MRS Internet Journal of Nitride Semiconductor Research

*Volume 2, Article 32*

# Exciton dynamics in thick GaN MOVPE epilayers deposited on sapphire.

J. Allègre, P. Lefebvre, J. Camassel
Groupe d'Etude des Semiconducteurs, GES-CNRS

B. Beaumont, Pierre Gibart
Centre de Recherche sur l'Hetero-Epitaxie et ses Applications, CRHEA-CNRS

This article was received on June 10, 1997 and accepted on September 15, 1997.

## Abstract

Time-resolved photoluminescence spectra have been recorded on three GaN epitaxial layers of thickness 2.5 µm, 7 µm and 16 µm, at various temperatures ranging from 8K to 300K. The layers were deposited by MOVPE on (0001) sapphire substrates with standard AlN buffer layers. To achieve good homogeneities, the growth was in-situ monitored by laser reflectometry. All GaN layers showed sharp excitonic peaks in cw PL and three excitonic contributions were seen by reflectivity. The recombination dynamics of excitons depends strongly upon the layer thickness. For the thinnest layer, exponential decays with $\tau$ ~ 35 ps have been measured for both $X_A$ and $X_B$ free excitons. For the thickest layer, the decay becomes biexponential with $\tau_1$ ~ 80 ps and $\tau_2$ ~ 250 ps. These values are preserved up to room temperature. By solving coupled rate equations in a four-level model, this evolution is interpreted in terms of the reduction of density of both shallow impurities and deep traps, versus layer thickness, roughly following a $L^{-1}$ law.

## 1. Introduction

The recombination dynamics of excess carriers in group III-nitrides is increasingly appearing as a key issue for the optimization of blue-light emitting diodes and lasers based on various combinations of GaN, GaInN and GaAlN layers - more particularly, concerning GaN, the relationship between the different growth parameters and the free and bound exciton intensities. The recombination dynamics has been considered by several groups. The following has been found. First, for micrometric layers of hexagonal GaN deposited on sapphire, the near-band edge emission spectrum appears dominated by excitonic recombinations. In most cases, the salient contribution arises from donor-bound excitons ($D^0X$) while free excitons associated with the two upper valence bands ($X_A$ and $X_B$) have been also identified in high quality material. A safe way to confirm the assignment of the residual-strain dependent photoluminescence (PL) lines is to perform a close comparison with reflectance spectra. Second, once properly identified, different investigations have provided reliable measurements of the decay time constant associated with the various recombination channels.

Concerning the free excitons, mainly fast decay times have been reported. At 10K, they range from 14 ps to 35 ps for MOVPE micrometric layers grown on $Al_2O_3$ substrates [1] [2] [3] [4] [5] [6] [7]. Strongly different values, ranging from 6 ps [8] to ~170-200 ps [9] have been published for thick HVPE layers. Finally, decay times of up to 0.22 ns in high-quality MBE-grown samples have been reported [10] [11] [12]. The latter value was obtained, however, by using a ~70 ps temporal resolution setup. All fast decay times have been unanimously assigned to parasitic non-radiative processes. Similar results have been reported for the so-called $I_2$ line, i.e. the shallow-donor-bound exciton ($D^0X$). Decay times of ~50-260 ps [1] [2] [3] [4] [5] [6] [7] [9] have been reported for MOCVD and up to ~600 ps in better MBE-grown layers. While convincing attempts have been made to correlate fast decays to various parameters such as, for instance, the intensity of the low-energy "yellow luminescence" [3] [13] or the presence of defects near the substrate-layer interface [7], up to now, no significant attempt to reach a limit close to the high value reported in MBE has been done using MOVPE.

https://doi.org/10.1557/S1092578300001587 Published online by Cambridge University Press

Since the local density of defects in most hetero-epitaxial systems is a sensitive function of the sample thickness [14], we investigate in this work the change of excitonic recombination time versus sample thickness. We have used 3 epitaxial layers of hexagonal GaN deposited on sapphire by MOVPE. Their respective thicknesses were 2.5, 7 and 18 μm. We have performed time-resolved PL measurements at various temperatures ranging from 8K to 300K, and found a strong influence of the thickness on the excitonic recombination time. Our results are consistent with an $L^{-1}$ dependence of the concentration of deep traps near the sample surface.

