Early manifestation of localization effects in diluted Ga(AsN)

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The electron effective mass, m_e, and extent of exciton wave function, r_{exc}, were derived in $GaAs_{1-y}N_y$ ($y=0.043\%-0.5\%$) from magnetophotoluminescence measurements. With an increase in nitrogen concentration, we find that m_e and r_{exc} undergo a rapid increase and squeezing, respectively, even for $y\approx 0.1\%$. This quite early manifestation of nitrogen-induced localization effects imposes important constraints on existing theoretical models. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1586787]

Of all the isoelectronic impurities nitrogen has recently attracted much attention for the peculiar effects it has on the electronic properties of GaAs.[1] At the very early stage of N incorporation into GaAs (N concentration, y, less than 0.001%), narrow recombination lines appear in the emission spectra at energies below the GaAs band gap.[2,3] These lines are attributed to carrier recombination from electronic levels due to N pairs and/or clusters. As the nitrogen concentration is increased further (up to $y\sim 0.1\%$), the band gap starts redshifting very rapidly, coexisting with and taking in levels associated with N complexes, whose energies remain pinned upon varying y.[4–6] Eventually at higher concentrations (alloy limit, $y>0.1\%$) the $GaAs_{1-y}N_y$ band gap keeps redshifting[7] and reaches values of interest for fiber optical communications and solar cell applications.[1] At the same time, the electron effective mass increases,[8–10] a sizable Stokes shift between emission and absorption is observed,[5,11,12] the band gap dependence on the temperature[13,14] and hydrostatic pressure[15–17] decreases, and N resonant states move towards higher energy.[4,17,18] This phenomenology can be described by three different approaches. The band anticrossing model accounts for the N-induced effects in terms of repulsive interaction between the GaAs conduction band minimum and a level induced by a *single* nitrogen atom in the conduction band.[17] A second model focuses on the possible role of interaction among nitrogen *pairs* and/or *clusters* at high N concentration.[6,9] Finally, a third model emphasizes localization effects on the carrier energy levels produced by the breaking of crystal translational symmetry following the introduction of N into the GaAs lattice.[19]

Here, evidence of the early development of carrier localization (i.e., carrier effective mass increase and wave function size decrease) in $GaAs_{1-y}N_y$ is provided by magnetophotoluminescence at very low N concentrations. Usually, with an increase in the magnetic field intensity highly localized states remain at fixed energy, while extended states blueshift. A combined analysis of this blueshift in the case of the energy of free-electron to neutral-carbon recombination (e,C) and of free exciton recombination was performed. It allowed us (i) to measure directly the electron effective mass, m_e, which sharply increases for $y>0.043\%$ before showing a tendency to saturate at $\sim 0.13\ m_0$ for $y\sim 0.1\%$ (m_0 is the electron mass in vacuum); (ii) to get an estimate of the variation with y of the free exciton wave function size.

The samples studied are four $GaAs_{1-y}N_y$/GaAs epilayers ($y=0.043\%$, 0.095%, 0.21%, and 0.5%) grown by metalorganic vapor phase epitaxy.[4,11] A N-free GaAs sample was studied for comparison. Nitrogen concentrations were determined by high-resolution x-ray diffraction measurements. Photoluminescence (PL) was obtained by exciting the samples with the 532 nm line of a vanadate-YAG laser. The luminescence was dispersed by a 3/4 m monochromator and detected by a N-cooled (InGa)As linear array. The spectral resolution of our experimental apparatus was 0.1 nm. A magnetic field, B, was applied along the growth axis of the samples.

Low-temperature photoluminescence spectra of the samples investigated are shown in Fig. 1. At the lowest N concentration (0.043%), a number of sharp, weak lines and two broad, intense bands appear on the low and high energy sides of the PL spectra, respectively. As y increases (0.095%), the sharp lines remain fixed in energy, while the two broad bands redshift, progressively swallowing the low energy recombination lines for higher y (0.21% and 0.5%). The low energy features in the PL spectra are ascribed to impurity-like states from nitrogen pairs and higher order clusters and their longitudinal optical (LO) phonon replica.[2–6] The high energy bands are related, instead, to radiative recombination that involve *extended* states of the $GaAs_{1-y}N_y$ lattice. The lower energy PL band (and its LO phonon replica) is attributed to the free-electron to neutral-carbon transition (e,C)[5] on grounds of its behavior upon variation of temperature and excitation density (not shown here). The PL band located at the highest energy is due to exciton recombination from the $GaAs_{1-y}N_y$ band gap, hereafter called E_-. The separation in energy between the (e,C) and the E_- transitions is equal to 20 meV for $y=0.043\%$ and decreases to ~12 meV in the samples with higher N concen-

