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Unusual carrier thermalization in a dilute $GaAs_{1-x}N_x$ alloy

P. H. Tan[a] and Z. Y. Xu
State Key Laboratory for Superlattices and Microstructures, Institute of Semiconductors, Beijing 100083, China

X. D. Luo and W. K. Ge
Department of Physics, HongKong University of Science and Technology, HongKong, China

Y. Zhang[b] and A. Mascarenhas
National Renewable Energy Laboratory, 1617 Cole Boulevard, Golden, Colorado 80401

H. P. Xin and C. W. Tu
Department of Electrical and Computer Engineering, University of California at San Diego, La Jalla, California 92093

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Photoluminescence (PL) properties of the E_0, $E_0+\Delta_0$, and E_+ bands in an $x=0.62\%$ $GaAs_{1-x}N_x$ alloy were investigated in detail, including their peak position, linewidth, and line shape dependences on the excitation energy, excitation power, and temperature, using micro-PL. The hot electrons within the E_+ band are found to exhibit highly unusual thermalization, which results in a large blueshift in its PL peak energy by $>2k_BT$, suggesting peculiar density of states and carrier dynamics of the E_+ band. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2454552]

The giant band gap bowing in dilute $GaAs_{1-x}N_x$ alloy is a subject of intensive experimental and theoretical research in recent years because of its promising application in the optoelectronic fields and its peculiar fundamental physical properties.[1–3] In addition to the unexpected large reduction of the fundamental band gap even with small amount of N incorporation, an electronic transition far above the band gap E_0, known as the E_+ transition, has been detected in several measurements, such as modulation reflectance (MR), resonant Raman scattering, and microphotoluminescence (μ-PL).[2–6] With increase of the nitrogen concentration, contrasting to the redshift of E_0, E_+ is found to blueshift with a magnitude of around 2/3 of that for E_0.[3,6] It is well known that the PL spectrum depends strongly on the thermal distribution of carriers, and has been widely used to characterize the optical properties of the band gap emissions in Ga(In)NAs alloys.[6–9] Recently, the deeply resonant E_+ band has been detected by μ-PL at low temperature (80 K) in dilute $GaAs_{1-x}N_x$ alloys with x as low as 0.1%, and the behavior of E_+ is found to be very different from another resonant transition $E_0+\Delta_0$.[6] The intrinsic optical transitions can be more clearly investigated with the μ-PL technique because of the saturation of localized states by high excitation density. Although the broadening parameter of E_+ in MR is only 6% on average larger than those of E_0 and $E_0+\Delta_0$ over a wide concentration range from MR measurements,[4] the PL bandwidth of E_+ remains about 70 meV for x being as low as 0.1%, which is much greater than that (25 meV) of E_0.[6] It has been concluded that E_+ is originated from a rather large set of perturbed host states of GaAs near the L point.[6] In this letter, using μ-PL and a sample with $x=0.62\%$, we provide a comprehensive study on the temperature dependence of the E_+ transition between 80 and 300 K. The result shows that the E_+ band exhibits very unusual density of states and carrier thermalization compared to E_0 and $E_0+\Delta_0$, which results in an unusually large thermalization-induced blueshift of its PL peak energy.

The $GaAs_{1-x}N_x$ sample ($x=0.62\%$) investigated here was grown by a gas-source molecular beam epitaxy on semi-insulating (001) GaAs substrates with an epilayer thickness of 400 nm. The detailed growth process has been described elsewhere.[10] The μ-PL is measured by a μ-Raman system of Dilor Super Labram, which consists of a LN_2 cooled Si charge-coupled detector. The laser excitation energies are 1.959 eV of a He–Ne laser, 2.410 and 2.541 eV of an Ar^+ laser, and 2.089 and 1.848 eV of two diode pumped solid-state lasers. In order to avoid the strong interference of the Raman lines to the PL peak of E_+, a forbidden scattering configuration for longitudinal optical phonons at Γ point was used for the PL measurements when excited by the 1.959 eV laser. The sample temperature was controlled by a programmable hot-stage THMS600 from Linkam Scientific Instruments Ltd.

