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H. Mariette, J. Kash, D. Wolford. BOUND EXCITON TRANSFER IN WEAKLY DISORDERED SYSTEMS: III-V ALLOYS. Journal de Physique Colloques, 1985, 46 (C7), pp.C7-197-C7-201. 10.1051/jphyscol:1985737 . jpa-00225061

HAL Id: jpa-00225061

<https://hal.science/jpa-00225061>

Submitted on 1 Jan 1985

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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 $\text{Ga}_x\text{In}_{1-x}\text{P:N}$ et $\text{GaAs}_{1-x}\text{P}_x\text{:N}$ 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 $\text{Ga}_x\text{In}_{1-x}\text{P:N}$ and $\text{GaAs}_{1-x}\text{P}_x\text{:N}$ 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 $\text{A}_x\text{B}_{1-x}\text{C}$ 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 $\text{GaAs}_{1-x}\text{P}_x$ and $\text{Ga}_x\text{In}_{1-x}\text{P}$ alloys as well. In such studies, the influence of the differing local atomic configurations surrounding the nitrogen atoms has already been reported^{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_x (isolated N) exciton line in $\text{GaAs}_{1-x}\text{P}_x$ (N_x band)^{1,3}, or a splitting and broadening of this isolated N-exciton level in $\text{Ga}_x\text{In}_{1-x}\text{P}$ (N_x and A_0 bands)². Moreover the exciton lines due to the repartition of N impurities like neighboring pairs of N atoms, denoted NN_s , and which are prominent in GaP:N^4 , disappear in low-temperature PL spectra upon alloying^{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_s) and the inhomogenously broadened bands (N_x, A_0)

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_x 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

Fig. 1 cw-photoluminescence (PL) and PL-excitation spectra (PLE) of $\text{GaAs}_{1-x}\text{P}_x\text{:N}$, $x = 0.96$ [N] = 10^{18}cm^{-3} , $T = 8\text{K}$ (a) PL spectrum (solid curve) under above band gap pumping and PLE (dashed curve) observed at the LO phonon replica of the N_x 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 $\text{GaAs}_{1-x}\text{P}_x\text{:N}^7$ and in Fig. 2 for $\text{Ga}_{1-x}\text{In}_x\text{P:N}^8$. 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 (N_x and A_0) for GaP-rich $\text{Ga}_{1-x}\text{In}_x\text{P}$, 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 $\text{GaAs}_{1-x}\text{P}_x\text{:N}$ this local disorder occurs on the second nearest neighbor shell from the N impurity and the broadening of the N_x band (dashed line Fig. 1a) corresponds to the envelope of the histogram arising from the 13 exciton states due to the 13 possible As-P configurations¹. In contrast, in $\text{Ga}_{1-x}\text{In}_x\text{P:N}$ 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 A_0/N_x in $\text{Ga}_{1-x}\text{In}_x\text{P}$ is completely 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 ($< 1\text{nsec}$) resemble the cw excitation spectra. As times increases after the laser pulse, however, the TRL spectra become progressively similar to the cw luminescence one. We may also notice three main features which appear in the TRL spectra as time increases:

- (i.) The ratio between the two dominant bands A_0 (3Ga-1In neighbors) and N_x (4 Ga neighbors) in GaP-rich $\text{Ga}_{1-x}\text{In}_x\text{P:N}$ 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 N_x band in the $\text{Ga}_{1-x}\text{In}_x\text{P}$ (Fig. 2b) and for the higher energy part of the N_x band in $\text{GaAs}_{1-x}\text{P}_x$ (Fig. 1b).

Fig. 2 Same as Fig. 1 for $\text{Ga}_{1-x}\text{In}_x\text{P:N}$, $x = 0.99$ [N] = 10^{18}cm^{-3} , $T = 8\text{K}$ (a) PL spectrum (solid curve) and PLE (dashed curve). (b) Time-resolved luminescence spectra.

Fig. 3. cw-photoluminescence spectra of GaP:N and $\text{Ga}_{0.99}\text{In}_{0.01}\text{P:N}$. both (a) and (b) show PL spectra at 2K while (c) corresponds to 33K.