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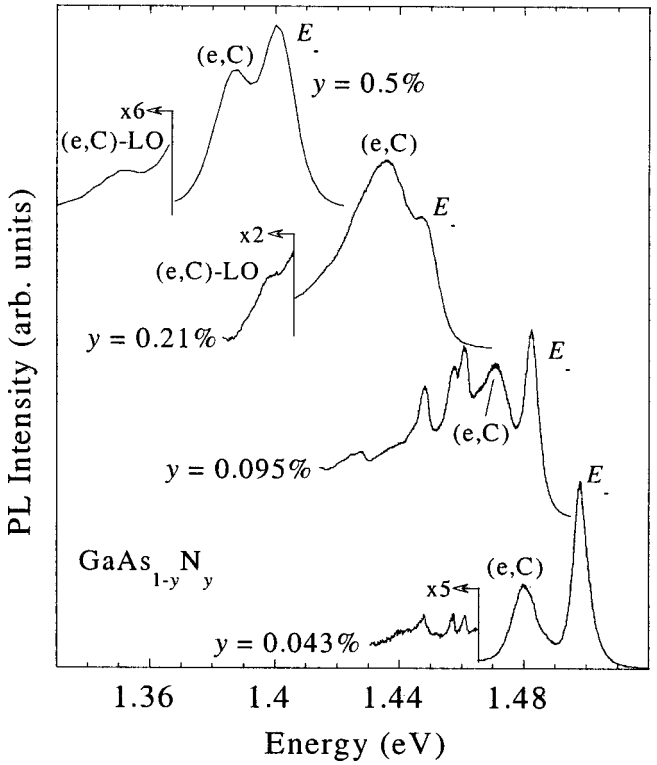

FIG. 1. Low-temperature PL spectra of $GaAs_{1-y}N_y$ epilayers with different y. The laser power density and temperature ($T=10-30$ K) were chosen in order to better highlight the contribution from the (e,C) and E_- transitions.

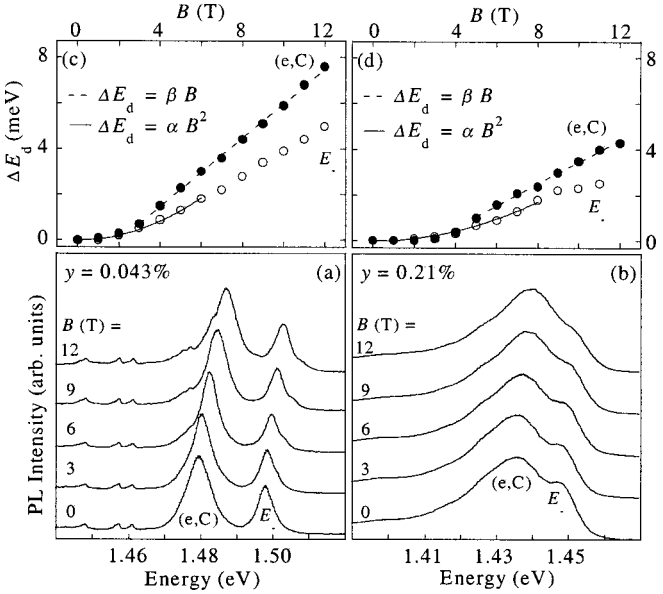

FIG. 2. (a), (b) PL spectra of $GaAs_{1-y}N_y$ samples with $y=0.043\%$ and 0.21%, respectively, taken at different magnetic fields ($T\approx 30$ K). (c), (d) value of the B-induced shift, ΔE_d, of the (e,C) (closed symbols) and E_- (open symbols) peak energy, as a function of the magnetic field, for corresponding samples shown in the lower panels (a) and (b). The continuous (dashed) lines are fits of the quadratic (linear) B dependence to the ΔE_d values of the E_- ((e,C)) peak. Note that the data for the E_- transition in the $y=0.21\%$ sample were derived from magneto-PL spectra recorded at higher laser power to better determine the transition peak energy (not shown here).

tration. This is most likely due to increasing tensile strain with an increase in y, which gives the top of the valence band a more pronounced light hole character and, hence, a smaller binding energy for acceptor impurity.

The application of a magnetic field supports the previous attributions. The PL spectra of samples with $y=0.043\%$ (dilute limit) and 0.21% (alloy limit) are shown in (a) and (b) of Fig. 2, respectively, for different B values. The PL spectra were taken at about 30 K to reduce the contribution from possible N-related localized states[14] and donor–acceptor pair recombination, the latter ionized with the temperature before (e,C) recombination. As B increases, the energy position of the sharp lines remains fixed by the strongly localized character N pairs and clusters have. But the E_- and the (e,C) bands blueshift. The B-induced shift, ΔE_d, of the E_- and (e,C) recombination lines is shown as a function of B in Figs. 2(c) and 2(d) for the same samples displayed in Figs. 2(a) and 2(b), respectively. The E_- band shifts with B at a lower rate than the (e,C) band due to larger Coulomb attraction between the electron and hole in the former case.