## 2. Presentation of samples

The three different GaN layers are referred to as samples 1 to 3. They were grown at atmospheric pressure by MOVPE on nominal C face sapphire substrates. After nitridation of the sapphire at 1050°C in $NH_3$ ambient, a 10 nm thick AlN buffer layer is first deposited at low temperature (800°C) followed by the growth at 1080°C of the GaN epilayer. These layers were grown with the same condition i.e. partial pressure of trimethyl gallium and ammonia respectively being $10^{-4}$ and 0.33 Atm in $N_2$ carrier gas. The growth rate was about 2.3 μm/h.

Preliminary measurements by time-integrated PL spectroscopy, cw PL, reflectivity, X ray diffraction and TEM (Transmission Electron Microscope) has been performed. Rocking curve FWHM (w scan) are 120, 240 and 320 arc-sec for sample 1 (2.5 μm), 2 (7 μm) and 3 (18 μm) respectively. The increase in the FWHM is correlated to the increasing curvature. For the thicker sample, a curvature radius as small as 0.9 m has been deduced from X Ray measurements. TEM plane view of the thinner sample yields an emerging dislocation density in the range of $10^9$ $cm^{-2}$.

## 3. Time-resolved spectroscopy setup

The samples were kept at a regulated temperature ranging from ~8 K to 300 K, by gluing them onto the cold finger of a helium closed-cycle cryostat. The excitation consisted of UV-laser pulses with temporal width of ~2 ps, centered at λ~270 nm. The repetition frequency was 82 MHz. The UV pulses have been produced by tripling the λ~802 nm radiation of a Ti-sapphire cavity, by using a nonlinear crystal. The emitted light was analyzed through a 0.5 m focal length spectrometer, and detected by a Hamamatsu synchroscan streak camera. The temporal response of this setup to ultrashort laser excitation is broadened to a typical full width at half maximum of ~15 ps. After deconvolution of the PL decay from this response, the temporal resolution of the setup,is of the order of 5 ps. The current repetition rate of one pulse every 12 ns prevents any accurate measurement of decay times larger than ~15 ns.

## 4. Experimental results

Figure 1 displays the change in time-integrated PL spectrum observed on sample 1 versus temperature. Mainly three lines are seen and have been identified, according to the cw measurements. The energy difference between the $D^0X$ line (3.476 eV) and the recombination of free $X_A$ excitons (~3.482 meV) is 5.7 meV. The strong thermal quenching of the low-energy component comes from the increasing rate of excitation from the $D^0X$ state to the free exciton continuum [3] [4] [7]. This experimental observation warrants our previous identification. The PL spectrum of sample 2 is not shown but presents very similar features, with $D^0X$, $X_A$ and $X_B$ lines at 3.473, 3.479 and 3.485 eV, respectively. Coming now to the time-integrated spectrum of sample 3, we find a totally different behavior. This is shown in Figure 2. Clearly the separate contributions of $D^0X$, $X_A$ and $X_B$ lines are no longer resolved and the overall line shape remains unchanged up to 100 K. Since, in this case, the line at 3.475 eV cannot be assigned to the recombination of $D^0X$ states, we conclude that only free excitons are seen. The recombination dynamics of exciton states at T = 8K appears strongly dependent of the layer thickness. This is shown in Figure 3. In this case both $X_A$ and $X_B$ excitons exhibit an exponential decay, with τ ~ 35 ps for sample 1 and τ ~ 80 ps for sample 2. The temporal behavior of emission for sample 3 appears very different. First the decay rate is the same in all regions of the spectrum between 3.47 and 3.49 eV . Second (see Figure 3) this decay is much slower than noticed for samples 1 and 2. Third, it is not really monoexponential. Indeed, standard fitting procedures can yield either a biexponential decay (with ~80 ps and ~250 ps time constants) or an average value of about 160 ps (if a single exponential rate is assumed) with a smaller correlation coefficient. It is interesting to notice that, due to the unusual layer thickness, the free exciton decay times observed on samples 2 and 3 are among the largest values observed so far on any MOVPE-grown GaN sample. Another difference to be noticed between our 3 samples lies in the rise times of the PL. It increases slightly with layer thickness. Finally, as shown in Figure 4, the dynamics of

