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BOUND EXCITON TRANSFER IN WEAKLY DISORDERED SYSTEMS: III-V ALLOYS*

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Résumé - Les mécanismes de transfert des excitons liés à l'azote dans les alliages GaInAsP:N et GaAsP:N sont observés en fonction de la température par des mesures de luminescence résolue en temps (laser picoseconde). Les résultats (saut direct entre des états localisés et piégeage multiple via les excitons libres) sont différents de ceux obtenus pour le binaire GaP:N. Nous montrons ainsi l'importance du désordre d'alliage sur la dynamique des excitons.

Abstract - Transfer mechanisms of N-bound excitons in GaInAsP:N and GaAsP:N alloys are studied as a function of temperature using picosecond time resolved photoluminescence. The results, direct exciton tunneling between localized states and multiple trapping via free excitons, are different from those seen in the binary GaP:N. Thus, we demonstrate the importance of alloy disorder on the exciton dynamics.

I. INTRODUCTION

Ternary A\textsubscript{x}B\textsubscript{1-x}C semiconductor alloys may be considered as model systems for investigation of the microscopic disorder inherent in alloys especially when results may be compared with those of a related binary (i.e. n=0 or n=1). An example is the spectroscopic study of excitons bound to substitutional nitrogen impurities in III-V compounds. Here cw-photoluminescence (PL), PL-excitation (PLE) and time resolved luminescence spectra of N-bound excitons are observed not only in the GaP binary but in the GaAs\textsubscript{x}P\textsubscript{1-x} and Ga\textsubscript{x}In\textsubscript{1-x}P alloys as well. In such studies, the influence of the differing local atomic configurations surrounding the nitrogen atoms has already been reported\textsuperscript{1,2}. Each configuration gives rise to an excitonic state with different energy. Depending on the importance of the energy difference between these states, we observe either a broadening of the N\textsubscript{e} (isolated N) exciton line in GaAs\textsubscript{x}P\textsubscript{1-x} (N\textsubscript{e} band)\textsuperscript{1,3}, or a splitting and broadening of this isolated N-exciton level in GaIn\textsubscript{x}P (N\textsubscript{e} and A\textsubscript{e} bands)\textsuperscript{2}. Moreover the exciton lines due to the repartition of N impurities like neighboring pairs of N atoms, denoted NN\textsubscript{p}, and which are prominent in GaP:N\textsuperscript{4}, disappear in low-temperature PL spectra upon alloying\textsuperscript{5,6}. In this paper we concentrate on the exciton dynamic of these partially disordered systems by reviewing all the mechanisms contributing to both spatial and spectral transfer of N-bound-excitons between these discrete levels (NN\textsubscript{p}) and the inhomogenously broadened bands (N\textsubscript{e},A\textsubscript{e}).

II. EXPERIMENT

Samples were excited with 20 psec pulses from a synchronously-pumped, cavity-dumped dye laser operating with coumarin 6 dye. Laser wavelengths were selected to be either resonant with the N\textsubscript{e} line or above the band gap. Average power and pulse repetition rates were typically 1mW and 700 KHz. The samples were held at constant temperature in a He-gas-exchange cryostat. Photoluminescence was analyzed with a double-grating spectrometer, a Varian VPM 154A1 photomultiplier, and a time-correlated single photon counting system. Time resolved luminescence spectra are obtained with a time resolution of 250 psec.

III. RESULTS

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Fig. 1 cw-photoluminescence (PL) and PL-excitation spectra (PLE) of GaAs₁ₓPₓ:N, x = 0.96 [N] = 10¹⁸cm⁻³, T = 8K (a) PL spectrum (solid curve) under above band gap pumping and PLE (dashed curve) observed at the LO phonon replica of the Nₓ band. (b) Time-resolved luminescence spectra under above bandgap pumping.

