M R S Internet Journal of Nitride Semiconductor Research

Volume 2, Article 28

Yellow luminescence in Mg-doped GaN

F. J. Sánchez, F. Calle, D. Basak, J. M. G. Tijero, M. A. Sánchez-García, E. Monroy, E. Calleja, E. Muñoz
Dpt. Ingeniería Electrónica, E.T.S.I. Telecomunicación, Politécnica, Ciudad Universitaria

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

J.J. Serrano, J.M. Blanco
Dpt. Ingeniería Electrónica, E.T.S.I. Telecomunicación, Politécnica, Ciudad Universitaria

This article was received on June 11, 1997 and accepted on September 12, 1997.

Abstract

Optical thresholds, that correspond to a level located at 1 eV above the valence band, are observed by photocapacitance techniques in n-type Mg-doped GaN. In undoped GaN, this level has been previously related to the yellow emission detected by photoluminescence. In Mg-doped GaN, this yellow luminescence is only observed for excitation energies below the Mg-related band (2.9 - 3 eV). This result evidences that Mg-doping may reduce but not avoid the formation of the yellow band related defects in n-type and semiinsulating Mg-doped samples. The fact that the yellow luminescence is not observed for excitation energies above the bandgap may be justified by a higher efficiency of the Mg-related recombination path.

1. Introduction

The group III nitrides technology has reached in the recent years a great development in the short-wavelength emitting devices field. The first blue cw laser operating at room temperature has been demonstrated [1]. Concerning blue and UV emitters, care must be paid to non radiative recombinations or alternative radiative recombination paths, which may be detrimental to the device performance. This may be the case of the yellow luminescence, a broad band centered at 2.2 eV, which is observed in undoped and n-type doped GaN, regardless the growth technique used. This emission was interpreted by Ogino and Aoki [2] and later by Hofmann et al. [3] as a transition from a shallow donor to a deep acceptor located at about 1 eV above the valence band (VB). Recent experimental and theoretical results support this model [4] [5] [6] [7].

Several authors have reported on the reduction of the yellow band in n-doped GaN, like Nakamura et al. that observed a moderate decrease of the absolute intensity of the yellow band in Ge and Si doped samples [8]. The yellow emission can also be reduced and even suppressed by doping with Mg [9], or growing on Ga-rich conditions [10]. Neugebauer and Van de Walle suggest from first principles calculations that the yellow emission is related to a deep level generated by a complex defect involving Ga vacancies [7], whose formation energy increases in semiinsulating or p-type GaN. That result would explain the abscence of the yellow band in highly Mg-doped GaN [9].

In this work, photocapacitance measurements of Mg-doped GaN are performed over a photon energy range of 0.5 to 3.5 eV, to study the presence of deep levels. The results are compared with photoluminescence (PL) spectra excited above and below the bandgap.

2. Experimental.

https://doi.org/10.1557/S109257830000154X Published online by Cambridge University Press

The GaN samples were grown at 1080°C by metal organic vapour phase epitaxy (MOVPE) on (0001) oriented sapphire substrates [11]. Ammonia and trimethylgallium (TMG) served as precursors, and biscyclopentadienil magnesium (cp_2Mg) was used for the Mg doping. Typical thickness was 1-3.5 μm, and an AlN buffer layer (100Å) was incorporated to the structure. The doping level was controlled with cp_2Mg flux, from 50 to 300 sccm. Just after growth, samples were annealed at 750 - 800°C for 30 minutes in a nitrogen atmosphere, in order to activate the Mg acceptors. In spite of that, they resulted n-type ($n \approx 10^{17}$ - $10^{18} cm^{-3}$) or semiinsulating. Figure 1 shows the Mg concentration profiles of three samples with different doping levels, measured by secondary ion mass spectroscopy (SIMS). The concentration varies from $10^{18} cm^{-3}$ (150 sccm) to $3 \times 10^{19} cm^{-3}$ (300 sccm), with a rather flat profile for high Mg-doping. Mg concentration profile is not shown for samples doped with Mg-flux of 50 sccm, because the Mg concentration was below the detection limit of the technique (less than 10^{16} atoms/cm^3).