https://doi.org/10.1557/S1092578300001587 Published online by Cambridge University Press

excitonic recombinations in sample 3 does not change much when heating the sample up to 300 K.

To account (at least qualitatively) for the above observations, we have solved the coupled rate equations corresponding to the four-level model sketched in Figure 5. All usual transfer channels have been shown by arrows. The number of adjustable parameters (time constants, donor and deep trap densities) as well as the simplicity of the initial conditions (we assume that all excitons are in a single free-exciton state FX at t=0) allow us only to deduce general trends. Nevertheless, the interesting point is that we could reproduce the measured decay times and the relative time-integrated intensities of the $D^0X$ and FX recombination lines, observed at various temperatures, by using only a restricted series of parameters. More important, we have found that the difference between our three samples can be interpreted, using this simple model, in terms of a simple diminution of donor and deep trap densities, with respect to the constant density of photo-injected carriers. For the three samples, all measurements have been reproduced by assuming the following :

i. a long-lived population of deep traps with $\tau_{DT} \sim 20$ ns (this value can be tuned down to 5 ns with no real change in results) ;

ii. a radiative decay time of 300 ps for the free excitons at 8K (this value is in reasonable agreement with previous evaluations [4] and has a decisive influence on the resulting time-integrated relative amplitudes of the $D^0X$ and FX emissions) ;

iii. a thermal emission time of $\tau_{\infty} = 5$ ps, also comparable to previously reported values [7]. An overall decay time for the donor-bound exciton $\tau_{DX} \sim 35$ ps has been kept to describe all samples at all temperatures.

Assuming this rather standard series of parameters, the entire set of data could be satisfactorily reproduced by changing only the densities of donors ($N_D$) and deep traps ($N_{DT}$). Moreover, for simplicity, we always kept the density of donors equal to the density of deep traps. Finally, it is important to remark that we assume a variation of $\tau_{FXDX}$ and $\tau_{FXDT}$ capture times compatible with classical Shockley-Read processes, i.e. $\tau_{FXDX}{}^{-1} \sim N_D \cdot T^{1/2}$ and $\tau_{FXDT}{}^{-1} \sim N_{DT} \cdot T^{1/2}$. In this case, the sensitive parameter becomes only the ratio of the density of deep traps to the density of injected free excitons at t = 0.

The main result of our systematic approach is to show that the density of impurities decreases from sample 1 to sample 3 by following, roughly speaking, a 7 - 3 - 1 sequence. The corresponding capture times are $\tau_{FXDX}$ = 170, 400 and 1200 ps and $\tau_{FXDT}$ = 55, 130 and 400 ps, respectively.

## 5. Discussion and conclusion

It is interesting to notice that the deduced density of deep traps varies almost linearly with the inverse layer thickness L. In other words we find from our simple model that the effective densities of traps, probed near the surface of the sample, should follow a 1/L law. Keeping the latter proposal as a working hypothesis, we obtain the prospective graph of Figure 6. It displays the expected layer thickness dependence of the decay time of free excitons in GaN epitaxial layers grown by MOVPE on sapphire substrates, assuming three asymptotic values of the radiative free exciton lifetime. Up to now, the comparison with data extracted from the literature is difficult, since all available measurements lie in the 1-4 µm range (when the layer thickness is given). Nevertheless, we have put a few points from other works on this graph. We believe that the central curve in Figure 6 constitutes a comparison basis for further investigation of the overall decay time of free excitons versus layer thickness.

