Evolution of the electron localization in a nonconventional alloy system GaAs$_{1-x}$N$_x$ probed by high-magnetic-field photoluminescence

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We demonstrate that a high magnetic field can be used effectively not only to probe the nature of the photoluminescence (PL) in a semiconductor, but also to reveal emission peaks that are unobservable at zero field since the magnetic field can alter energy relaxation processes and the statistical distribution of the photocarriers. Our systematic magneto-PL study of GaAs$_{1-x}$N$_x$ ($0.1\% \leq x < 2.5\%$) in fields up to 30 T indicates that the character of the low-temperature PL in this system changes drastically with varying nitrogen composition x and exhibits transitions with applying strong magnetic fields. For $x < 0.7\%$, the PL spectrum shows many discrete features whose energies remain nearly stationary up to the highest applied field. However, the magnetic confinement gives rise to a feature emerging on the higher energy side of the zero-field spectrum. This feature does show a diamagnetic shift, but it is much slower that that of the GaAs band-edge transition. For $x > 1\%$, the PL spectrum evolves into a broad band, and its diamagnetic shift resembles the band-edge transition in a conventional semiconductor, and the rate of shift is comparable to that of GaAs. From the diamagnetic shift of the band, the reduced effective masses for different composition of nitrogen have been derived for this system using the standard theory for the magneto-exciton in a three dimensional semiconductor. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1584789]

The dilute nitrogen GaAs$_{1-x}$N$_x$ alloy has been extensively studied both theoretically and experimentally over the past few years, because of its important applications in electro-optics and interesting fundamental physical properties created by the doping of nitrogen. It has been found that doping nitrogen into GaAs greatly reduces the band gap of GaAs.[1,2] A lot of experimental and theoretical investigations have been carried out to study the origin of this giant band-gap reduction.[3–11] It is generally understood that in the dilute doping limit, N impurities introduce highly localized states either above or below the conduction band edge of GaAs. These impurity states, originating from isolated N atoms, N pairs, and N clusters, have progressively lower energy levels in GaAs and emerge sequentially with increasing doping of nitrogen.[12–14] The emission lines of those nitrogen bound states have been shown to broaden and turn into a continuous spectrum with increasing nitrogen doping.[14] The GaAs-like band-edge excitonic absorption feature has also been found to broaden drastically with increasing nitrogen doping,[4,5] presumably due to a strong interaction of the down shifting host state with nitrogen-bound states in its vicinity. However, the exact nature of those bound states or emission lines and their evolutions with increasing nitrogen doping remain unclear.[6,7,14,15]

In order to better understand the nature of various nitrogen-induced bound states, the impurity–host interaction, and to what extent the wisdom for conventional alloys is still applicable to this "unconventional" alloy system, we have carried out systematic magneto-photoluminescence (PL) measurements on a set of GaAs$_{1-x}$N$_x$ samples (with x ranging from 0.1% to 2.5%) in magnetic fields up to 30 T. The biggest advantage of performing magneto-PL measurements at high magnetic fields is that this technique can clearly distinguish the extended states and localized states without any ambiguity.

The samples were grown by gas-source molecular-beam epitaxy on semi-insulating (001) GaAs substrates at 420 °C and a growth rate of 0.8 μm/h using a rf nitrogen radical beam source with a mixture of N$_2$ and Ar in a ratio of 1:9. The epilayer thickness is nominally 4000 Å with a 2000-Å GaAs buffer for $x < 1\%$, and 1000 Å with a 2500-Å GaAs buffer and a 250-Å GaAs cap for $x > 1\%$. The nitrogen concentrations of all these samples were determined by high-resolution x-ray rocking curve measurement, as well as theoretical dynamic simulation. For our PL measurements, a 200-μm-diameter optical fiber was used to direct laser light to the sample, with a typical power of 1 mW at the 5145-Å wavelength, resulting in a nominal excitation intensity of $\sim$0.1 W/cm^2. The PL signal was collected by a 600-μm-diameter optical fiber and dispersed by a McPherson 3/4m spectrometer. A Princeton Instrument CCD array detector was used for measuring PL signals between 300 and 1100
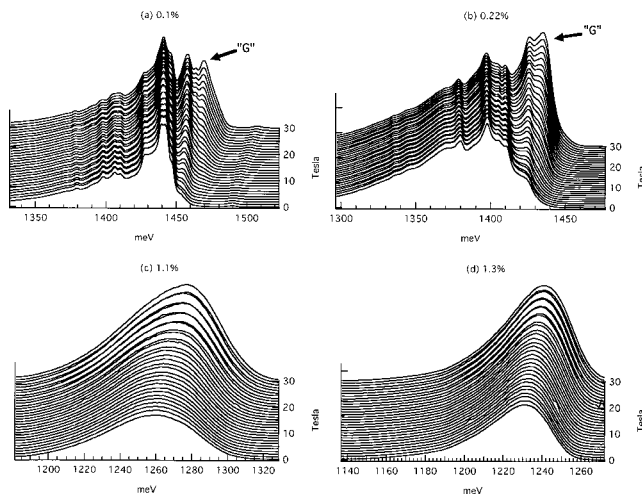
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FIG. 1. Waterfall plots of PL spectra of GaAs$_{1-x}$N$_x$ at magnetic field up to 30 T: (a) $x=0.1\%$, (b) $x=0.22\%$, (c) $x=1.1\%$, and (d) $x=1.3\%$.

nm and a North-Coast EO-817L germanium detector for the long-wavelength regime from 1 to 1.7 μm.

