x$ dilute alloys that use a full-hybridization approach to treat the incorporation of N-pair (cluster) states.

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I. INTRODUCTION

The presence of relatively small amounts of nitrogen (as an isoelectronic anion substituent) in $GaAs_{1-x}N_x$ alloys strongly affects the formation of the alloy's conduction-band (CB) structure as the N composition exceeds $x\sim 0.001$. The most apparent of the changes—a decrease in the fundamental band gap E_g driven by excessive negative bowing,[1] an accompanying increase in the electron mass m_e^*,[2] and a decrease in dE_g/dP (the band-gap pressure shift[3])—are decidedly outside of the virtual crystal approximation, and contrary to other established trends in conventional direct band-gap III-V materials, where one usually finds $\Delta m_e^*/m_e^* \sim \Delta E_g/E_g$ and $dE_g/dP\sim$const. according to Paul's rule.[4] Other $III\text{-}V_{1-x}N_x$ dilute alloys exhibit similar nonstandard effects, and the detailed understanding of these phenomena is being actively pursued.[5]

The general origin of the unconventional behavior is understood to be the high mismatch, in electronegativity and in size, between N and the host anion, leading to a variety of N-related localized states at energies near (both below and above) the CB edge (CBE).[6] However, the detailed evolution of these states during formation of the alloy CB structure is not well established. In particular, the mechanism by which the N-related states delocalize with increasing x, and incorporate into the extended states of the alloy's CB continuum, remains quite controversial. The potential impact of dilute $III\text{-}V_xN_{1-x}$ ternary and quaternary alloys on near-infrared light-emitting devices,[7] multijunction solar cells,[8] and heterojunction bipolar transistors[9] provides additional impetus to resolve these issues.

It is well known that nitrogen, at impurity concentrations (e.g., $\leqslant 10^{18}$ cm^{-3}) in $GaAs_{1-x}N_x$ and other $III\text{-}V_{1-x}N_x$ systems, introduces localized states associated with N centers in isolation, N pairs, and more complex N clusters.[10,12,13] Depending on the alloy system, N composition, and external pressure, the energy spectrum of these states can span the CBE, so that different states may be either bound or resonant with (i.e., degenerate with) the CB continuum. In $GaAs_{1-x}N_x$ at 1 atm, the isolated N center generates a resonant level,[14] and considerable experimental and theoretical work has shown that this lowest unoccupied level of N_{As} (which has a_1 symmetry) is subject to strong coupling (increasing as $\sqrt{x}$) with the extended CB-states of the alloy.[3,15–21]

This coupling has been described theoretically based on the two-band anticrossing model[3,19–22] and on supercell calculations that consider multiband hybridization.[23–26] Both types of these band-mixing approaches are able to describe the main observations concerning the CBE in $GaAs_{1-x}N_x$ alloys up to several atomic percent N content—in particular, the composition and pressure dependencies of E_g and m_e^*. In the treatment of Ref. 25, the effects of N-pair and N-cluster states on the formation of the alloy CB structure in large relaxed supercells was calculated explicitly. It was predicted that the multiband mixing of the N-pair/-cluster states should become sufficient to cause transitions of their wave

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functions to a quasilocalized bandlike character as the states are overtaken by the descending CB continuum. Besides the preceding band-mixing approaches, it has been proposed that impurity-band formation, via overlap between N-pair/-cluster states, controls the evolution of the CBE properties in dilute $GaAs_{1-x}N_x$ and $GaP_{1-x}N_x$ alloys.[27,28] In particular, the observed scaling of the band-gap reduction as $\delta E_g \propto x^{\alpha}$, with exponents in the range $0.55 \leqslant \alpha \leqslant 0.65$, was attributed to this mechanism.[29] All of these interpretations allow for fluctuations in the CBE energy (as expected in highly mismatched alloys), either by including a lifetime for the resonant N state in the two-band anticrossing model,[22] by direct calculation of random geometries in supercells with multiple N atoms,[25] or by the disorder inherent in impurity-band states.[27]

The present photoluminescence (PL) experiments use applied hydrostatic pressure to explore changes in the spectrum of the localized N related states in $GaAs_{1-x}N_x$/GaAs multiple quantum wells (MQWs) within the range of N compositions where these states are expected to undergo transitions to a delocalized bandlike character. Prior work indicates that such transitions most likely occur in the range $0.001 \leqslant x \leqslant 0.006$.[25,27,30,31] Our measurements exploit the ability of pressure to "filter" the energy levels of localized and extended states by virtue of their different pressure behaviors. Localized electron states generally exhibit blueshifts with pressure that are 3–5 times slower than the blueshifts of extended CBE states in direct-gap III-V materials.[4] This filtering property is well known, and in fact was instrumental in first identifying the hierarchy of resonant N-pair states in N-doped GaAs and $GaP_{1-x}As_x$.[10,11,14] Here we investigate the effects of pressure on the PL spectra due to recombination of excitons bound to N-pair/-cluster states and/or to CB-tail states. We focus on the mechanisms for spectral broadening and increase in Stokes shift under pressure, and on the pressure-induced appearance (or not) of N-pair/-cluster features that are associated with CB-resonant states at 1 atm. As is seen below, our results provide experimental evidence that *selected* resonant N-pair states in $GaAs_{1-x}N_x$ are able to incorporate, *via band-mixing processes*, into the extended states of the CB continuum prior to impurity-band formation. This selective delocalization (in a narrow range of N compositions) has not been established in earlier measurements. It offers important criteria for testing theoretical predictions on the formation of the CB structure in dilute $GaAs_{1-x}N_x$ alloys.