## References


[1] C. I. Harris, B. Monemar , H. Amano, I. Akasaki , *Appl. Phys. Lett.* ***67***, 840-842 (1995).

[2] G. D. Chen, M. Smith, J. Y. Lin, H. X. Jiang , M. Asif Khan, C. J. Sun , *Appl. Phys. Lett.* ***67***, 1653-1655 (1995).

[3] W. Shan, T. Schmidt, X. H. Yang, J. J. Song , B. Goldenberg , *J. Appl. Phys.* ***79***, 3691-3696 (1996).



https://doi.org/10.1557/S1092578300001587 Published online by Cambridge University Press

[4] A Hangleiter, JS Im, T Forner, V Härle, F Scholz, *Mater. Res. Soc. Symp. Proc.* ***395***, 559 (1996).

[5] K Okada, Y Yamada, T Tagushi, F Sasaki, S Kobayashi, T Tani, S Nakamura, G Shinomiya, *Jpn. J. Appl. Phys.* ***35***, L787 (1996).

[6] Y Kawakami, ZG Peng, Y Narukawa, S Fujita , S Fujita , S Nakamura, *Appl. Phys. Lett.* ***69***, 1414-1416 (1996).

[7] BK Meyer, D Volm, C Wetzel, L Eckey, JC Holst, P Maxim, R Heitz, A Hoffmann, I Broser, EN Mokhov, PG Baranov, C Qiu, *Mater. Res. Soc. Symp. Proc.* ***378***, 521-6 (1995).

[8] L. Eckey, R. Heitz, A. Hoffmann, I. Broser, B. K. Meyer, K. Hiramitsu, T. Detchprohm, H. Amano, I. Akasaki, *Inst. Phys. Conf. Ser.* ***142***, 927 (1996).

[9] J. P. Bergman, B. Monemar, H. Amano, I. Akasaki, K. Hiramatsu, N. Sawaki, T. Detchprohm, *Inst. Phys. Conf. Ser.* ***142***, 931 (1996).

[10] M. Smith, G. D. Chen, J. Y. Lin, H. X. Jiang , A. Salvador, B. N. Sverdlov, A. Botchkarev, H. Morkoc , *Appl. Phys. Lett.* ***66***, 3474-3476 (1995).

[11] G. D. Chen, M. Smith, J. Y. Lin, H. X. Jiang , A. Salvador, B. N. Sverdlov, A. Botchkarv, H. Morkoc , *J. Appl. Phys.* ***79***, 2675-2683 (1996).

[12] M. Smith, G. D. Chen, J. Z. Li, J. Y. Lin, H. X. Jiang , A. Salvador, W. K. Kim, O. Aktas, A. Botchkarev, H. Morkoc , *Appl. Phys. Lett.* ***67***, 3387-3389 (1995).

[13] J. J. Song, W. Shan, T. Schmidt, X. H. Yang, A. Fisher, S. W. Hwang, B. Taheri, B. Goldenberg, R. Horning, A. Salvador, W. Kim, Ö. Atkas, A. Botchkarev, H. Morkoç, *Proc. SPIE* ***2693***, 86-96 (1996).

[14] L. A. Falkowsky, J. M. Bluet, J. Camassel, *Phys. Rev. B* ***55***, R14697 (1997).

