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Optical density of states in ultradilute GaAsN alloy: Coexistence of free excitons and impurity band of localized and delocalized states

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Optically active states in liquid phase epitaxy-grown ultra-dilute GaAsN are studied. The feature-rich low temperature photoluminescence spectrum has contributions from excitonic band states of the GaAsN alloy, and two types of defect states—localized and extended. The degree of delocalization for extended states both within the conduction and defect bands, characterized by the electron temperature, is found to be similar. The degree of localization in the defect band is analyzed by the strength of the phonon replicas. Stronger emission from these localized states is attributed to their giant oscillator strength.

Since the discovery of giant bandgap bowing in GaAs$_{1-x}$N$_x$ ($x \leq 5\%$), these pseudo-binary alloys have been actively studied.1–5 GaAs$_{1-x}$N$_x$ belongs to a class of mismatched semiconductor alloys (other examples include InSb$_{1-x}$As$_x$, ZnTe$_{1-x}$Se$_x$), where the virtual crystal approximation, so successful in modeling the alloys like Ga$_{1-x}$Al$_x$As or Ga$_{1-x}$In$_x$P, breaks down. A number of unusual properties are observed in GaAs$_{1-x}$N$_x$ alloys. For example, contrary to the prediction of $k \cdot p$ theory, the electron effective mass increases even as the energy gap is reduced on alloying.7 Furthermore, due to the relatively large difference in size and electronegativity between the anion elements, GaAs$_{1-x}$N$_x$ is thought to have a miscibility gap in the growth phase diagram.8 This leads to its tendency to phase-separate and form clusters. The optical and electronic properties are often dominated by the electronic states associated with these localized cluster states.9,10 The localized states manifest in an order of magnitude larger alloy disorder than in the continuum of states forming the defect band,18–20 address the controversy whether the low energy peaks in the emission spectra are phonon-assisted transitions or from a separate set of cluster states,21–23 and finally discuss the quantum mechanical enhancement of the excitonic oscillator strength on account of the localization of its center of mass.24

GaAs-GaN alloys can normally only be grown under highly non-equilibrium conditions using molecular beam epitaxy, metal-organic vapor phase epitaxy, or forced incorporation of nitrogen into GaAs by ion bombardment, followed by annealing and possibly hydrogenation steps.2–4 In each case, the nitrogen atoms may be located at metastable positions and the electronic and optical properties may differ between samples and between different growth techniques.

We, on the other hand, have previously demonstrated that epitaxial GaAs$_{1-x}$N$_x$/GaAs can be grown by the liquid phase epitaxy (using GaAs + Ga + GaN melt with 2% molar Li$_3$N as a flux for nitrogen dissolution in GaAs) under close to equilibrium conditions.25 The advantage of studying such melt-grown samples is that GaAs$_{1-x}$N$_x$ is more likely to be in an equilibrium phase and the conclusions of the studies based on such samples may have more generic (sample-independent) validity. With such samples, one is of course limited to the ultra-dilute alloy limit. Photoluminescence (PL) measurements were conducted in a helium closed-cycle optical cryostat in the temperature range of 4–80 K. The sample was excited with a 643 nm diode laser and the spectra were dispersed with 500 mm spectrograph equipped with a charge-coupled device. The incident excitation power was varied between samples and between different growth techniques.