Experimental data at low T for the high energy part of the PL, PLE and time resolved luminescence spectra are presented in Fig. 1 for GaAs₁ₓPₓ:N and in Fig. 2 for GaIn₁ₓPₓ:N. The PLE spectra (Fig. 1a and Fig. 2a) reflect the density of states of the different isolated nitrogen centers in the alloys. We interpreted the splitting into two bands (Nₓ and A₀) for GaP-rich Ga₁InₓP, and the broadening of all the bands in both types of alloys, as resulting from the various possible atomic configurations surrounding the N atoms. In GaAs₁ₓPₓ:N this local disorder occurs on the second nearest neighbor shell from the N impurity and the broadening of the Nₓ band (dashed line Fig. 1a) corresponds to the envelop of the histogram arising from the 13 exciton states due to the 13 possible As-P configurations¹. In contrast, in GaIn₁ₓP:N the principal energy variation of exciton bound to isolated nitrogen are due to the 5 possible Ga-In configurations which may occur statistically within the shell of the nearest neighbors to the N impurity. The energy difference between each of these levels is sufficiently large (≈ 12 mev) that we observe a splitting of the nitrogen levels² with each of them broadened by more distant Ga-In configurations (dashed line Fig. 2a). The PL spectra (Fig 1a and 2a full line) which correspond to the relaxed exciton distribution are shifted towards lower energies and the ratio A₀/Nₓ in Ga₁InₓP is completed inverted compared to the corresponding PLE spectra. These important differences observed between the PL and PLE spectra may be understood from the time resolved luminescence (TRL) spectra of Fig. 1b and 2b. The TRL spectra at very short times (< 1nsec) resemble the cw excitation spectra. As times increases after the laser pulse, however, the TRL spectra become progressively similar tho the cw luminescence one. We may also notice three main features which appear in the TRL spectra as time increase:

(i.) The ratio between the two dominant bands A₀ (3Ga-1In neighbors) and Nₓ (4 Ga neighbors) in GaP-rich Ga₁InₓP:N becomes completely inverted, taking place over a period of 80 nsec following the laser pulse (Fig 2b)

(ii.) Most of the energy shift occurs within the first nanosecond for the Nₓ band in the Ga₁InₓP (Fig. 2b) and for the higher energy part of the Nₓ band in GaAs₁ₓPₓ (Fig. 1b).

Fig. 2 Same as Fig. 1 for GaIn₁ₓPₓ:N, x = 0.99 [N] = 10¹⁸cm⁻³, T = 8K (a) PL spectrum (solid curve) and PLE (dashed curve). (b) Time-resolved luminescence spectra.
(iii). The dynamic energy shift within the lower energy part of the N\textsubscript{i} band in Ga\textsubscript{As\textsubscript{1-x}}P\textsubscript{x} (Fig. 1b) and within the A\textsubscript{0} band in Ga\textsubscript{In\textsubscript{1-x}}P\textsubscript{x} (Fig 2b) occur over a longer time scale (50 nsec).

Taken together, these low temperature results demonstrate that excitons bound to differing N centers transfer from site-to-site by spatial and spectral diffusion. This exciton migration (spatial diffusion) to lower energy states with energy dissipation (spectral diffusion) has been attributed to tunneling processes through the bound excitonic bands assisted by emission of appropriate acoustic phonons\textsuperscript{7,8} (this process is usually called hopping). At such low T, an exciton trapped at a given N atom may tunnel only to those N atoms that are both spatially nearby (e.g. within an exciton radius) and at the same or lower energy. By modeling\textsuperscript{6} this direct tunneling with the usual form for the hopping rate between localized states one may account for the main experimental features noted above in Ga\textsubscript{In\textsubscript{1-x}}P\textsubscript{x} and GaAs\textsubscript{1-x}P\textsubscript{x}.\textsuperscript{6} We found in accord with the experiment, that the tunneling within the N\textsubscript{i} band in Ga\textsubscript{In\textsubscript{1-x}}P\textsubscript{x} and within the higher energy part of the N\textsubscript{i} band in GaAs\textsubscript{1-x}P\textsubscript{x} is much faster (≈ 1 nsec) than that within the A\textsubscript{0} band in Ga\textsubscript{In\textsubscript{1-x}}P\textsubscript{x} and within the lower energy part of the N\textsubscript{i} band in GaAs\textsubscript{1-x}P\textsubscript{x} (≈ 50 nsec) and between the two bands N\textsubscript{i} and A\textsubscript{0} in Ga\textsubscript{In\textsubscript{1-x}}P\textsubscript{x} (≈ 80 nsec.). This result is a natural consequence of the smaller density of states of the A\textsubscript{0} centers (N surrounded by 3Ga and 1In) in GaP-rich Ga\textsubscript{In\textsubscript{1-x}}P\textsubscript{x} and at the bottom of the N\textsubscript{i} band (N surrounded by As-rich configurations) in GaP-rich Ga\textsubscript{As\textsubscript{1-x}}P\textsubscript{x} as reflected in the PLE. Other spectral changes observed for the N\textsubscript{i} and A\textsubscript{0} PL-bands as a function of N concentration and excitation power\textsuperscript{10} are consistent with this hopping model.