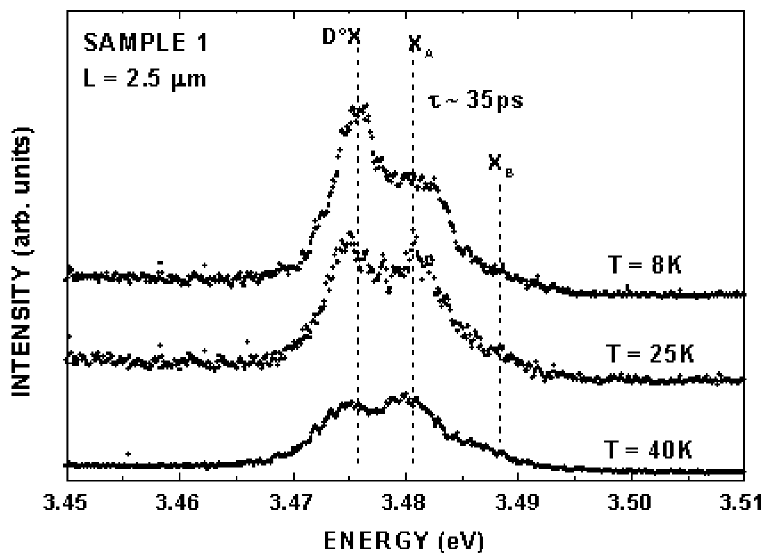


**Figure 1**. Evolution of the time-integrated spectrum of sample 1 versus temperature.

https://doi.org/10.1557/S1092578300001587 Published online by Cambridge University Press

