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## Direct Observation of NN Pairs Transfer in GaP<sub>1-x</sub>N<sub>x</sub> ( $x = 0.12\%$ ) \*

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*Time-resolved photoluminescence (TRPL) was applied to investigate the transient process in GaP<sub>1-x</sub>N<sub>x</sub> ( $x = 0.12\%$ ) alloy. The filling, transferring and decay processes among nitrogen pairs are directly observed. The NN<sub>4</sub> pair, either not present or only a small obscure peak under a proper excitation condition in the steady-state photoluminescence spectrum, is well resolved by TRPL.*

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GaP<sub>1-x</sub>N<sub>x</sub> alloys, or referred to as heavily nitrogen doped GaP in some articles, are known for their “Giant bowing effect” along with other modifications to the band structure and have attracted increasing studies not only for their theoretical interests but also for their potential applications in optical devices, such as light-emitting diodes (LEDs) and violet laser diodes.<sup>[1–7]</sup> The conventional nitrogen-doped GaP is usually referred to as isoelectronic impurities in semiconductors that can date back to a research field more than thirty years ago.<sup>[8–13]</sup> Since the large differences in lattice structures (GaP:zincblende, GaN:wurtzite) and the limitation of growth techniques, the doping level of nitrogen was difficult to exceed 10<sup>19</sup> cm<sup>-3</sup>, i.e. the dilute doping limit. Recently, some new growth techniques under nonequilibrium conditions have made it possible to successfully incorporate high nitrogen into GaP. Miyoshi *et al.*<sup>[2]</sup> obtained 4% in GaP<sub>1-x</sub>N<sub>x</sub>, using metalorganic vapour phase epitaxy (MOVPE). Baillargeon *et al.*<sup>[3]</sup> reported up to 7.6% N incorporation into GaP by molecular beam epitaxy (MBE), corresponding to 1.9×10<sup>21</sup> cm<sup>-3</sup> nitrogen concentration. Bi and Tu<sup>[4]</sup> showed that as high as 16% N incorporation into GaP can be achieved by gas-source molecular beam epitaxy (GSMBE), which is the highest N concentration reported previously.

At very low N concentration ( $\sim 10^{16}$  cm<sup>-3</sup>), an isolated N introduces a highly localized state in GaP. With increasing N concentration, N forms a set of bound exciton NN<sub>*i*</sub> ( $i = 1, 2, \dots, 10$ ) pairs, which exhibit a number of sharp lines with phonon replicas in photoluminescence (PL) spectra. Further increasing N concentration, the bound exciton PL bands evolve into a broad emission band, whose energy exhibits a significant red shift, i.e. a band gap reduction.<sup>[14,15]</sup> Several models have been developed to explain the band gap reduction. A phenomenological model, the

so-called “band anti-crossing” model suggests that the primary effect of nitrogen doping is to cause a repulsion between the isolated nitrogen level and the  $\Gamma$  conduction band edge.<sup>[16–18]</sup> However, the absorption spectrum of Zhang *et al.*<sup>[14,19]</sup> indicated that the peak positions of nitrogen pair states barely move with respect to the dilute limit, but they strongly broaden and merge with each other, which unambiguously disapprove the N- $\Gamma$  repulsion suggested by the band anti-crossing model.<sup>[16]</sup> Another suggested mechanism for the band gap reduction is the impurity band formation of the nitrogen bound states.<sup>[14]</sup> All existing experimental data of GaP<sub>1-x</sub>N<sub>x</sub> seem to indicate the weak role of any perturbed host states in the band edge absorption, and instead point to the formation of an impurity band from various nitrogen bound exciton states.<sup>[8,9,20–22]</sup> However, recent theoretical calculations<sup>[23]</sup> claimed that the nitrogen impurity states can not interact sufficiently so as to broaden and form an impurity band, and the band gap reduction is due to the host state “plunging down” as a result of nitrogen perturbation.

One of the significant phenomena in GaP<sub>1-x</sub>N<sub>x</sub> is that, with increasing N concentration, the sharp lines due to nitrogen pairs at the higher energy side broaden and quench sequentially in the order of increasing energy. At the same time, a broad emission band arises at the lower energy side of the NN<sub>*i*</sub> line. The selective excitation PL spectrum of Zhang *et al.*<sup>[14]</sup> reveals that the states in the broad emission band are nothing but nitrogen bound exciton states with different local environments. Such a phenomenon is interpreted as carriers transferring effect, from the higher energy side of nitrogen pairs to the lower energy side, and has been identified during the thermal quenching process or by the intensity-dependent PL spectrum,<sup>[10,11]</sup> but not been directly observed yet.