PL at 4 K at a low excitation power of 16 $\mu$W is shown in Fig. 1. The peaks above 1.46 eV are attributed to usual free and bound exciton states from the GaAs substrate. In addition to these, we observe a distinct peak at 1.450 eV and a set of peaks below 1.408 eV. If the free-exciton transition arising from the hybridized conduction band due to alloying in GaAs$_{1-x}$N$_x$ identified with the 1.450 eV peak, one infers $x \approx 0.25\%$.16,23 The structure in the transitions below 1.408 eV is attributed to phonon replicas. This is discussed in detail later.
In Figs. 2 and 3, we have plotted the excitation power and temperature dependence of PL, respectively. To facilitate a direct comparison between the emission channels associated with various transitions, spectra are arbitrarily scaled so that the peak around 1.408 eV has nearly the same intensity in the particular figure. Consider the excitation power-dependent spectra (Fig. 2) first. Especially at the highest excitation power, the spectrum consists of broad continuous emission between 1.30 and 1.45 eV with a busy structure indicating the presence of many different types of excitonic states. The peak at 1.450 eV, which is about a factor of 5 weaker than 1.408 eV peak at the lowest power, progressively gains strength, and, at the highest excitation power, exceeds the 1.408 eV peak by about a factor of 2. This implies that the density of states responsible for the emission from the peaks marked as NP_A and NP_B and its various satellites is much smaller than those responsible for the free exciton peak at 1.450 eV. This fact is also borne out in the temperature-dependent spectra (Fig. 3). The bound state emission in comparison with the band states is clearly more robust against the increase in temperature, as it is for defect states in In_xGa_{1-x}N alloys and quantum dots. Second, continuum emission between 1.41 and 1.45 eV, which was missing in Fig. 1, becomes progressively prominent at high excitation powers (Fig. 2). For spectra measured at lower excitation powers (Fig. 3), these states are visible in the high energy tail at elevated temperatures. The exponential form of the tail implies that the carriers have a Maxwell-Boltzmann distribution with an effective “carrier temperature” \( T_e \), inferred by fitting \( PL \sim \exp[-(E - E_0)/k_B T_e] \) in this energy window (Fig. 4). Here, \( E_0 \) represents the relevant energy gap. The rationale behind this fit is that...
while the lower energy cut-off of the PL emission spectrum arises from the density of states, the high energy region (assuming that the band width is very large compared to $k_B T_e$) tail represents the carrier distribution function. The occupation probability can thus be characterized by a single parameter, $T_e$. Fits for spectra measured at two representative temperatures (15 K and 50 K) are shown in Fig. 4 (inset).

It has been previously shown that not just the kinetic energy but also the extent of carrier localization can be characterized by $T_e$. If photoexcited carriers are created with equal probability anywhere within a band, once trapped they will end up recombining from higher energy states. From the above expression for PL, complete trapping would imply a uniform occupation probability within a band and thus an infinite carrier temperature. In Fig. 4, carriers from both the free excitonic states ($\sim$1.45–1.47 eV) and states between $\sim$1.41 and 1.45 eV have nearly the same $T_e$. That $T_e$ for both bands closely follows each other for a large range of lattice temperatures indicates that carriers in both these states are equally delocalized and experience similar disorder. Fig. 4 thus independently establishes the existence of two separate sets of extended states within two distinct bands.

The second band of extended states between $\sim$1.41 and 1.45 eV are identified with states where the excitons percolate through the crystal by overlaps with their neighbors. It is also evident from Figs. 2 and 3 that the localized states within the defect band continuously (in energy) merge with the delocalized (supercluster) states. The value of energy where this transition occurs is marked with an arrow in Figs. 2 and 3. While this has previously been called the “mobility edge,” it is emphasized that this designation is not quite conventional. Historically, the “mobility edge” had been predicted to appear within a band as the result of a subtle wave interference phenomenon resulting solely on account of disorder (Anderson transition). In principle, there should be two such mobility edges, appearing on both the high and the low energy band edges where the density of states is small. In the present case, however, the sharp boundary between the localized and the extended states within the defect band is more perhaps a percolation phenomenon. The classification of various states inferred from the above analysis is schematically depicted in Fig. 5.

**Phonon replicas.** Most of the low energy peaks below 1.41 eV can be identified with one of the two prominent transitions, labeled “NP$_A$,” and “NP$_B$,” as they occur at a separation of the longitudinal-optical (LO) (36 meV) and/or the transverse-acoustic (TA) (9 meV) phonon modes from these two no-phonon lines (Fig. 1). While the correct energy separation alone is not sufficient to mark these transitions as phonon replicas, the combination of the observations in Figs. 2 and 3 give additional support to this assertion. In Fig. 2, intensity of the phonon replicas scales linearly with the strength of the no-phonon transitions, even though the excitation power is varied by almost three orders of magnitude. The relative intensities of the replicas between themselves and with respect to the no-phonon peaks are (almost) preserved. This is only likely to happen if it is the same set of states that are involved for emission at various energies. The relative intensities of other transitions in the broad continuum below $\sim$1.35 eV, on the other hand, are found to be strongly power-dependent and non-monotonic. In Fig. 3, the phonon-assisted transitions broaden and gain in strength due to larger occupation probability of phonons at higher temperature.