(iii). The dynamic energy shift within the lower energy part of the N_x band in $\text{GaAs}_{1-x}\text{P}_x$ (Fig. 1b) and within the A_0 band in $\text{Ga}_x\text{In}_{1-x}\text{P}$ (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 processing through the bound excitonic bands assisted by emission of appropriate acoustic phonons^{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 (eg. within an exciton radius) and at the same or lower energy. By modeling⁹ 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 $\text{Ga}_x\text{In}_{1-x}\text{P}$ and $\text{GaAs}_{1-x}\text{P}_x$ ⁸. We found in accord with the experiment, that the tunneling within the N_x band in $\text{Ga}_x\text{In}_{1-x}\text{P}$ and within the higher energy part of the N_x band in $\text{GaAs}_{1-x}\text{P}_x$ is much faster ≈ 1 nsec) than that within the A_0 band in $\text{Ga}_x\text{In}_{1-x}\text{P}$ and within the lower energy part of the N_x band in $\text{GaAs}_{1-x}\text{P}_x$ (≈ 50 nsec) and between the two bands N_x and A_0 in $\text{Ga}_x\text{In}_{1-x}\text{P}$ (≈ 80 nsec.). This result is a natural consequence of the smaller density of states of the A_0 centers (N surrounded by 3Ga and 1In) in GaP-rich $\text{Ga}_x\text{In}_{1-x}\text{P}$ and at the bottom of the N_x band (N surrounded by As-rich configurations) in GaP-rich $\text{GaAs}_{1-x}\text{P}_x$ as reflected in the PLE. Other spectral changes observed for the N_x and A_0 PL-bands as a function of N concentration and excitation power¹⁰ are consistent with this hopping model.

This direct tunneling assisted by phonons was first observed in GaP:N between the NN_a pair levels¹¹ 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 center¹² (triplet configuration) account for the strong intensities of all the NN_a lines at low temperature. In contrast, in the alloys we do not see any efficient $N_x \rightarrow NN_a$ transfer at low temperature (Fig. 3b). However, as the temperature

Fig. 4. Kinetics of the NN_1 luminescence at different temperatures with the laser excitation in the N_x band, for $\text{GaAs}_{0.04}\text{P}_{0.96}\text{:N}$, $[N] = 10^{18}\text{cm}^{-3}$ (a), and $\text{Ga}_{0.99}\text{In}_{0.01}\text{P:N}$, $[N] = 10^{18}\text{cm}^{-3}$ (b)

is raised, the NN_a pair lines appear in the PL spectra of both $GaAs_{1-x}P_x$ ¹³ and $Ga_xIn_{1-x}P$ (Fig 3c) while the N_x and A_o bands rapidly diminish. This evolution could be explained by the time dependence study of the NN_1 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_1 luminescence risetime¹³. For example, for $GaAs_{0.04}P_{0.96}$, the $N_x \rightarrow NN_1$ transfer takes 150 nsec at 30K and only 400 psec at 50K. At lower T the NN_1 emission is too weak compared to the underlying N_x 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 $N_x \rightarrow NN_1$ interband transfer rate progressively increases, i.e. it becomes thermally activated. By studying this T -dependence¹³ 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 (ie. free excitons of free carriers) with subsequent retrapping at either a different isolated N-site or an NN_a site. The second process is similar to variable range hopping and results from excitons tunneling solely within the N_x and A_o bands until they reach an NN_a 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_x line is mainly monoenergetic, the direct tunneling from N_x to NN_a is always unimpeded and efficient even at low temperature. Therefore, in $GaP:N$ the PL intensity increases observed for NN_a pair lines with temperature^{12,14} before the thermal quenching¹⁵ 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_x line is such that the isolated N bound exciton can tunnel efficiently to the NN_a 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_a 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 $N_x(A_o) \rightarrow NN_a$ transfer.

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

(a) GaP low T : $N_x \rightarrow NN_a$ transfer by hopping between different equivalent N_x states until the excitons reach an NN_a state on which they hop.

(b) Alloys low T : intraband and interband transfer within and between the N_x and A_o bands due to the statistical distribution of the energy levels by the alloy local disorder.

(c) GaP , $T > 10K$: $N_x \rightarrow NN_a$ transfer by hopping and multiple trapping through extended states (free excitons).

(d) Alloys, $T > 10K$: $N_x(A_o) \rightarrow NN_a$ 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 $\text{GaAs}_{1-x}\text{P}_x\text{:N}$ and $\text{Ga}_x\text{In}_{1-x}\text{P:N}$. 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_x), broadened in the $\text{GaAs}_{1-x}\text{P}_x\text{:N}$ alloy by different As-P local configurations around nitrogen atoms (disorder broadening). The same direct tunneling is also observed in $\text{Ga}_x\text{In}_{1-x}\text{P:N}$. 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 from the N_x band to deeper NN_a traps. GaP shows such $\text{N}_x \rightarrow \text{NN}_a$ 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 $\text{N}_x (\text{A}_o) \rightarrow \text{NN}_a$ 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_x and A_o bands, and the $\text{N}_x (\text{A}_o) \rightarrow \text{NN}_a$ 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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+We gratefully acknowledge support by the ONR (N00014-80-C-0376)

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