II. EXPERIMENT

The $GaAs_{1-x}N_x$/GaAs MQW samples investigated in this work were grown by chemical beam epitaxy (ChBE) using, as sources, 1,1-dimethylhydrazine, triethylgallium, cracked arsine, and a growth temperature of 490 ± 5 °C. The growth procedures and ultrahigh vacuum ChBE reactor have been described elsewhere.[32,33] The samples were deposited on buffered (001) semi-insulating GaAs substrates with no postgrowth annealing, and were characterized by standard x-ray diffractometry, and secondary ion mass spectroscopy (SIMS) methods. The quantum walls (QWs) were fully strained. Their nitrogen compositions were deduced from the lattice constant of the $GaAs_{1-x}N_x$ layers observed in triple crystal rocking curves about the GaAs (004) Bragg peak. It was assumed that Vegard's law holds, and a linear interpolation of Poisson's ratio between GaAs and cubic GaN (Ref. 34) was used to correct for the biaxial strain in the $GaAs_{1-x}N_x$ layers. SIMS measurements were then performed to confirm the x-ray-determined compositions. Extensive earlier work has shown that $GaAs_{1-x}N_x$ material grown by ChBE under similar conditions yields high-quality epitaxial layers, with essentially full substitutional incorporation of nitrogen up to 7% N composition.[32]

The two MQW samples studied in the present work each have 86-Å-thick $GaAs_{1-x}N_x$ quantum wells and 230-Å-thick GaAs barriers; there are 15 well/barrier repetitions. The molar N fractions are measured to be $x=0.0025$ (sample number 615) and $x=0.004$ (sample number 616), with an estimated uncertainty in x of $\pm 10\%$. Specimens are prepared for measurement by carefully thinning the substrates and cleaving into $\sim 80 \times 80 \times 10$-$\mu m^3$chips.

PL experiments are performed under applied pressures (to $P=62$ kbar) and at low temperatures ($T=9$ K) using a ruby calibrated diamond-anvil cell (DAC) and a He cryostat with a bottom optical window.[35] Concurrent tuning of the pressure ($\sim$0.5-kbar minimum step size) and temperature is possible by means of a hydraulic press and resistive heating of the He-exchange gas surrounding the DAC. The accuracy of the ruby barometer is $\pm 3\%$,[36] and the temperature is controlled to ± 1 K by Si-diode thermometers contacting the DAC. We load superfluid He into the DAC sample chamber (a hole initially 450 $\mu m \phi \times 90$ μm deep in an Inconnel gasket) to maximize the isotropy of the pressure environment. Even so, on changing the pressure (up or down for $T \leqslant 40$ K), the ruby R lines broaden sufficiently to justify annealing the He medium (150 K is adequate below 100 kbar) after *changes* of $\sim$20 kbar. Frequent and thorough annealing of the pressure medium is carried out to ensure that none of the observed PL features derive from spurious strain gradients.

The PL spectra are measured in the reflection geometry using a 1-m double monochromator and photon counting detection. PL excitation is provided by $\sim$5-mW 5145-A radiation from a continuous wave Ar^+ laser, focused into a 25-μm spot at the sample. The same system is used to measure the ruby R lines, except that the signal is recorded with an alternative multichannel detector. This permits real-time monitoring while changing the pressure or annealing the medium. The quoted pressure for each sample spectrum is the average of two ruby runs recorded just before and just after taking that spectrum. Besides the PL studies, we also carried out transmission measurements on the $x=0.0025$ MQW sample by imaging DAC-loaded specimens (back lit by a tungsten source) onto the monochromator slits. Above ambient pressure, the transmission tends to be partially attenuated by debris that gathers on the upper diamond anvil during the process of capturing He in the gasket hole.

III. RESULTS

Figures 1 and 2 show the effects of applied pressure on the PL spectra of the MQW samples with $x=0.0025$ and x