Figure 1 shows waterfall plots of magneto-PL spectra of GaAs$_{1-x}$N$_x$ at four typical compositions with $x=0.1\%$, 0.22%, 1.1%, and 1.3% in magnetic fields up to 30 T at intervals of 1 T. These samples can be roughly divided into two groups: $x<0.7\%$ and $x>1\%$, based upon their distinct differences in their spectra and response to the magnetic field. For $x<0.7\%$, as shown in Figs. 1(a) and 1(b), many transitions with discrete energies were observed at zero magnetic field. Comparing with previously published results (Ref. 14 and the references therein), all these transitions are identified to be nitrogen-induced bound states. When the applied magnetic field is increased, the positions of these impurity transitions do not shift with magnetic field, indicating that they originate from strongly localized states of "deep" impurity centers. However, starting from around 10 T, at the high-energy edge of the spectrum, an additional feature (at ~ 1.47 eV for the 0.1% sample, and at ~ 1.44 eV for the 0.22% sample) emerges with increasing magnetic field, and becomes a well-developed peak at 30 T. Its peak energy is close to but always lower than the excitonic band gap (the excitonic band gap has been found to be ~ 1.475 and ~ 1.442 eV for the $x=0.1\%$ and 0.22% samples, respectively).[6,16] This additional PL feature, hereafter referred to as G, exists for all the dilutely doped samples (with $x<0.7\%$) studied in this work. Right below the dominant G-line, there are other features as well (two for 0.1% sample, and one for 0.22% sample) that seem to change with the applied magnetic field. The combination of two factors may be responsible for the observed behavior. (1) The linewidth of G is very broad, and its tail distribution contributes to the intensity enhancement of features next to it. (2) The states associated with these features are very close to the states that give rise the G-line, therefore these features and G-line might come from the same origin, explained in detail in the following. For $x>1\%$, the discrete impurity-like transitions observed in the low-N-composition samples are no longer observable; instead a broad band becomes the only feature in the spectra. Figures 1(c) and 1(d) show the PL spectra for two typical x values of 1.1% and 1.3%. It is clear that the
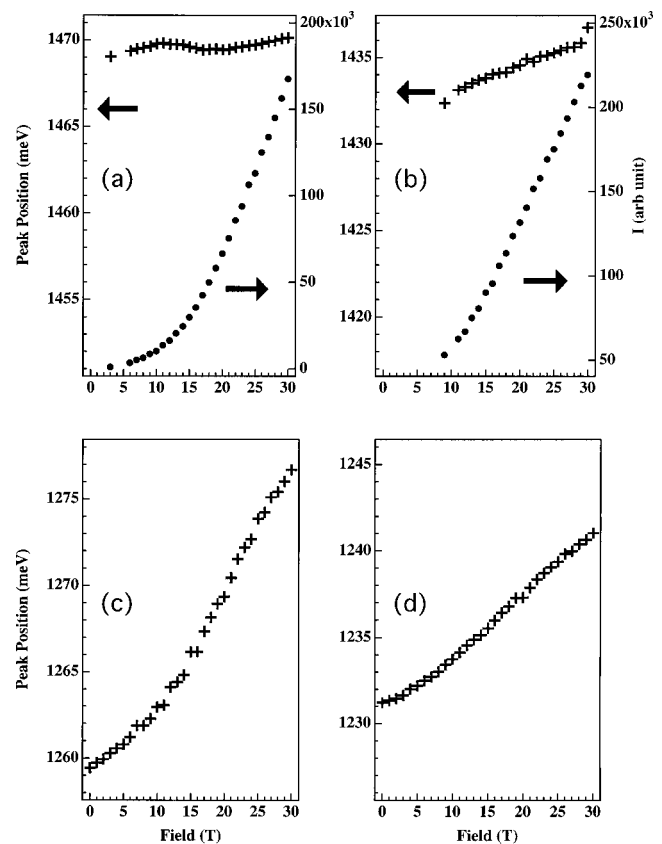

FIG. 2. The energy (+, left axis) and peak intensity (●, right axis) as a function of magnetic field. (a) and (b) for the transition G in the $x=0.1\%$ and 0.22% samples, respectively; (c) and (d) for the broad emission bands in the 1.1% and 1.3% samples, respectively.

peak position of the broad band shifts to the higher energy with increase of magnetic field at a significantly fast rate than for the low-x samples, resembling the behavior for conventional alloys. However, for the samples with $x>2.2\%$, further broadening and diminishing of the emission make it difficult to resolve any feature in the spectra, possibly due to the decrease in the sample quality.