Photoluminescence was excited at 4 K and room temperature with the 334, 458, 488, and 514 nm lines of an Ar+ laser. The emission was dispersed by a Jobin-Yvon THR1000 and a Jarrell - Ash 25-100 monochromators. The signal was detected with a GaAs photomultiplier.

Schottky diodes were fabricated by Au evaporation, and ohmic contacts were obtained with Ti/Al. Photocapacitance measurements were performed at 20 K, using a Boonton 7200 capacitance meter and a 600W Globar (quartz-tungsten) lamp, with a Jobin-Yvon H-25 monochromator.

3. Results and discussion.

PL spectra of Mg-doped samples with increasing Mg concentration under above-bandgap excitation (334nm) are shown in figure 2. The shape and position of the PL Mg-related peak evolves with increasing Mg doping level from a narrow peak at 3.28 eV with clear LO phonon replicas (samples C and D), to a broad band centered at 2.9 - 3 eV (samples A and B) [12]. The structure resolved in sample A corresponds to Fabry-Perot interferences. In a recent work, Smith et al. [13] attribute the 2.9 eV band observed by PL to a free electron to bound hole recombination involving Mg complexes in p-type Mg-doped GaN. Myoung et al. [14] find by PL two different Mg-related complex levels at 2.43 and 2.87 eV in p-type samples ($p \approx 2.7 \times 10^{18}$ cm^{-3}).

Photocapacitance measurements have been performed in undoped samples ($n \approx 10^{17} cm^{-3}$) and Mg-doped samples. Typical photocapacitance spectra for an n-type Mg doped GaN sample (curve 1b) and an undoped sample (curve 1a) are shown in figure 3. The spectra were recorded after cooling the samples down to 20 K in the dark, at zero bias. The photon energy scan was then performed from 0.5 eV to 3.5 eV. Just like in undoped material [4] [5], there is an optical threshold between 2.0 and 2.5 eV, and the band edge absorption is also observed at 3.5 eV in both samples. The arrow at 3 eV in curve 1b (figure 3b) indicates a region where an increase in capacitance might correspond to absorption by Mg-related levels. The capacitance step at 2.5 eV was associated to a level located at 2.5 eV below the conduction band in undoped GaN [4] [5], and it is likely the same level observed in Mg doped GaN (see the 2.5 eV transition from that level to the CB in the insets of figure 3a and 3b). Yi and Wessels [15] obtain similar spectra for highly Mg-doped n-type GaN, detecting a clear capacitance step at 2.5 eV, and a continuous increment between 2.9 eV and 3.2 eV, and Götz et al. [16] report on the same photocapacitance features at 2.1 eV and 3 eV for p-type samples.In a very recent work, Qiu et al [17] obtained similar results by photocurrent spectroscopy, observing photocurrent steps at 2 and 3 eV in p-type material with room-temperature electric resistivity around 10^4 Ωcm.

Curves 2a and 2b (figure 3a and 3b) show the photocapacitance spectra obtained for undoped and Mg-doped GaN respectively, after illuminating the samples at 20 K with photons of 3.5 eV for 1 hour, switching off the light and waiting for 1 hour in the dark, until capacitance reaches a persistent steady state, as described previously [4] [5]. The illumination with a photon energy of 3.5 eV empties all the levels in the diode space charge region, and the electric field generated by the Schottky barrier sweeps out the photoexcited electrons, reducing the recombination rate and leading to a persistent photocapacitance value higher than that measured in the dark, for both kind of samples. When the photon energy scan proceeds, a continuous decrease in the photocapacitance is observed from 0.5 eV to 0.9 eV for the Mg-doped sample. In spite of Mg-doping, the material is n-type, thus a decrease in the capacitance is interpreted as a positive charge reduction in the space charge region. This reduction is produced by the capture of electrons from the VB by levels located in this energy range, which agrees with the position of the Mg-related blue band observed by PL in samples A and B (figure 2). When the photon energy scan starts, electrons are emitted from the VB, filling these levels, and therefore the total device capacitance is reduced (see the transition from the VB to the band centered 0.6 eV above in the inset of figure 3b). In contrast, this decrease is not observed in undoped material for the energy range from 0.5 to 0.9 eV.

https://doi.org/10.1557/S109257830000154X Published online by Cambridge University Press

The abrupt step detected at 1 eV in the undoped sample (curve 2a in figure 3a) is related to the electron capture from the VB by a level located 1 eV above, and was previously related to the yellow emission in undoped GaN [4] [5]. A weak step in the photocapacitance can also be observed at 1 eV for Mg-doped GaN (curve 2b in figure 3b), that is likely related to the filling of a level at 1 eV from the VB (see the 1 eV transition in the insets of figures 3a and 3b). Thus, the level responsible for the yellow band might be still present in Mg-doped samples, although in less concentration than in undoped samples, considering the capacitance step amplitude.