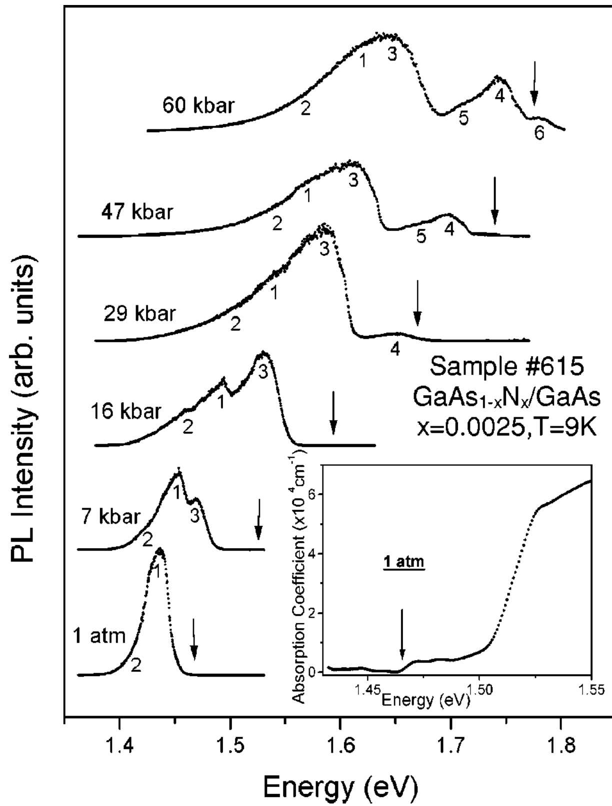

FIG. 1. PL spectra at several pressures for the MQW sample with N-composition $x = 0.0025$ in the QWs. Numbers 1–6 label distinct PL features, as assigned in the text. The inset shows the measured absorption spectrum of the QW and substrate in this sample at 1 atm. Vertical solid arrows mark the calculated energy of the sample's QW band gap at each pressure. Note that the E_o gap in bulk GaAs is at 1.52 eV.

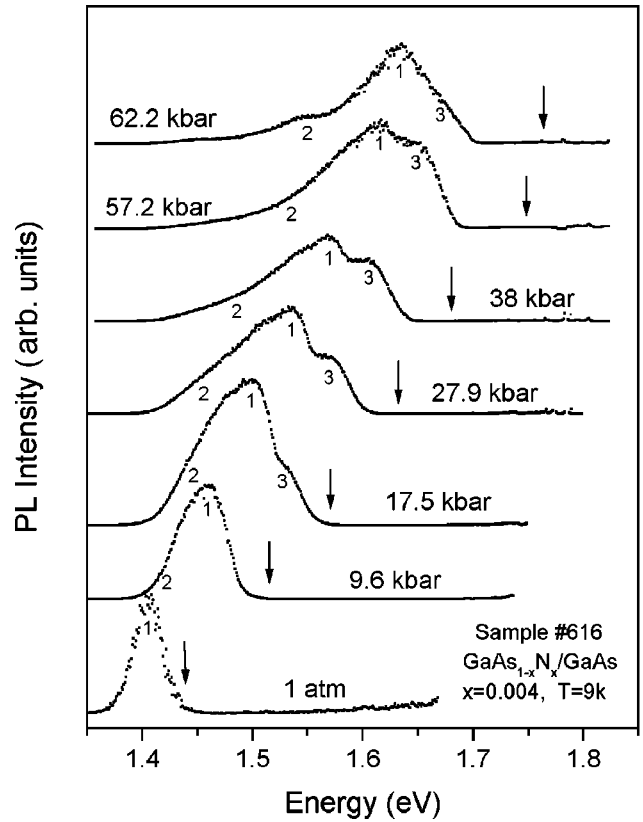

FIG. 2. PL spectra at several pressures for the MQW sample with N-composition $x = 0.004$ in the QWs. Numbers 1–3 designate the same PL features as in Fig. 1; note that features 4–6 are missing in this sample. Vertical arrows mark the calculated energy of the QW band gap in this sample at each pressure.

$= 0.004$, respectively; the Fig. 1 inset displays the measured absorption spectrum for the $x = 0.0025$ sample at 1 atm. In all cases, the solid arrows mark the calculated position of the effective band gap in the $GaAs_{1-x}N_x$ QWs, as obtained (see discussion below) using the band anticrossing model.[22,37] The PL spectra in Figs. 1 and 2 are quite consistent with a number of previous results obtained at 1 atm,[13,38–40] or at pressures significantly lower than reported here,[10,30] in measurements on $GaAs_{1-x}N_x$ epilayers and QWs having similar dilute N compositions.

The observed PL spectra are a mixture of two types of components—emission by localized excitons trapped at different energies in a quasicontinuum of *fluctuation* states, and emission by excitons bound to *specific N-related centers* derived from N pairs and N clusters.

The fluctuation states result from random spatial variations in the average N composition $\sim \sqrt{x(1-x)}$, and/or in the internal strain environment.[41,42] This gives rise to broad structureless low-energy wings associated with the CBE's band-tail emission *and* with each of the PL features due to specific N-related centers. The fluctuation states also contribute to the Stokes shift of the PL via the approximate correlation between energy and lifetime among these states, as discussed in Sec. IV. In Figs. 1 and 2, the low-energy wings and the Stokes shift of the different PL features relative to the absorption edge (indicated by the solid arrows) are clearly visible for both samples. We find that both the low-energy broadening and the Stokes shift increase under applied pressure, in accord with prior results.[30,43]

Recombination of excitons bound to specific types of N-related centers, especially N pairs, leads to a number of distinct features in the PL spectra at 1 atm and higher pressures in Figs. 1 and 2. For the N compositions investigated here, a hierarchy of N-pair (and N-cluster) centers gives rise to different spatially localized states (see, e.g., Ref. 25). Some of these states are bound below the CB edge at all pressures, while others are resonant with the CB continuum at 1 atm but are expected to become (energetically) deep states, able to bind excitons, as pressure shifts the CBE successively above the levels of particular centers.[10,14,30] The PL transitions associated with N-pair (-cluster) states are a complicated mixture of zero-phonon and phonon-replica lines. However, the energies of these transitions are known to be relatively insensitive to the N composition,[30,38] and, in fact, for any given pressure at which like-numbered PL features (refer to Figs. 1 and 2) are present in both samples, we find that these features are coenergetic. Hence, based on a comparison to prior results for N-doped GaAs containing two orders-of-magnitude less nitrogen $(x \approx 2.5 \times 10^{-5})$,[10] we conclude that the N centers that are most likely to make