Figure 1 shows the PL spectra of $GaAs_{1-x}N_x$ with $x=0.62\%$ by different excitations at 80 K. The PL peaks at 1.374, 1.721, and 1.860 eV are assigned as the optical transitions, E_0, $E_0+\Delta_0$ (the spin-orbit split-off valence band), and E_+, respectively.[6] The linewidth (full width at half maximum intensity) of E_0 is about 25 meV, and its peak energy and linewidth are found to be independent of the excitation energy. In contrast, the E_+ peak shows a surprisingly large linewidth, and both the peak position and linewidth vary significantly with excitation energy: a 13 meV blueshift in the peak energy (as indicated by two dashed lines in Fig. 1) and a change in the linewidth from 68 to 84 meV when excitation energy increases from 1.959 to 2.541 eV. The larger linewidth of E_0 in GaNAs alloys relative to that in GaAs is mostly from the usual inhomogeneous broadening, meaning that the energy variation of a specific state with the fluctuation in the local atomic configuration. However, the width of the E_+ band should have two contributions: the inhomogeneous broadening, which should be in the same order of magnitude of the E_0,[6] and the energy spread of different

[a]Electronic mail: pt290@cam.ac.uk and pinghengtan@hotmail.com
[b]Electronic mail: yong_zhang@nrel.gov

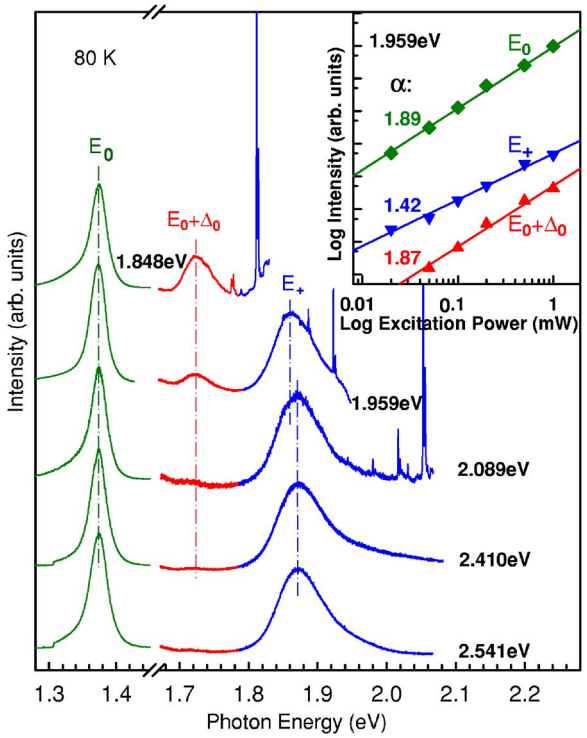

FIG. 1. (Color online) Peak normalized PL spectra of $GaAs_{1-x}N_x$ with $x=0.62\%$ for different excitations (1.848, 1.959, 2.089, 2.410, and 2.541 eV) at 80 K. All the spectra are vertically shifted for clarity. The inset shows the integrated PL intensity of the PL peaks excited by the 1.959 eV laser as a function of the excitation power in a double logarithmic plot.

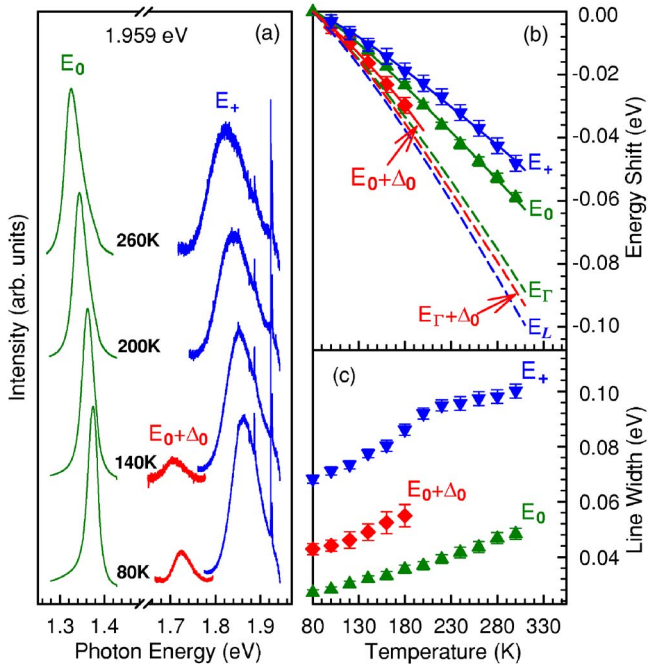

FIG. 2. (Color online) (a) Temperature dependent PL spectra of the 0.62% GaAsN alloy excited by 1.959 eV laser. (b) Energy shifts of the E_0, $E_0+\Delta_0$, and E_+ transitions with temperature relative to that at 80 K in the GaAsN alloy. The dashed lines represent the temperature dependence of the direct or indirect band gaps at Γ and L points in GaAs. The solid lines represent their peak energy fits to the Bose-Einstein expressions. (c) The PL peak widths of the three transitions as a function of temperature.