Described photocapacitance experiments suggest that there should be a level located at 1 eV from the VB very similar to that reported in undoped samples. As it was described above, a correlation between this level and the yellow emission was previously established. However, the yellow band observed by PL in undoped GaN has not been detected in Mg-doped samples (see figure 2). This fact might be related either to the reduction of the defects that generate the level at 1 eV by Mg doping, or to the introduction of a new and more efficient recombination path, which competes with the yellow emission. In order to excite the yellow band emission, avoiding the Mg related band (2.9 - 3 eV), PL under below-bandgap excitation was performed, and the results are shown in figures 4a and 4b. Four different laser lines have been used, 334 nm (3.71 eV), 458 nm (2.71 eV), 488 nm (2.54 eV) and 514 nm (2.41 eV). In these figures, we can compare the yellow emission observed with above and below bandgap excitation in undoped material [5] (figure 4a) with that generated in a Mg-doped sample (figure 4b). The yellow emission is not observed for above bandgap excitation (3.71 eV) in the Mg-doped sample. The decrease in the emission intensity observed in figure 4b when exciting with smaller energies below bandgap, is probably due to a lower absorption. This behavior was previously reported by Hofmann et al. [3] in undoped material, where photoluminescence excitation (PLE) spectra of the yellow emission reveals a decrement of the absorption with decreasing energy from 2.8 to 2.4 eV.

From the measurements described above, we conclude that the yellow emission related levels are still present even in n-type highly Mg-doped GaN (sample A). Thus, Mg-doping in the range measured by SIMS may reduce but not avoid completely the formation of the defects that produce the acceptor levels involved in the yellow emission. However, the yellow luminescence is only effectively by PL detected in highly Mg-doped GaN for excitation energies below the Mg -band (2.9 -3 eV). On the other hand, free to bound or donor-acceptor pair transitions involving Mg-related levels might be much more efficient than the yellow band recombination. This is supported by the reported recombination lifetimes of both transitions. Hofmann et al. [3] found a strongly non exponential decay for the yellow luminescence, with a time dependent lifetime varying from 0.1 μs to 1 ms, at 1.8 K. On the other hand, Smith et al. [12] measured recombination lifetimes below 1 ns in the temperature range of 10 K to 300 K, for the 3.21 eV and 2.95 eV Mg-related bands. Thus, for excitation energies above 2.9-3 eV, most of the photogenerated electrons recombine through the much faster Mg related path, and the yellow emission is either sharply reduced or not observed.

In summary, photocapacitance and PL studies have been performed on Mg doped GaN samples grown by MOVPE, showing that the yellow emission can be detected, under excitation below the Mg-related band (2.9 - 3 eV). This result evidences the existence of the yellow band related defects in n-type or semiinsulating Mg doped samples, although may be in reduced concentration compared to undoped GaN. The fact that the yellow luminescence is not observed for excitation energies above the bandgap may be justified by a higher efficiency of the Mg related recombination path.

Acknowledgments

This work has been partially supported by the European Union ESPRIT LTR contract LAQUANI 20968.

References

[1] S Nakamura, M Senoh, S Nagahama, N Iwasa, T Yamada, T Matsushita, Y Sugimoto, H Kiyoku, *Appl. Phys. Lett.* ***70***, 1417-1419 (1997).

[2] T. Ogino, M. Aoki, *Jpn. J. Appl. Phys.* ***19***, 2395 (1980).

[3] D. M. Hofmann, D. Kovalev, G. Steude, B. K. Meyer , A. Hoffmann, L. Eckey, R. Heitz , T. Detchprom , H. Amano, I. Akasaki , *Phys. Rev. B* ***52***, 16702-16706 (1995).