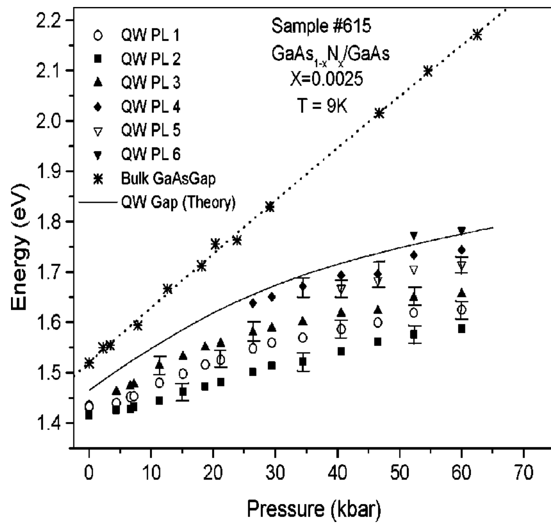

FIG. 3. Measured effects of pressure on the energies of the PL features in the $x=0.0025$ sample. The data symbols in the key are labeled using the same numbering as in Fig. 1. Also shown is the calculated pressure dependence of the sample's lowest-energy QW transition (solid curve), and the observed shift of the bulk-GaAs absorption edge (stars and dotted fit) in the substrate.

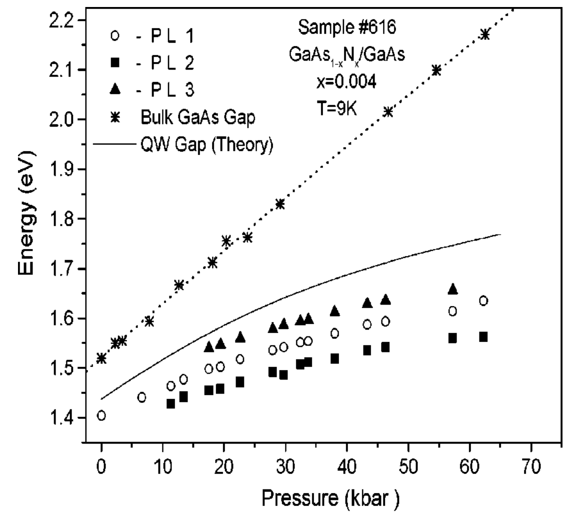

FIG. 4. Measured effects of pressure on the energies of the PL features in the $x=0.004$ sample. The data symbols in the key use the same numbering as in Fig. 2. Also shown is the calculated pressure dependence of the lowest-energy QW transition in this sample (solid curve), and the observed shift of the absorption edge in bulk GaAs (substrate of $x=0.0025$ sample; stars and dotted fit).

strong contributions to peaks 1, 2, and 3, *in both samples*, arise from N pairs at nearest-neighbor anion sites (denoted NN_1). The one phonon replica NN_1-LO is the best choice for peak 3, whereas the energies of the higher-order phonon replicas NN_1-2LO and NN_1-3LO are appropriate for assignment to peak 1 and feature 2, respectively. However, as remarked, it is likely that the observed spectra are a mixture of emission both from N-related centers *and* from CB fluctuation states. The relative strength of these components is difficult to assess, but both can be substantial. The competing recombination paths that contribute to the PL spectra are considered further (see Fig. 6) below.

The assignment of peaks 4–6 to specific N-pair (-cluster) centers is more problematic. First of all, we note that these features are present *only for the lower N-composition sample* ($x=0.0025$, Fig. 1), an important observation that is discussed at length in the next section. In the case of the $x=0.0025$ sample, the best choices for peaks 4 and 5, based on the results in Ref. 10 for N-doped GaAs, are low-order phonon replicas of NN_3 pairs. Alternatively, recent theoretical results, which take account of the orientation of N pairs, suggest that NN_2 oriented along the [2,0,0] axis, or perhaps NN_3 oriented along [2,1,1], figure importantly in peaks 4 and 5.[24,25,44] Both experiment and theory allow other assignments, but these seem less likely to us. We make no attempt to assign peak 6 in Fig. 1, for which there are just two data points.

The energies of the numbered features in the PL spectra of the $x=0.0025$ and $x=0.004$ samples depend on pressure as plotted in Figures 3 and 4, respectively. The data points give the positions of the component peaks obtained in optimized multioscillator fits to the observed PL spectra. The error bars represent the typical variations among several fits to the same spectra using slightly different starting parameters. The stars (and least-squares dotted line) show the effect of pressure on the absorption edge of the GaAs substrate in the $x=0.0025$ sample, as found in our DAC transmission studies. It was possible to observe the substrate edge at all pressures, but the much weaker QW absorption edge could be measured only at 1 atm (inset to Fig. 1) because of the debris that obscured the upper diamond anvil, as mentioned in Sec. II.