perturbed **k** states, meaning that even N atoms are distributed in an ordered manner, there will still be an E_+ band (rather than a single state), which explains why the linewidth of E_+ is much larger than that of E_0. It is interesting to contrast the broadening of the E_+ band in GaAs:N with an extensively studied problem, the broadening of the N bound state in $GaP_{1-x}As_x$:N.[11] For the latter, the alloy fluctuation of the host material has caused a broadening of the impurity state. Here, we investigate how the impurity perturbation causes the broadening of a spectral feature of certain host states. As shown in the inset of Fig. 1, the PL peak intensity is found to increase superlinearly with increase of the excitation power, following a power law of $I_{PL} \propto P^{\alpha}$, where I_{PL} is the integrated intensity of the PL peak and P is the excitation power. The measured exponent α for E_0 (~1.89) and $E_0+\Delta_0$ (~1.87) in the GaAsN alloy are, in fact, very close to that (1.92) of E_0 in undoped GaAs, showing a typical behavior for the free-exciton emission,[12] whereas the exponent $\alpha \sim 1.42$ for E_+ is distinctly different from the others. It appears that the carrier dynamics for E_0 and $E_0+\Delta_0$ are primarily determined by the electrons in the conduction band edge, while the carrier dynamics of the E_+ states is rather different from that near the conduction band edge, as the states in the E_+ band are strongly perturbed by N doping.

The temperature dependence of PL spectra in the GaAsN alloy excited by 1.969 eV laser is shown in Fig. 2(a). Figure 2(b) depicts the energy shifts of the E_0, $E_0+\Delta_0$, E_+ peaks, and the E_Γ and E_L band gaps in bulk GaAs relative to their 80 K values,[13] and Fig. 2(c) shows their bandwidths versus temperature. The overall shifts are found to be 59 and 48 meV for E_0 and E_+, respectively. While the E_0 bandwidth appears to increase smoothly with increasing temperature, the E_+ bandwidth exhibits an abnormal temperature dependence, reflecting the unusual density of states and thermalization within the E_+ band. The shift of E_+ is found to be smaller than that of E_0, even though the temperature variation of the unperturbed host states at the L point is larger than that at the Γ point in GaAs,[13] as indicated by the dashed lines in Fig. 2(b).

In a very similar sample, GaAsN alloy with 0.6% N, Francoeur *et al.* recently reported that the energy shifts of E_0 (~80 meV) and E_+ (~90 meV) between 80 and 300 K in MR measurements[4] are fairly close to those of the band gaps at the Γ (~85 meV) and L (100 meV) point in GaAs.[13] MR is a differential spectroscopy that amplifies the roles of few states near the "singularity" of the electronic density of states, and thus reflects the energies of critical points. PL, being a linear spectroscopy, may probe the contributions of states in a more broad range. If we assume approximately that the temperature change causes a rigid shift of the band structure in the MR measurement, the difference between the energy shift measured by MR and PL can then be attributed to the thermalization-induced blueshift. In general, the blueshift is determined by the density of states, the relative carrier relaxation time $\gamma = \tau_{rel}/\tau_{rad}$ (τ_{rel} is the relaxation time and τ_{rad} the radiative decay time), and excitation density. Under the assumption of parabolic dispersion and thermal equilibrium, the thermalization of free carriers will result in a blueshift of $k_BT/2 = 0.086T$ meV/K for the PL peak position relative to the band gap energy,[14] where k_B is Boltzmann's constant. The temperature variation from 80 to 300 K will yield a blueshift of ~10 meV. However, with respect to the critical energies determined by MR,[4] the blueshifts are found to be ~21 meV ($\sim 1.1k_BT$) and ~42 meV ($\sim 2.2k_BT$), respectively, for E_0 and E_+, indicating an unusual behavior of

TABLE I. Values of parameters E_B, a_B, Θ, and α_{CT}, obtained by fitting the peak energies of E_0, $E_0+\Delta_0$, and E_+ in the GaAsN alloy.