In order to give a more quantitative account for the origin of the feature G and the broad emission band, we have carried out a careful analysis of their magnetic field dependences. Figure 2 summarizes the shift of the peak position, the so-called diamagnetic shift, as a function of magnetic field, where (a) and (b) are for the field-induced feature G in the 0.1% and 0.22% samples, respectively, and (c) and (d) are for the broad emission bands in the 1.1% and 1.3% sample, respectively. For Figs. 2(a) and 2(b), the peak intensity of G has also been plotted. Because of the interference of other adjacent peaks, it is difficult to accurately extract the integrated intensity of G. We have, therefore, chosen to simply plot the peak intensity in order to qualitatively illustrate the general trend of the intensity change with the magnetic field. From the Figs. 2(a) and 2(b), one can clearly see that once the transition G becomes a well-developed peak at high enough magnetic field (>15 T), its peak position starts to shift monotonically to higher energy with applied magnetic field. The observed energy–field dependence is very much different from that of a band edge or shallow impurity transition in conventional semiconductors. Compared to those transitions on its lower energy side associated with truly

"deep" impurity like centers that remain stationary under magnetic field, the field dependence of G clearly indicates that it originates from a state somewhat less localized. The behavior of the stationary transitions observed here corroborates well with the conclusions that they are highly localized states drawn from the earlier selective excitation experiments.[14] Some states appear to always exist that can give rise to the transition G in the dilute doping region. These states seem to define a transition region between the bulk-like and impurity-like states, that is, the G transition might be considered as an onset of the delocalized state. The electronic structure near the band edge continues to evolve with adding more nitrogen. Figures 2(c) and 2(d) show the field dependence of the peak position for the 1.1% and 1.3% samples. It is clear that the field dependence shows the quadratic behavior at low magnetic field (below 15 T) and sublinear behavior at high magnetic field, very much like the dependence observed for the band-edge transition in a conventional semiconductor. This finding suggests that the impurity states and the host states are thoroughly hybridized over this nitrogen concentration region. Nevertheless, it does not necessarily mean that there are no more localized states embedded in the unusually broad emission band. We notice that the band has become more symmetric under high field, with its peak intensity enhanced at the expense of the low-energy tail.

We have fitted the diamagnetic shift for samples with $1.1\% \leqslant x \leqslant 1.7\%$, using a numerical scheme in the framework of standard theory for the magneto-exciton in a three-dimensional semiconductor.[17] The diamagnetic shift is given as $\delta E(B) = E(B) - E(0) = R\,\delta e(\gamma)$, where E is the transition energy, R the effective Rydberg $\mu e^4/(2\hbar^2\varepsilon_0^2)$, ε_0 the dielectric constant for GaAs, $\delta e(\gamma)$ a dimensionless energy shift as a function of effective field $\gamma = \frac{1}{2}\hbar\omega_c/R$, and $\omega_c = eB/(c\mu)$. $\delta e(\gamma)$ is an interpolation function obtained by numerical data in a range $\gamma \leqslant 50$ (in a step size 0.1). The reduced mass μ is the only fitting parameter. The masses derived for 1.1%, 1.3%, and 1.7% are 0.063, 0.090, and 0.083, respectively. Please note that the mass first increases and then decreases with increasing nitrogen composition. Since the magnetic field dependence of the broad band (in samples with $x>1\%$) is very similar to that of a conventional semiconductor, and its overall diamagnetic shift from 0 to 30 T is comparable with that of GaAs, we believe that the emission mainly originates from delocalized states, and the derived reduced masses are reliable. Therefore, the observed nonmonotonic dependence indicates the complexity of the evolution process. It is known that there are a number of nitrogen-induced bound states below the GaAs band gap, and the GaAs conduction band edge moves down with increasing x. It is then conceivable that the impurity–host interaction is enhanced when the band edge arrives at the vicinity of one particular bound state and gives rises to a heavy effective mass. Of course, this conjecture needs to be validated in the future study. The conduction band effective mass in GaAsN or InGaAsN with dilute indium has been measured by various techniques,[10,18–20] and the disagreement in terms of its absolute value is rather large. The results presented here might shed some light on this controversial issue.

We have demonstrated that the interaction between nitrogen-induced bound states and bulk-like states plays a very important role in the electronic properties of $GaAs_{1-x}N_x$. Using a magnetic field to generate a tunable confinement, we are able to explore the characters of various bound states near the conduction band edge. Under high magnetic field, for $x<0.7\%$, the transition energies for many nitrogen related bound states remain stationary up to 30 T, revealing that they are highly localized states; an optical transition G is observed at the onset of localized to delocalized transition region in the energy spectrum, showing very small diamagnetic shift and thus a weak delocalization. For $x>1\%$, a broad optical transition band is observed with a diamagnetic shift similar to that in a conventional semiconductor alloy, exhibiting extended host-state-like behavior. The reduced masses derived from our data are found to vary nonmonotonically with x and differently from those obtained from other techniques with x, which suggests a complex interaction between nitrogen impurities and the GaAs host.

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