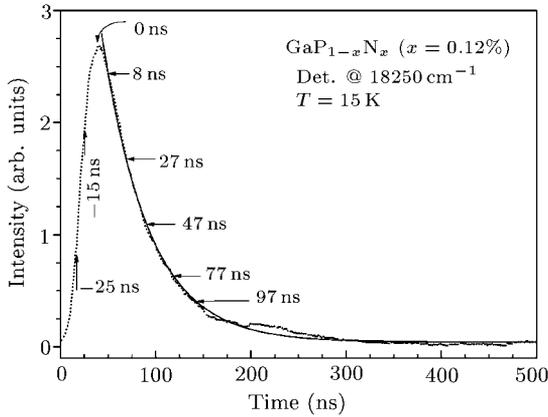
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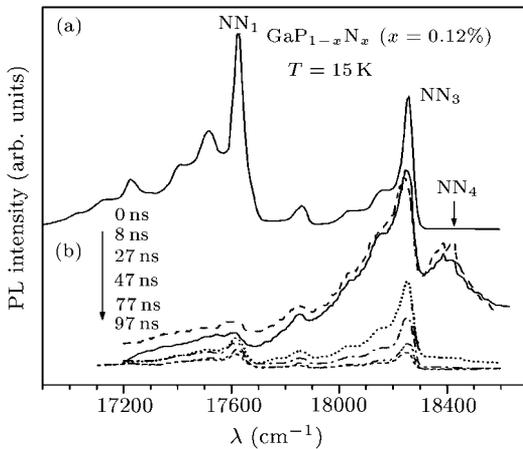
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In this Letter, time-resolved photoluminescence (TRPL) was applied to investigate the transient process in  $\text{GaP}_{1-x}\text{N}_x$  ( $x = 0.12\%$ ) alloy. The filling, transferring and decay processes among nitrogen pairs are directly observed. The  $\text{NN}_4$  pair, either not present or only a small and obscure peak under a proper excitation condition in the steady-state PL spectrum, is well resolved by TRPL.

The  $\text{GaP}_{1-x}\text{N}_x$  sample was grown on a (100) GaP substrate by gas-source molecular beam epitaxy. For the GaP buffer layer, the growth temperature was  $640^\circ\text{C}$ . For GaPN epitaxy layer (250 nm in thickness), the growth temperature was decreased to  $520^\circ\text{C}$  to incorporate N. The sample was mounted in a CSA-202E closed cycle cryostat with the temperature changed within 15–80 K.



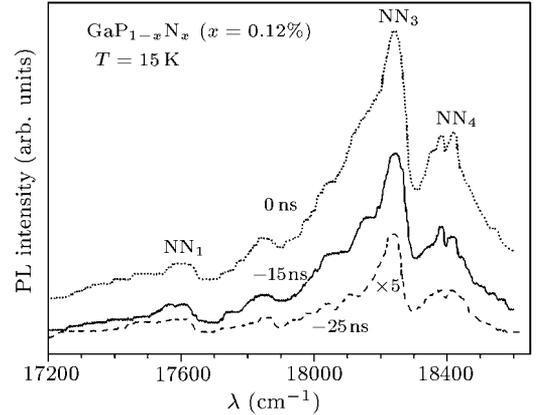
**Fig. 1.** Rising and decay process of  $\text{NN}_3$  bound exciton pair in  $\text{GaP}_{1-x}\text{N}_x$  ( $x = 0.12\%$ ) at 15 K with the detected wavenumber set at  $18250\text{ cm}^{-1}$ .



**Fig. 2.** (a) Steady-state PL spectrum of  $\text{GaP}_{1-x}\text{N}_x$  ( $x = 0.12\%$ ), excited by cw  $\text{Ar}^+$  laser. (b) TRPL spectra of  $\text{GaP}_{1-x}\text{N}_x$  at 15 K, demonstrating the transferring effect of carriers. The delay time is labelled in Fig. 1.

For the steady-state PL measurement, the 514.5 nm line of a cw  $\text{Ar}^+$  laser was used as the excitation source. A pulsed Nd:YAG laser operated at

532 nm with 30 Hz repetition rate, 5-ns pulse FWHM, and about 20 kW peak power was applied for the TRPL and lifetime measurement. The signal was collected and analysed by a 1.0-m GDM-1000 double grating monochromator, a cooled C31034 photomultiplier and a PAR124A lock-in amplifier (for steady-state PL measurement), a 165Boxcar averager (for TRPL and lifetime measurement).



**Fig. 3.** TRPL spectra of  $\text{GaP}_{1-x}\text{N}_x$  ( $x = 0.12\%$ ) at 15 K, displaying the filling process of carriers during excitation. The monitored time is labelled in Fig. 1.