The solid curves in Figs. 3 and 4 are calculated results for the pressure dependence of the effective band-gap energy in the $GaAs_{1-x}N_x$ QWs of each sample. This calculation is carried out using the band-anticrossing model of Walukiewicz and co-workers,[19,22,37,45] with the QW confinement energy of the lowest electron level found from a finite square-well treatment. Based on the results of previous experiments and calculations, the pressure coefficients (relative to the valence band) of the GaAs CBE and the isolated N level are taken to be $dE_M/dP=10.8\times10^{-3}$ eV/kbar (Ref. 46) and $dE_N/dP=1.9\times10^{-3}$ eV/kbar,[14] respectively, and for the coupling coefficient between E_N and E_M at low temperature, we use $C_{NM}=2.5$ eV.[37] The best agreement with our 1-atm absorption edge data is obtained for $E_N(P=0)=1.7$ eV, also in reasonable accord with the value 1.65 eV employed in Ref. 37. The hole confinement energy, and the splitting of the heavy- and light-hole valence bands due to mismatch strain, have been neglected, omissions that introduce less than 5-meV error for the N compositions of interest here.[47] The solid arrows in Figs. 1 and 2 also are obtained using this calculation. The band-anticrossing model is employed here chiefly to assess the magnitude of the Stokes shift in our samples as a function of pressure. Although still controversial, this model is known to replicate rather well the pressure and composition dependencies of the CBE in dilute $GaAs_{1-x}N_x$ alloys.

IV. DISCUSSION

We focus on three important aspects of the preceding pressure-PL results: (i) The PL spectra are a combination of

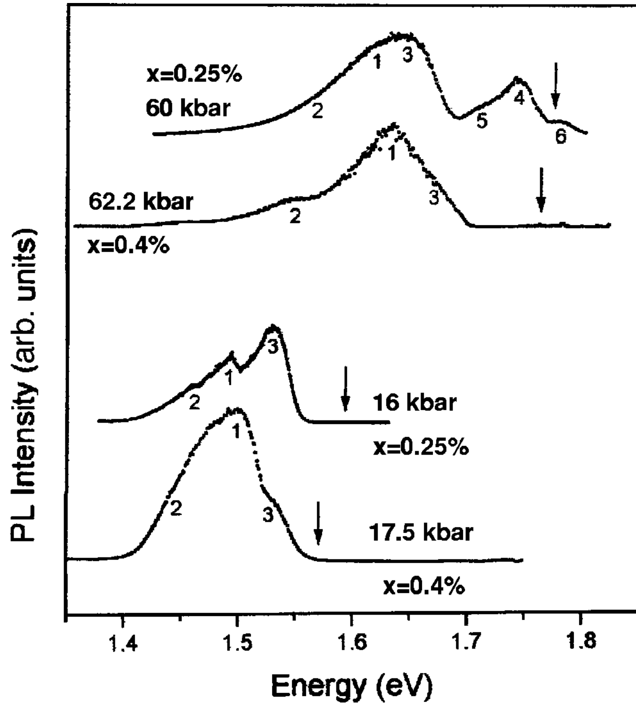

FIG. 5. PL spectra of the $x=0.0025$ and $x=0.004$ samples compared at similar pressures. Vertical arrows mark the calculated energies of the effective QW band gaps in each sample.

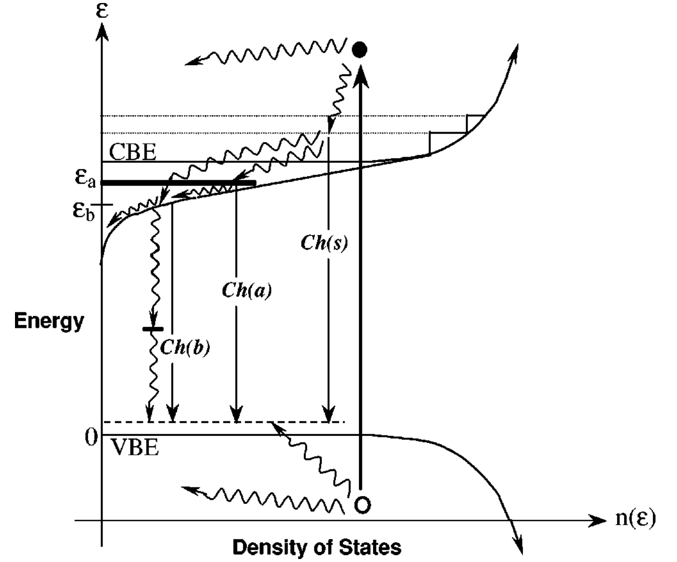

FIG. 6. Density-of-states model of competing recombination processes which contribute to the observed PL spectra. Absorption and PL emission are shown by up and down solid arrows; wavy arrows indicate nonradiative processes. CBE and VBE label the edges of the conduction and valence bands in bulk GaAs (dashed line accounts for exciton Coulomb energy). Dotted lines represent electron quantum levels. ε_a and ε_b designate the energies of a deep N-pair/-cluster state (bold line) and a band-tail fluctuation state (short tick mark), respectively.

emission from a quasicontinuous density of fluctuation states and from sharper features related to specific N-pair/-cluster centers (principally pairs). Under applied pressure, the fluctuation component broadens toward lower energy, and the number of N-pair features increases. (ii) The Stokes shift between the observed PL peaks and the absorption edge of the $GaAs_{1-x}N_x$ QWs tends to increase with pressure. (iii) Several of the N-related features that appear below the absorption edge for pressures greater than 29 kbar in the $x=0.0025$ sample are absent under similar circumstances in the $x=0.004$ sample. Points (i)–(iii) are clearly illustrated in Fig. 5, where we compare spectra for the two samples at similar intermediate pressures and similar high pressures.