This direct tunneling assisted by phonons was first observed in GaP:N between the NN\textsubscript{i} pair levels\textsuperscript{11} which dominate the PL spectra at low temperature (Fig. 3a). In that case a stochastic approach of exciton tunneling among the two nearest neighbors of a given center\textsuperscript{12} (triplet configuration) account for the strong intensities of all the NN\textsubscript{i} lines at low temperature. In contrast, in the alloys we do not see any efficient N\textsubscript{i} + NN\textsubscript{i} transfer at low temperature (Fig. 3b). However, as the temperature

Fig. 4. Kinetics of the NN\textsubscript{i} luminescence at different temperatures with the laser excitation in the N\textsubscript{i} band, for Ga\textsubscript{As\textsubscript{0.04}In\textsubscript{0.96}:N, [N] = 10\textsuperscript{19}cm\textsuperscript{-3} (a), and Ga\textsubscript{In\textsubscript{0.99}P\textsubscript{0.01}:N, [N] = 10\textsuperscript{18}cm\textsuperscript{-3} (b)
is raised, the NN\textsubscript{e} pair lines appear in the PL spectra of both GaAs\textsubscript{1-x}P\textsubscript{x} and Ga\textsubscript{1-y}In\textsubscript{y}P (Fig 3c) while the N\textsubscript{e} and A\textsubscript{e} bands rapidly diminish. This evolution could be explained by the time dependence study of the NN\textsubscript{e} luminescence intensity as a function of T (Fig. 4). The main result is that, as the temperature is increased, the luminescence intensity maximum shifts to shorter times, corresponding to a sharply decreasing of the NN\textsubscript{e} luminescence risetime\textsuperscript{13}. For example, for GaAs\textsubscript{0.64}P\textsubscript{0.36}, the N\textsubscript{X}→NN\textsubscript{e} transfer takes 150 nsec at 30K and only 400 psec at 50K. At lower T the NN\textsubscript{e} emission is too weak compared to the underlying N\textsubscript{e} background. At T = 50K, the risetime is sufficiently short as to approaching the system resolution (250 psec). These results clearly demonstrate that with increasing temperature, the N\textsubscript{e}→NN\textsubscript{e} interband transfer rate progressively increases, i.e. it becomes thermally activated. By studying this T-dependence\textsuperscript{13} we concluded that the thermal energy (kT) greatly increases the effective spatial diffusion of the isolated N-bound excitons, a consequence we attributed to two coexisting mechanisms. The first is multiple trapping in which a N-exciton may be thermally excited from the isolated center to extended states (i.e. free excitons of free carriers) with subsequent retrapping at either a different isolated N-site or an NN\textsubscript{e} site. The second process is similar to variable range hopping and results from excitons tunneling solely within the N\textsubscript{e} and A\textsubscript{e} bands until they reach an NN\textsubscript{e} site on which they can directly tunnel. In the alloy, due to the disorder broadening, this direct tunneling must be activated thermally to proceed efficiently. By contrast, in GaP:N, because the N\textsubscript{e} line is mainly monoenergetic, the direct tunneling from N\textsubscript{e} to NN\textsubscript{e} is always unimpeded and efficient even at low temperature. Therefore, in GaP:N the PL intensity increases observed for NN\textsubscript{e} pair lines with temperature\textsuperscript{12,14} before the thermal quenching\textsuperscript{15} are mainly due to multiple trapping.