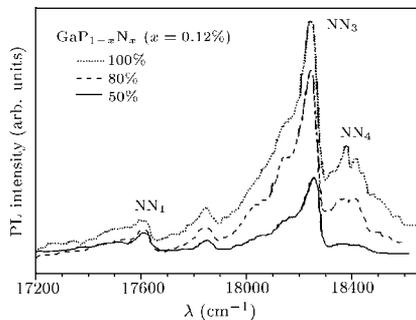
Figure 1 shows a typical rising and decay spectrum of  $\text{GaP}_{1-x}\text{N}_x$  with the detected wavenumber set at  $18250\text{ cm}^{-1}$ . To measure the TRPL spectrum, the peak in the spectrum shown in Fig. 1, where the excitation procedure ceases, is defined as zero time, i.e. the starting reference time for the TRPL spectrum. With a set of delay times, the TRPL spectra are shown in Fig. 2 together with a steady-state PL spectrum for comparison. As shown in Fig. 2(a), the  $\text{NN}_4$  Ga bound exciton pair does not appear in the steady-state PL spectrum, although its absorption energy level has been identified in the photoluminescence excitation (PLE) spectrum,<sup>[14,19]</sup> (in Ref. [14] the  $\text{NN}_4$  bound exciton pair is shown as a small and obscure peak, with proper excitation energy adjusted). However, in the transient PL spectra as shown Fig. 2(b), the fine structure of  $\text{NN}_4$  pairs is clearly observed and its peak position keeps stable as compared with the energy position at lower nitrogen concentration  $\text{GaP}_{1-x}\text{N}_x$  alloys.<sup>[14,15]</sup> Thus, this fact, in coherent with the PLE result, further disapproves the band anti-crossing model, in which an N- $\Gamma$  repulsion is predicted.<sup>[16]</sup> From the TRPL spectra, one can also observe the different decay and transferring speeds of different  $\text{NN}_i$  pairs. Apparently,  $\text{NN}_4$  has a decay speed larger than  $\text{NN}_3$  and  $\text{NN}_1$ , and carriers transfer from the  $\text{NN}_4$  level to lower energy levels during their decay process, leading to comparatively enhanced intensities of lower energy levels, which can be clearly seen from the PL spectrum at 8-ns delay time. After

47-ns delay, the  $NN_4$  can hardly be observed in the PL spectrum. On the contrary, the  $NN_1$  has little change in intensity with the delay time, and gradually dominates the luminescence. After 97-ns delay, the profile of the transient PL spectrum is very similar to that of the steady-state PL spectrum.

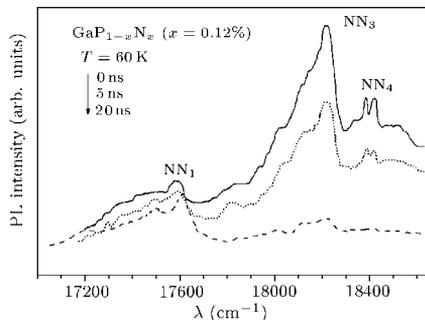
To examine the filling process of carriers during excitation, two points before the zero time are set to monitor the PL spectra at 15 K, as shown in Fig. 3. The filling process of carriers displays a reverse procedure as compared with the decay process, i.e., a “last-in-first-out” procedure. The luminescence of  $NN_4$  pairs is very weak at the beginning of excitation, but gradually enhanced with the filling of  $NN_1$  and  $NN_3$  pairs in sequence. The filling process is further identi-

fied by the excitation-intensity-dependent PL spectra, as shown in Fig. 4, with the sequential saturation of  $NN_1$  and  $NN_3$  pairs, the intensity of  $NN_4$  pairs gradually increases and displays fine structure.

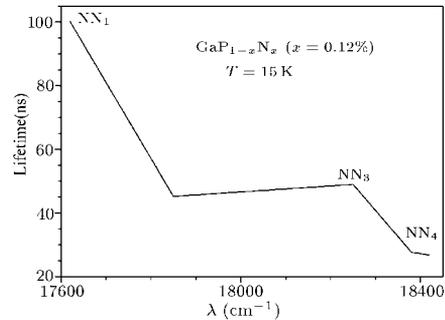
With increasing temperature up to 60 K, the more active thermal quenching speeds up the transferring process from  $NN_4$  to  $NN_3$  and  $NN_1$  pairs as revealed in Fig. 5, from which one can clearly see the transferring process almost ends up around 20 ns and is much faster than that at 15 K (see Fig. 2). It is believed that the transferring effect is responsible for the much longer lifetime of  $NN_1$  than that of  $NN_4$ , whose lifetime can be roughly used for estimating the transferring time, as shown in Fig. 6.



**Fig. 4.** PL spectra as a function of excitation intensity in  $\text{GaP}_{1-x}\text{N}_x$  ( $x = 0.12\%$ ) at 15 K.



**Fig. 5.** TRPL spectra of  $\text{GaP}_{1-x}\text{N}_x$  ( $x = 0.12\%$ ) at 60 K.



**Fig. 6.** Lifetime as a function of detected wavenumber in  $\text{GaP}_{1-x}\text{N}_x$  ( $x = 0.12\%$ ) at 15 K.

In summary, using TRPL, a useful tool for studying the transient PL spectra in  $\text{GaP}_{1-x}\text{N}_x$  ( $x = 0.12\%$ ) alloy, not only the excitation process but also the transferring and decay processes among carriers can be effectively studied. The  $NN_4$  pair, either not present or only a small and obscure peak under a proper excitation condition in the steady-state PL spectrum, is clearly observed in the transient PL spectrum. The filling and decay processes of  $NN_4$  pairs are completely reverse to that of  $NN_1$  pairs. Moreover, the transferring time between NN pairs can be roughly estimated by the lifetime of  $NN_4$  pairs. The phenomenon further disapproves the N-I repulsion predicted by the band anti-crossing model.

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