It is useful to discuss the interpretation of these findings by way of the generic model depicted in Fig. 6. We consider three radiative recombination channels: The PL of confined excitons associated with the lowest electron quantum level, the PL of excitons bound by a deep N-pair (-cluster) center at energy ε_a, and the PL of excitons bound within band-tail states at energy ε_b. After photoexcitation, electrons and holes in the QWs rapidly thermalize to the lowest confined levels and easily form excitons (especially at low temperature). These shallow excitons can emit PL (channel s), or become trapped in the states associated with the N complex (ε_a) or the band tail (ε_b). A N-complex-bound exciton at ε_a can emit PL (channel a), or decay directly into a band-tail exciton at ε_b. In turn, the ε_b exciton may either emit PL (channel b), decay nonradiatively, or relax to lower band-tail states. Due to the low temperature of our experiments, this model treats only energy relaxation processes. In principle, one should include the PL from band-tail excitons at energies above ε_a, but this is neglected because the observed PL spectra fall off more sharply at high energy than at low energy. Although the model in Fig. 6 is clearly oversimplified, it has sufficient content to account for our main findings.

Within this model, the relative strengths of the PL emitted via the different channels under steady-state and low-level excitation conditions are given by the intensity ratios

$$\frac{I_a}{I_s}=(QE)_a^r n_a \beta_{as} \tau_s^r,$$

$$\frac{I_b}{I_a}=\frac{(QE)_b^r n_b \beta_{bs} \tau_s^r}{I_a/I_s}+(QE)_b^r n_b \beta_{ba} \tau_a^r, \qquad (1)$$

where $(QE)^{\mathrm{r}}_{a(b)}$ is the radiative quantum efficiency of channel-a (or b), $n_{a(b)}$ is the density of deep nitrogen-complex states at ε_a (or band-tail states at ε_b), $\beta_{as(bs)(ba)}$ is the capture coefficient for trapping a shallow exciton into state a (or into state b, or for exciton capture directly from state a to state b), and $\tau^r_{a(s)}$ is the radiative lifetime of an exciton in state a (or a shallow exciton).

A. PL line-shape changes under pressure

Based on these expressions, the mixture of band-tail and N-pair (-cluster) emission observed in the sub-band-gap PL spectrum at a given pressure can depend on several factors. The most important of these factors is the state densities n_a and n_b. Clearly, in the limit in which n_a goes to zero, I_a also will vanish, and [multiplying together the two expressions in Eq. (1)] we see that I_b will then arise only from the capture

of shallow excitons. For the N compositions in our samples and 1-atm pressure, all of the N-pair levels at energies above NN_1-2LO are expected to be CB resonant,[10,25] and the density n_a of sub-band-gap pair levels is relatively low. It increases, however, under applied pressure, as N-pair states enter the band gap. This provides a simple explanation for the smooth PL line shape dominated by a single peak at low pressure, and the increasing number of sharper N-pair features appearing at elevated pressures.

Density-of-states arguments can also account for the low-energy broadening of the band-tail PL under pressure. As mentioned, the band-tail emission arises from excitons localized in potential wells due to composition and/or strain fluctuations in the CBE. The deepest fluctuations bind the most localized excitons, and their energy levels are expected to be the least sensitive to pressure—with pressure coefficients similar in magnitude to that of excitons localized at N-related centers.[4,10,14] It follows that the rate of pressure shift (to higher energy) should be slower for the deeper band-tail states, resulting in low-energy broadening of the corresponding PL line shape with increasing pressure, as observed. Hence, these changes are driven by the ability of applied pressure to *filter localized and extended states that overlap in energy* by virtue of their different pressure shifts.

B. Increase in the Stokes shift

The Stokes shift of the observed PL features relative to the QW absorption edge is due to the relaxation of excitons by successive capture into lower-energy states.[49] For the PL structure associated with specific N-pair centers, the pressure-induced increase in the Stokes shift can be explained in a straightforward manner by the filtering effect of pressure, which tends to move the localized N-pair states to deeper energies below the extended states at the CBE. In this case the increase in Stokes shift directly reflects the difference in pressure coefficients between N-pair states and the CBE.

For the PL component arising from fluctuation states, there is an added contribution to the Stokes shift that also can depend on pressure. The filtering effect is again the mechanism, but here it operates through the influence of lifetime *and* density-of-states changes on the PL intensity. This can be understood qualitatively using the model in Fig. 6. Band-tail states that are deeply bound and localized, such as state b in Fig. 6, tend to retain excitons longer than tail states near the CBE that are more extended. According to Eq. (1), this favors [via the efficiency $(QE)_b^r$] PL emission at lower energy; on the other hand, the density of band-tail states n_b falls off sharply with decreasing energy, favoring PL at higher energy. The resulting Stokes shift depends on the balance between these factors, and applied pressure, by broadening the band tails, modifies this balance to enhance the PL strength at deeper energies below the CBE. Again one expects an increase in the Stokes shift.

