Unusual carrier thermalization in a dilute GaAs\textsubscript{1-x}N\textsubscript{x} alloy

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Photoluminescence (PL) properties of the \(E_0\), \(E_0+\Delta_0\), and \(E_+\) bands in an \(x=0.62\%\) GaAs\textsubscript{1-x}N\textsubscript{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.

The giant band gap bowing in dilute GaAs\textsubscript{1-x}N\textsubscript{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.\textsuperscript{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).\textsuperscript{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 \(E_0\).\textsuperscript{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.\textsuperscript{6,9} Recently, the deeply resonant \(E_+\) band has been detected by µ-PL at low temperature (80 K) in dilute GaAs\textsubscript{1-x}N\textsubscript{x} alloys with \(x\) as low as 0.1%, and the behavior of \(E_+\) is found to be very different from another resonant transition \(E_0+\Delta_0\).\textsuperscript{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,\textsuperscript{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 \(E_0\).\textsuperscript{6} It has been concluded that \(E_+\) is originated from a rather large set of perturbed host states of GaAs near the L point.\textsuperscript{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\textsubscript{1-x}N\textsubscript{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.\textsuperscript{10} The µ-PL is measured by a µ-Raman system of Dilor Super Labram, which consists of a LN\textsubscript{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\textsuperscript{+} 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 \(\Gamma\) 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\textsubscript{1-x}N\textsubscript{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.\textsuperscript{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 \(E_0\), and the energy spread of different
perturbed k states, meaning that even N atoms are distributed in an ordered manner, there will still be an $E_0$ band (rather than a single state), which explains why the linewidth of $E_0$ is much larger than that of $E_0$. It is interesting to contrast the broadening of the $E_0$ band in GaAs:N with an extensively studied problem, the broadening of the N bound state in GaP$_{1-x}$As$_x$N.\textsuperscript{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 $\alpha$ for $E_0$ ($\sim 1.89$) and $E_0 + \Delta_0$ ($\sim 1.87$) 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,\textsuperscript{12} whereas the exponent $\alpha \sim 1.42$ for $E_0$ 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 $E_0$ states is rather different from that near the conduction band edge, as the states in the $E_0$ 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 $E_0$, $E_0 + \Delta_0$, $E_\gamma$, peaks, and the $E_\Gamma$ and $E_L$ band gaps in bulk GaAs relative to their 80 K values,\textsuperscript{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 $E_\gamma$, respectively. While the $E_0$ bandwidth appears to increase smoothly with increasing temperature, the $E_\gamma$ bandwidth exhibits an abnormal temperature dependence, reflecting the unusual density of states and thermalization within the $E_\gamma$ band. The shift of $E_\gamma$ 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 $\Gamma$ point in GaAs,\textsuperscript{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.\textsuperscript{14} recently reported that the energy shifts of $E_0$ ($\sim 80$ meV) and $E_\gamma$ ($\sim 90$ meV) between 80 and 300 K in MR measurements\textsuperscript{4} are fairly close to those of the band gaps at the $\Gamma$ ($\sim 85$ meV) and $L$ (100 meV) point in GaAs.\textsuperscript{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 $\gamma = \tau_{rel}/\tau_{rad}$ ($\tau_{rel}$ is the relaxation time and $\tau_{rad}$ 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 $k_B T/2 = 0.086 T$ meV/K for the PL peak position relative to the band gap energy,\textsuperscript{14} where $k_B$ is Boltzmann’s constant. The temperature variation from 80 to 300 K will yield a blueshift of $\sim 10$ meV. However, with respect to the critical energies determined by MR,\textsuperscript{4} the blueshifts are found to be $\sim 21$ meV ($\sim 1.1 k_B T$) and $\sim 42$ meV ($\sim 2.2 k_B T$), respectively, for $E_0$ and $E_\gamma$, indicating an unusual behavior of the $E_\gamma$ state. The PL peak widths of the three transitions as a function of temperature.
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 $\Gamma$ and $L$ in GaAs as approximations for those of $E_0$ and $E_x$. 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,

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

where $\Theta$ represents the average phonon temperature, $a_B$ the electron-phonon interaction strength, and $a_{CT}$ the temperature coefficient for the carrier thermalization. Using the fitting parameters of GaAs at $\Gamma$ and $L$ points, we can fit the experimental data very well with Eq. (1). 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 gap change in GaAsN alloy with small amount of N incorporation. The temperature, excitation energy, and density. The temperature variations of the peak energies of $E_0$ and $E_x$ in 0.6% GaAsN alloy have been found to be reduced, respectively, by 24 and 46 meV compared to those of the $E_T$ and $E_{pl}$ in bulk GaAs. The thermalization-induced unusually large blueshift suggests that the $E_x$ 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 $E_x$ band with excitation energy and/or power, and the abnormal variation of linewidth with temperature can all be explained consistently.

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