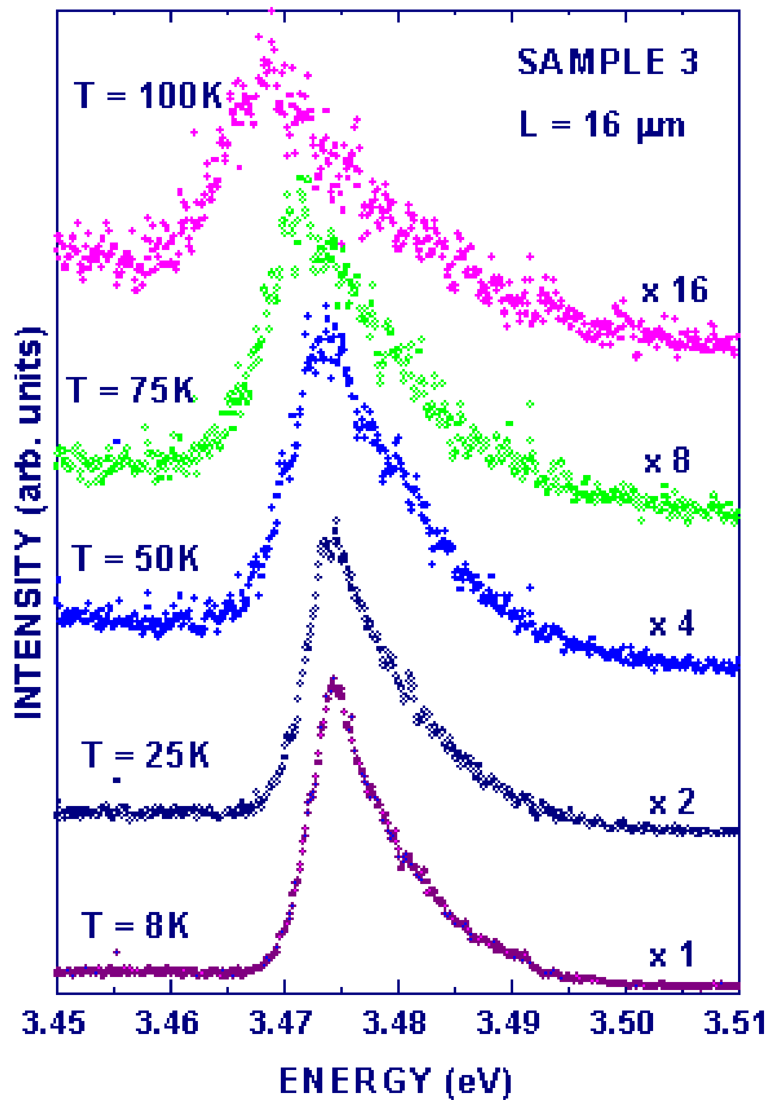


**Figure 2**. Evolution of the time-integrated PL spectrum of sample 3 versus temperature.

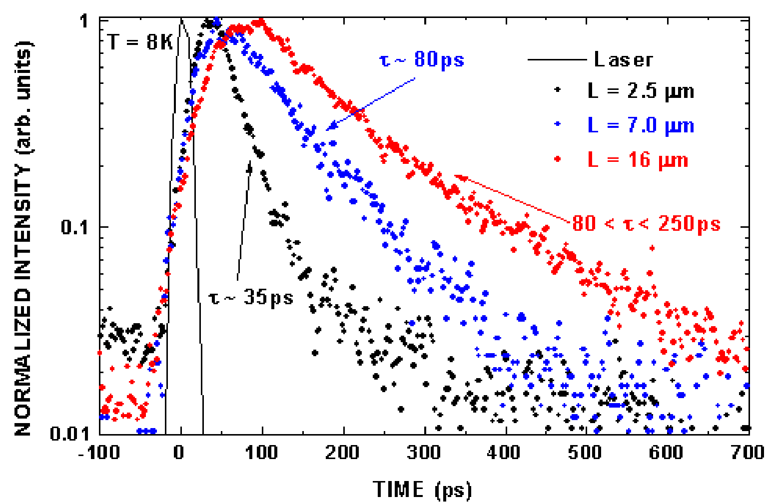


**Figure 3**. Decays of the free-exciton PL intensities recorded for samples 1-3.

https://doi.org/10.1557/S1092578300001587 Published online by Cambridge University Press