The physics of this mechanism has been discussed at length by Mott and others in relation to the PL of band-tail states in amorphous semiconductors.[48] We point out that the Stokes shifts of the PL bands in amorphous Si:H and in As-chalcognide glasses are also observed to increase under applied pressure.[35,50]

C. Missing PL peaks

The N compositions in the two $GaAs_{1-x}N_x/GaAs$ samples studied here, $x=0.0025$ and $x=0.004$, are not very different, and the geometry and growth of each sample is otherwise the same. Yet, for pressures above 29 kbar, the PL spectra of the samples exhibit a striking qualitative difference that has not been reported prior to the present work to our best knowledge. (See Figs. 1, 2, and 5.) The two prominent PL features that appear below the QW band edge in the $x=0.0025$ sample (numbers 4 and 5 in Fig. 1; probably NN_3 replica) do not appear in the $x=0.004$ sample, even though their energies are expected to fall below the QW band edge at high pressures in both samples. There could be two probable explanations for this behavior: First, the N-pair (or N-cluster) states that give rise to features 4 and 5 still cross below the QW band edge in the $x=0.004$ sample, but the corresponding PL transitions are forbidden or much weaker than in the $x=0.0025$ sample. Second, the N-related states associated with features 4 and 5 no longer cross below the QW band edge in the $x=0.004$ sample, but remain CB resonant because their pressure behaviors are strongly modified compared to the lower N-composition case. Let us examine these alternatives in greater detail.

In GaAs-based systems, the Γ-X crossover provides a natural mechanism by which forbidden (or weak) transitions can be driven into the band gap. (In pure GaAs this crossing occurs at 39 kbar.[14]) If the N-pair states responsible for features 4 and 5 are able to hybridize with the host band structure such that they acquire appreciable X-like character, this wave-function character would control both their oscillator strength and their pressure dependence. The states would then enter the gap at a pressure near the Γ-X crossover, but their transition probabilities [which underlie the quantum efficiencies in Eq. (1)] would be much reduced. For this to explain the behavior of features 4 and 5, the coupling with the X minimum in the Γ-X crossover regime must be such that the small change in N composition, from $x=0.0025$ to $x=0.004$ causes a large increase in the X-like character. Recent ambient pressure calculations for N pairs with various orientations in large GaAs and GaP supercells find that the X-like character of pair states is small in the GaAs case, but can be large for GaP (e.g., $\sim 50\%$ X character for NN_2 along [200], or for NN_3 along [211]).[25] Hence, one may also expect the X character of pair states in $GaAs_{1-x}N_x$ to become significant *for pressures near the* Γ-X *crossover*, where the band structure becomes indirect, and thus more like $GaP_{1-x}N_x$ at 1 atm. However, in $GaAs_{1-x}N_x$ with $x=0.004$, the Γ-X crossover is unlikely to take place within the pressure range studied here, due to the effects of N in reducing both the band gap and its pressure shift. The supercell calculations, in fact, indicate that this crossing should occur in our samples at ~ 80 kbar.[17,25,26] Thus, we discount an explanation along these lines for the observed high-pressure behavior of features 4 and 5 in the PL spectra.

The second explanation is more promising. Clearly, the effect of applied pressure on a localized resonant state is subject to strong modification via mixing with nearby (in energy) extended states of the host band structure. It is known that the resonant state of the isolated N_{As} center in $GaAs_{1-x}N_x$ becomes sufficiently mixed with the conduction band for increasing x ($\geqslant 0.001$) that applied pressure no longer can drive this state, as a distinct level, below the absorption edge. This finding is supported both by experiment and theory. It accounts very well for the weak sublinear pressure shift and the reduced oscillator strength at high pressure of the observed E_- absorption edge,[3,23,30,51,52] and it is obtained in both the band-anticrossing[16,22,45] and the full-hybridization treatments.[17,23–26] The inability of pressure to filter the N_{As} state from the CB continuum strongly indicates that band mixing has progressed to the point where the N_{As} state is substantially delocalized.

In view of the findings for the isolated N_{As} center, it is reasonable to expect that the pressure behavior of resonant N-pair/-cluster states should be similarly affected by enhanced band mixing and delocalization with increasing N composition. The pressure response of these states also should become more bandlike until, eventually, it would not be possible to drive their levels below the CBE at elevated pressure. This provides a straightforward explanation for the missing PL peaks in the $x=0.004$ sample. Essentially, the absence of features 4 and 5 is understood as evidence that the corresponding states (probably related to NN_3 or NN_2 pairs) have mixed into the CB continuum, and, attendant to this incorporation, have become substantially delocalized. If so, the present experimental results require (i) that the localized to delocalized transition for the states contributing to features 4 and 5 must onset quickly in the range $x=0.0025$–0.004, and (ii) that this process is energy selective and/or state selective. The basis for the latter statement is clear, since, in the same N-composition range, we observe little effect on deeper bound or resonant states, e.g., the state associated with feature 3 (assigned to NN_1-LO), which still enters the band gap at ~ 15 kbar in the $x=0.004$ sample. See Figs. 1 and 2.