The electron-phonon coupling is expected to enhance on account of localization in the cluster states. No replicas are observed for the extended excitonic states and above the mobility edge in the impurity band (Energy $\gtrsim$1.408 eV). The Huang-Rhys’ single frequency configuration coordinate model provides a standard method to analyze these phonon-assisted transitions within bound states. The strength of vibronic coupling resulting in $n^{th}$ phonon-replica is parameterized by a temperature-dependent dimensionless number $S_n = n I_n / I_0$, where $I_0$ and $I_n$ are the strengths of the zero-phonon transition and its $n^{th}$ phonon-replica. Following Stoneham, the calculation of the Huang-Rhys factor $S$ can be done assuming Fröhlich coupling of polar-optical phonons with the localized electronic wave functions. Focussing on the first replica

$$S_1 = e^2 / \pi \hbar \Theta (1 - 1/e_0) \int_0^1 F(q) dq.$$  \hspace{1cm} (1)

Here $F(q)$ is the overlap of the bound state wave functions with the phonon plane waves of momentum $q$. Here the notation is standard and we have completely followed Ref. 32. Given that the estimated binding $E_B \approx 43$ meV, the bound states associated with nitrogen cannot be treated as simple hydrogenic levels and perhaps a better (though still arbitrary) choice of the wave function would be those corresponding to a delta-function potential, $\phi_0(r) = (\beta/2 \pi)^{1/2} r^{-1} \exp(-\beta r)$, where the inverse localization length is simply estimated from the uncertainty argument, $\beta \approx \sqrt{2m E_B/\hbar^2}$. Since it is the electron which is bound to the isoelectronic nitrogen impurity, we take $m^* = 0.067$. This gives $\beta \approx [4.4 \text{ nm}]^{-1}$. $F(q) = [\pi/2 - \arctan(2\beta/q)]^2 (2\beta/q)^2$ when plugged into Eq. (1) yields a relatively large (though still very much in the weak coupling regime) value of $S \approx 0.25$. Experimentally, $S_1 = I_1/I_0$ for the NP$_A$ transition has a value of $S_1 = 0.35$ and for NP$_B$, $S_1 = 0.25$ (Fig. 1). The agreement between experiment and theory is only expected to be approximate because of the very simple nature of the analysis that ignores the non-adiabatic nature of the interaction.
Giant oscillator strength. It was recognized in the late 1990s that disorder-created localized states may not always be a nuisance but may actually be responsible for relatively strong and thermally stable emission both in InGaN and quantum dots.\textsuperscript{26} Note that there is expected to be an additional enhancement of the emission efficiency on account of the excitons being bound.\textsuperscript{24,34} Though this phenomenon has been known since 1962, it has received scant attention in the context of dilute nitrides.

As long as the size of the bound exciton is much smaller than the wavelength of light, coherence effects enhance the oscillator strength $f_{\text{bound}}$ of the bound exciton compared to that of the free exciton $f_{\text{free}}$ though the approximate relationship $f_{\text{bound}}/f_{\text{free}} \approx 4\pi (1/\beta)^3/\Omega_0 \approx 133$. Here, $\Omega_0 = 0.18$ nm$^3$ is the unit cell volume GaAs and $1/\beta \approx 4.4$ nm was already calculated earlier. Hence, these bound states have about two orders of magnitude higher radiative recombination efficiency compared to the free exciton states.

To summarize, this paper attempted an insight into the nature of the energy levels in the highly mismatched GaAs$_{0.9975}$N$_{0.0025}$ alloy by studying an equilibrium-grown sample in the ultra-dilute limit. The zoo of observed optical transitions (Fig. 1) could be consistently explained on account of two separate bands below the GaAs conduction band associated with free excitons and defect states (Figs. 2 and 3). The defect states continuum itself has coexisting localized and extended states. The degree of delocalization for the latter is similar to that of hybridized conduction band states (Fig. 4). (Only) The bound states transitions below the “mobility edge” were found to have strong phonon replicas. We have also pointed out that these bound state transitions should have more than two orders of magnitude enhanced optical activity due to the giant oscillator strength effect of account of exciton localization. This is an additional reason for observation of strong emission from these localized levels up to much higher temperature.

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\textsuperscript{2}Physics and Applications of Dilute Nitrides, edited by I. A. Buyanova and W. M. Chen (Taylor & Francis, New York, 2004).


\textsuperscript{6}A.-B. Chen and A. Sher, \textit{Semiconductor Alloys} (Plenum, New York, 1995).