To summarize we illustrate the differences between the exciton transfer mechanisms in the alloys compared to the binary in Fig. 5. At low temperature, hopping between differing localized states is the dominant process in both the alloy and the binary. However, for GaP:N the spatial diffusion of the excitons within the very narrow N\textsubscript{e} line is such that the isolated N bound exciton can tunnel efficiently to the NN\textsubscript{e} pairs (Fig. 5a). In the alloys, however, because of the disorder-broadening and splitting of the isolated nitrogen levels, the excitons soon become trapped at the sites of lower energy (Fig. 5b). Therefore the N-bound exciton spatial diffusion is greatly reduced and exciton tunneling to NN\textsubscript{e} pairs is inhibited. As the temperature increases multiple trapping processes are thermal activated in both the alloys and the binary (Fig. 5c and d). However, in the alloy the direct tunneling is also strongly temperature dependent (variable range hopping) and contributes efficiently to the observed increasing of the N\textsubscript{e} (A\textsubscript{e}) → NN\textsubscript{e} transfer.

Fig. 5. N-bound exciton transfer mechanisms in alloys (b and d) compared to the binary (a and c)

(a) GaP low T: N\textsubscript{e} → NN\textsubscript{e} transfer by hopping between different equivalent N\textsubscript{e} states until the excitons reach an NN\textsubscript{e} state on which they hop.

(b) Alloys low T: intraband and interband transfer within and between the N\textsubscript{e} and A\textsubscript{e} bands due to the statistical distribution of the energy levels by the alloy local disorder.

(c) GaP, T > 10K : N\textsubscript{e} → NN\textsubscript{e} transfer by hopping and multiple trapping through extended states (free excitons).

(d) Alloys, T > 10K : N\textsubscript{e}(A\textsubscript{e}) → NN\textsubscript{e} transfer by variable range hopping through the alloying states and multiple trapping through extended states (FX)
IV. CONCLUSION

We demonstrate and explain three distinct types of exciton transfer for excitons bound to substitutional N traps in GaAs$_{1-x}$P$_x$:N and GaIn$_{1-x}$P$_x$:N. These transfer mechanisms, related to the alloy disorder, are observed by picosecond time-resolved photoluminescence, depending on temperature. The first one occurs at low temperatures, when excitons tunnel only to lower energy sites within the band of excitons bound to isolated nitrogen (N$_i$), broadened in the GaAs$_{1-x}$P$_x$:N alloy by different As-P local configurations around nitrogen atoms (disorder broadening). The same direct tunneling is also observed in GaIn$_{1-x}$P$_x$:N. Here, however, the disorder broadening gives rise to several bands corresponding to different nearest neighbor Ga-In configurations.

The second and third types of transfer are exciton tunneling form the N$_i$ band to deeper NN$_o$ traps. GaP shows such N$_i$ $\rightarrow$ NN$_o$ transfer at low temperature; alloys do not. As the temperature is increased, however, this transfer appears in alloys with a transfer time which decreases sharply with T. Thus, the N$_i$ (A$_o$) $\rightarrow$ NN$_o$ interband transfer in alloys is thermally activated. This interband transfer happens either directly by variable range hopping, or indirectly via free excitons by multiple trapping. These two mechanisms are active here in the temperature range 30-50K.

These results, direct tunneling between and within the N$_i$ and A$_o$ bands, and the N$_i$ (A$_o$) $\rightarrow$ NN$_o$ transfers are different from those seen in GaP:N. Compared to the binary, the exciton spatial diffusion is greatly reduced in the alloy due to lower energy states which arise from the random disorder broadening and splitting. Thus, we show the importance of alloy disorder on the exciton dynamics.

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