To examine this band-mixing explanation further, it is clear that realistic calculations of the effects of applied pressure on explicit N-pair (or N-cluster) states in $GaAs_{1-x}N_x$, similar to the treatment of these states at 1 atm,[24,25] would be highly desirable. Given the wide variety of the resonant N-pair/-cluster states in $GaAs_{1-x}N_x$, and their complicated pressure dependencies, it seems to us that models in which hybridization with the full band structure is considered will be needed to understand the pressure-PL results. We note that the supercell calculations of Refs. 24 and 25 predict (at least at 1 atm) that all the N-pair/-cluster states should have become substantially delocalized, and incorporated into the CB, once the N composition attains the critical value $x_c \approx 0.006$. This prediction is, in fact, consistent with the observed absence of features 4 and 5 in the $x=0.004$ sample (Figs. 2 and 5). However, since the calculations pertain to ambient pressure, their validity cannot be judged directly in comparison with the present results. In particular, subsequent calculations on band mixing and delocalization in $GaAs_{1-x}N_x$ should be able to explain the key observations which underpin statements (i) and (ii) above,[53] namely, the rapid onset (in composition) and selectivity of the changes in pressure-PL behavior for the specific N-pair states associated with features 4 and 5.

Impurity-band formation also has been proposed as a means by which N-pair and N-cluster states may be incorporated into the conduction-band continuum of $GaAs_{1-x}N_x$ alloys[29,38] and $GaP_{1-x}N_x$ alloys.[28] In fact, for $GaP_{1-x}N_x$, PL experiments at 1 atm reveal that the N-pair lines observed on the low-energy side of the absorption edge undergo strong quenching for N compositions increasing through the range $x=0.0024$–0.007. Although this behavior is similar to the present PL results for features 4 and 5 at high pressure, it differs in an important respect. For the $GaP_{1-x}N_x$ system, the N-pair features that decrease in intensity lie just below the absorption edge, and these PL features are quenched on being overtaken by the absorption edge as it shifts to lower energy with increasing x. Such behavior is consistent with the formation of an impurity band at energies adjoining the lower edge of the CB continuum. In contrast, for the $GaAs_{1-x}N_x$ system, no significant intensity change in the PL features below the absorption edge is observed (Figs. 1 and 2.) Rather, we find that features associated with *resonant* N-pair states situated far above the edge at 1 atm, are quenched in the PL spectra. Hence, the pressure-PL results indicate that these N-pair states are incorporated into the CB continuum prior to the onset of impurity-band formation.

It is conceivable that impurity-band formation could begin for smaller x values among N-pair states at higher energies. The distance between N atoms in such pairs tends to be larger, thereby enhancing the overlap of pair-state wave functions at more dilute N compositions. In this way, a modified impurity-band picture might account for the selectivity in energy, and/or state, that we observe. However, for the $GaAs_{1-x}N_x$ system, we find it difficult to understand how such a mechanism could proceed for the CB-resonant N-pair states without very strong band-structure mixing effects. Therefore, it seems to us that the hybridization viewpoint[25] can provide a more reasonable explanation for the behavior of resonant N-pair/-cluster states observed under applied pressure in this study.

V. SUMMARY

High-pressure PL experiments are carried out on $GaAs_{1-x}N_x$/GaAs MQWs having dilute N compositions ($x=0.0025$, 0.004) in the range in which the electronic properties of $GaAs_{1-x}N_x$ alloys change rapidly via a process in which N-pair (-cluster) states delocalize and incorporate into the CB continuum. The PL spectra are found to consist of emission from excitons localized within a pressure-dependent mixture of fluctuation states and N-pair (-cluster) states, in accord with earlier work. With increasing pressure, the fluctuation component of the PL spectra broadens toward lower energy, the Stokes shift below the QW absorption edge increases, and several distinct N-pair features appear. The latter features most likely derive from low-phonon replica of NN_i ($i=1$–3) anion-site neighbors, whose states are CB resonant at 1 atm but become bound below the CBE at high

pressures. Two prominent features, which can be assigned to NN_3 replica, appear in the $x=0.0025$ sample but are absent in the $x=0.004$ sample, even though their transition energies should fall well below the QW absorption edge at high pressure in both samples.

A generic model of the PL recombination kinetics is used to assess the competition of shallow excitons, N-pair/-cluster bound excitons, and CB-tail excitons. The low-energy broadening and increase in Stokes shift follow from the ability of applied pressure to filter a mixed density of localized and extended states.

Three mechanisms are considered for the absence of features associated with particular CB-resonant (at 1 atm) N-pair states in the high-pressure spectra of the $x=0.004$ sample: The Γ-X crossover, delocalization of specific resonant N-pair states due to mixing with extended CB states, and impurity-band formation. The Γ-X crossover can be ruled out, since the crossing pressure in this sample is too high. Simple impurity-band formation is also unlikely, because the absent N-pair features derive from resonant states, not from states at or just below the CBE, as observed in $GaP_{1-x}N_x$ alloys. Hence, we find that the second mechanism is the most appropriate. Given the many types of N complexes, it seems to us that theories such as those proposed in Refs. 24 and 25, in which the mixing proceeds via hybridization of N-pair states with the full CB structure, have the best chance to explain the pressure results. In this regard, the selectivity and narrow onset range ($0.0025 \leqslant x \leqslant 0.004$) of the observed changes—occurring for specific resonant N-pair states and not for others—offer useful test criteria.

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