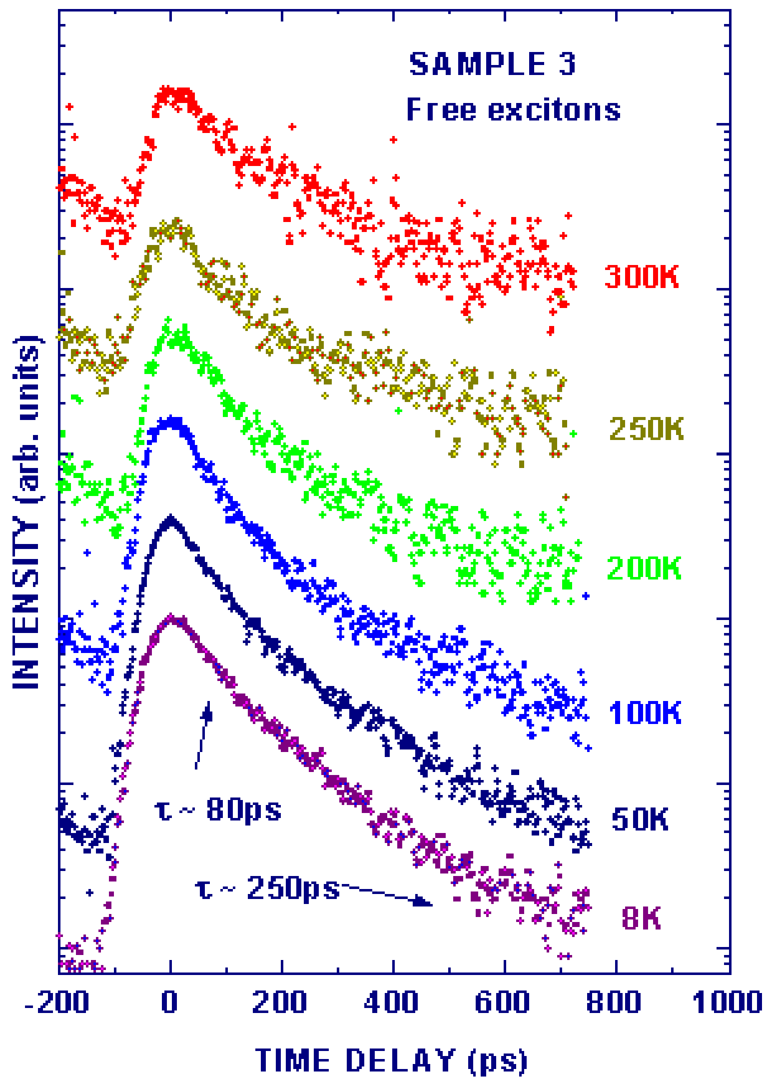


**Figure 4**. Evolution of the decay of free-exciton PL intensity, for sample 3, versus temperature.

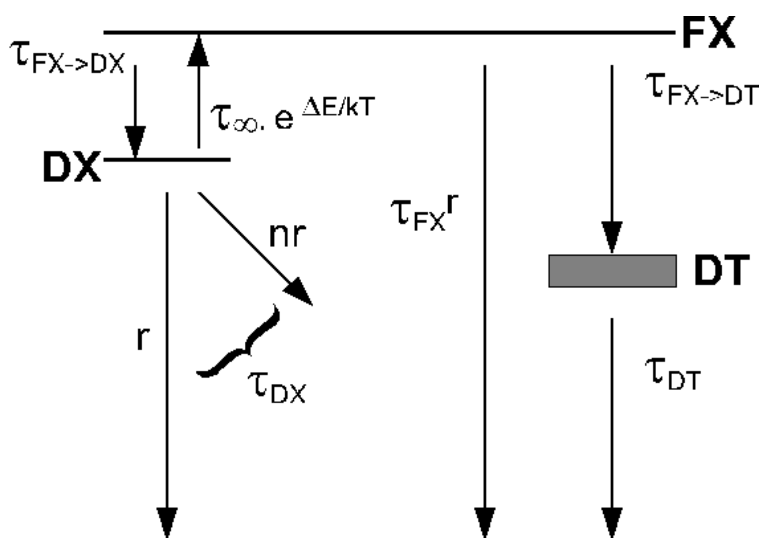


**Figure 5**. Schematic view of the 4-level model used to describe the present series of experimental results.

https://doi.org/10.1557/S1092578300001587 Published online by Cambridge University Press

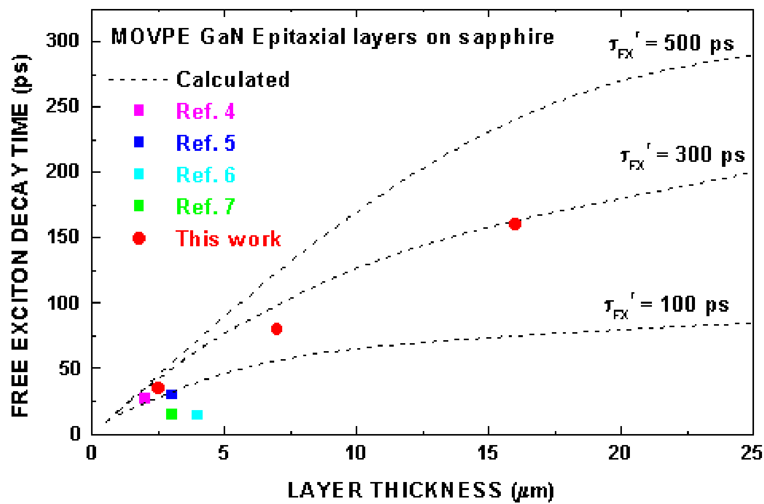


**Figure 6**. Dashed line : prospective estimate of the overall decay time constant of free excitons in MOVPE epitaxial layers of hexagonal GaN on sapphire, plotted versus layer thickness. Three asymptotic radiative lifetimes of 100, 300 and 500 ps have been considered.

© 1997 The Materials Research Society



https://doi.org/10.1557/S1092578300001587 Published online by Cambridge University Press