	E_B (eV)	a_B (eV)	Θ (K)	α_{CT} (10^{-3} eV/K)
E_0	1.427	0.058	249	0.11
$E_0+\Delta_0$	1.785	0.062	249	0.06
E_+	1.913	0.065	249	0.21

carrier thermalization in the studied GaAsN alloy.

To quantitatively evaluate the behavior of carrier thermalization in GaAsN alloy, we extract the unusual thermalization-induced blueshifts in the GaAsN alloy, by taking the energy variations of the critical-point energies at Γ and L in GaAs as approximations for those of E_0 and E_+. If the blueshift is assumed to be a linear function of T, the PL peak energy in GaAsN can be fitted by the Bose-Einstein expression[15] with an additional term for the thermalization-induced blue shift,

$$E(T) = E_B - a_B(1 + 2/(e^{\Theta/T} - 1)) + \alpha_{CT}T, \quad (1)$$

where Θ represents the average phonon temperature, a_B the electron-phonon interaction strength, and α_{CT} the temperature coefficient for the carrier thermalization. Using the a_B and Θ parameters of GaAs at Γ and L points, we can fit the experimental data very well with Eq. (1) and obtain α_{CT} =0.11, 0.06, and 0.21 meV/K for E_0, $E_0+\Delta_0$, and E_+ in the GaAsN alloy. The results are summarized in Table I.

The parameter E_B in Table I shows the significant band gap change in GaAsN alloy with small amount of N incorporation into GaAs, compared with the fitting values[15] for the critical-point energies of E_Γ(1.570 eV), $E_\Gamma+\Delta_0$ (1.910 eV), and E_L (1.872 eV) in GaAs. The fitting parameters α_{CT} yield the thermalization-induced blueshifts of 24 and 46 meV between 80 and 300 K for the E_0 and E_+ transitions in the GaAsN alloy, respectively, which is much larger than that (10 meV) of $k_BT/2$. On the other hand, the corresponding blueshift (13 meV) of $E_0+\Delta_0$ is close to $k_BT/2$. We note that E_0 and $E_0+\Delta_0$ are associated with the common conduction band states, which indicates that the larger blueshift for E_0 is mainly resulted from the thermalization of the holes near the top of the valence band, probably due to the fact that the carriers are not in thermal equilibrium as it often occurs under the high excitation density, and thus the carrier temperature could be different from the lattice temperature. The major difference between E_+ and E_0, which involves the same valence band states, should be attributed to the difference of the carrier thermalization for the conduction band states in the E_+ band and near the band edge. The difference is highly anticipated because the density of states and the relative carrier relaxation rates are expected to be very different near E_+ and E_0. The density of states near E_0 is likely to remain as a monotonic function of energy, whereas the density of the perturbed states of the E_+ band is not expected to be monotonic function of energy but with a limited extension.

Because of the unusual aspects of E_+ in its components and density of states and carrier relaxation, the E_+ line shape and the thermalization effect are also expected to depend on excitation energy and power. As revealed in Fig. 1, different numbers of perturbed states are excited with different excitation energies, and thus the E_+ line shape varies. These unusual aspects are also reflected in its excitation powder dependence, with a smaller exponent compared to E_0 or $E_0+\Delta_0$, as shown in the inset of Fig. 1. The smaller exponent of the E_+ band could be understood as the result of more photoexcited electrons being populated to higher energy states, as evidenced by the line shape change, which is, in fact, consistent with the larger thermalization-induced blueshift. Finally, the slow down of the bandwidth increase for E_+ above 240 K may indicate the finite bandwidth of the perturbed states because the states at the high-energy side are expected to be less and less perturbed.

In summary, we have reported a detailed photoluminescence study of the E_0 and E_+ bands in a dilute $GaAs_{1-x}N_x$ alloy with x=0.62% using micro-PL technique, with varying temperature, excitation energy, and density. The temperature variations of the peak energies of E_0 and E_+ in 0.62% GaAsN alloy have been found to be reduced, respectively, by 24 and 46 meV compared to those of the E_Γ and E_L in bulk GaAs. The thermalization-induced unusually large blueshift suggests that the E_+ band exhibits a unique density of states and carrier dynamics, which are very different from those of unperturbed host states in GaAs. The variations in the peak intensity and line shape of the E_+ band with excitation energy and/or power, and the abnormal variation of linewidth with temperature can all be explained consistently.

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