The electron effective mass, m_e, was estimated by fitting [dashed lines; Figs. 2(c) and 2(d)] the formula for the magnetic field dependence of the bottommost Landau level of the conduction band, $\Delta E_d=\beta B=(\hbar e/2m_e)B$, to the shift of the ($e$,$C$) transition in the B-linear region of ΔE_d.[20] At zero magnetic field, ΔE_d extrapolates to a negative value, of order of $k_BT/2$, as found in other magneto-PL measurements of the B-induced shift of free-electron to neutral-acceptor recombinations.[21–23] This behavior is usually attributed to a change in the density of states of the system from three to one dimensional due to a magnetic field being applied. The fitted values of m_e are shown versus y in Fig. 3 (bottom panel). The electron effective mass increases from 0.065 ($y=0\%$) to $0.074m_0$ ($y=0.043\%$) before tending to saturate at $\sim 0.13m_0$ for $y\geq 0.1\%$. The continuous lines in Figs. 2(c) and 2(d) are fits of $\Delta E_d=\alpha B^2=e^2\langle r_{eh}^2\rangle/(8\mu)B^2$ to the E_- diamagnetic shift in the low-field regime (small perturbation limit). r_{eh} and μ are, respectively, the electron-hole distance and the reduced effective mass of excitons. At very low N concentration, α rapidly decreases by a factor of ~ 2 with respect to the value it has in GaAs and tends to saturate for $y>0.1\%$. This behavior matches that found for m_e well. By using the m_e values determined previously, we get an estimate of $r_{exc}=\sqrt{\langle r_{eh}^2\rangle}$ for each sample from the diamagnetic

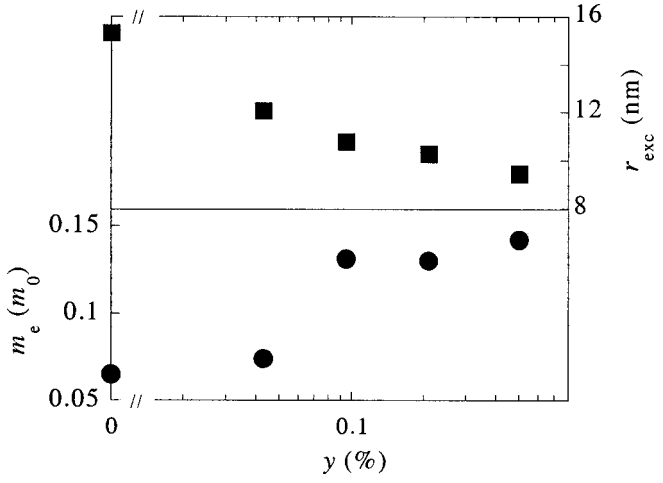

FIG. 3. Electron effective mass (bottom panel) and extent of exciton wave function (top panel) vs the N concentration, y.

shift formula $\Delta E_d = \alpha B^2$.[24] The r_{exc} values are shown as a function of y in Fig. 3 (top panel). We point out that this method provides a sound value of both m_e ($=0.065m_0$) and r_{exc} ($=15.3$ nm, which corresponds to an exciton Bohr radius of $a_0^{\mathrm{exc}} = r_{\mathrm{exc}}/\sqrt{2} = 10.8$ nm) for the GaAs reference. The fast decrease in r_{exc} provides further evidence that N-induced localization effects start at very low values of y.

The counterpart in the optical properties of the fast increase in the electron effective mass and of the decrease in the exciton wave function size at very low N concentration is the redshift of the E_- peak, which progressively swallows the N-related pair and cluster lines; see Fig. 1. The dependences on N concentration shown in Fig. 3 may serve as guidelines for theoretical models that attempt to describe the N-induced effects on the GaAs electronic properties. In particular, the band anticrossing model[17] provides a means by which to calculate the electron effective mass. However, this model underestimates the electron effective mass increase, at least for reasonable values of interaction potential. On the other hand, the N pair and cluster interaction model[6,9] as well as the translational symmetry breaking model[19] could provide a more comprehensive description of the $GaAs_{1-y}N_y$ electronic properties. However, neither model has yet provided quantitative estimates of the electron effective mass or the extent of the exciton wave function that can be compared with the present results.

In conclusion, localized and extended states in $GaAs_{1-y}N_y/GaAs$ epilayers behave quite differently in magneto-PL. At dilute N concentrations, N pairs and higher order clusters give rise to sharp lines, which do not move in energy upon the application of a magnetic field up to 12 T. On the contrary, the (e,C) and the E_- recombination bands exhibit for increasing B a clear linear and quadratic shift, respectively. The former shift provides a direct estimate of the electron effective mass, whose value rapidly increases at very low N concentrations and tends towards $\sim 0.13m_0$ for $y \sim 0.1\%$. Similarly, the extent of the exciton wave function, estimated by combined analysis of the (e,C) and E_- energy shift with B, exhibits significant localization with an increase in N concentration. These results are manifestations of strong localization effects at very low N concentration and they impose important constraints on existing and future theoretical models.

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[24] As for the hole effective mass, the increase in tensile strain with an increase in y modifies the character of the top of the valence band from predominantly heavy to light. We get an estimate of the variation in hole mass (m_{h}) from the measured change in the acceptor binding energy roughly estimated by the difference in energy between the free exciton and the (e,C) recombination and by setting $m_{\mathrm{h}} = 0.45m_0$ as the starting point for $y = 0\%$.