[4] F. J. Sanchez, D. Basak, M. A. Sánchez-García, E. Calleja, E. Muñoz, I. Izpura, F. Calle, J. M. G. Tijero,

https://doi.org/10.1557/S109257830000154X Published online by Cambridge University Press

B. Beaumont, P. Lorenzini, P. Gibart, T. S. Cheng, C. T. Foxon, J. W. Orton, *MRS Internet J. Nitride Semicond. Res.* ***1***, 7 (1996).

[5] E. Calleja, F. J. Sanchez, D. Basak, M. A. Sanchez-Garcia, E. Munoz, I. Izpura, F. Calle, J. M. G. Tijero, J. L. Sanchez- Rojas, B. Beaumont, P. Lorenzini, P. Gibart, *Phys. Rev. B* ***55***, 4689 (1997).

[6] M Ramsteiner, J Menniger, O Brandt, H Yang, KH Ploog, *Appl. Phys. Lett.* ***69***, 1276-1278 (1996).

[7] J Neugebauer, CG Van de Walle, *Appl. Phys. Lett.* ***69***, 503-505 (1996).

[8] S. Nakamura, T. Mukai, M. Senoh, *Jpn. J. Appl. Phys.* ***31***, 2883 (1992).

[9] W Kim, A Salvador, AE Botchkarev, O Aktas, SN Mohammad, H Morcoc, *Appl. Phys. Lett.* ***69***, 559-561 (1996).

[10] X Zhang, P Kung, D Walker, A Saxler, M Razeghi, *Mater. Res. Soc. Symp. Proc.* ***395***, 625-9 (1996).

[11] B. Beaumont, M. Vaille, T. Boufaden, B. el Jani, P. Gibart, *J. Cryst. Growth* ***170***, 316-320 (1997).

[12] M. Ilegems, R. Dingle, *J. Appl. Phys.* ***44***, 4234 (1973).

[13] M. Smith, G. D. Chen, J. Y. Lin, H. X. Jiang , A. Salvador, B. N. Sverdlov, A. Botchkarev, H. Morkoc , B. Goldenberg , *Appl. Phys. Lett.* ***68***, 1883-1885 (1996).

[14] JM Myoung, KH Shim, C Kim, O Gluschenkov, K Kim, S Kim, DA Turnbull, SG Bishop, *Appl. Phys. Lett.* ***69***, 2722-2724 (1996).

[15] GC Yi, BW Wessels, *Appl. Phys. Lett.* ***68***, 3769-3771 (1996).

[16] W. Gotz, N. M. Johnson, D. P. Bour , *Appl. Phys. Lett.* ***68***, 3470-3472 (1996).

[17] C. H. Qiu, J. Y. Pankove, *Appl. Phys. Lett.* ***70***, 1983 (1997).

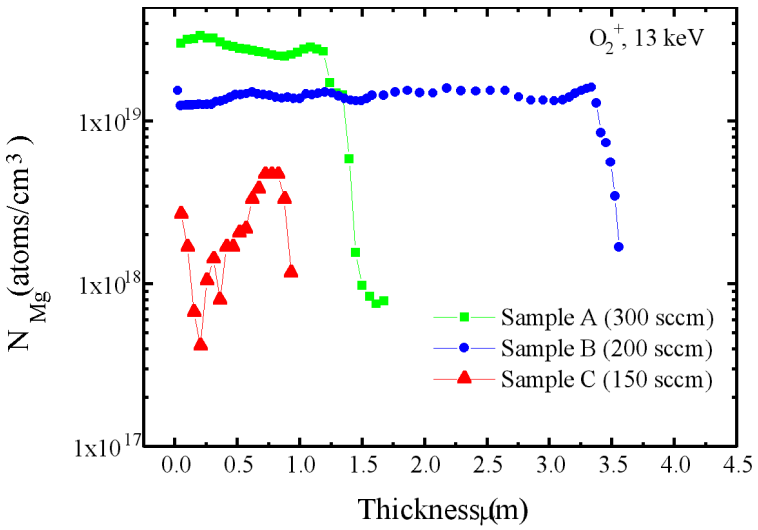

Figure 1. SIMS profiles of Mg-doped samples, with different cp_2Mg fluxes. Mg concentration of sample D (50 sccm) was below the detection limit of the system.

https://doi.org/10.1557/S109257830000154X Published online by Cambridge University Press

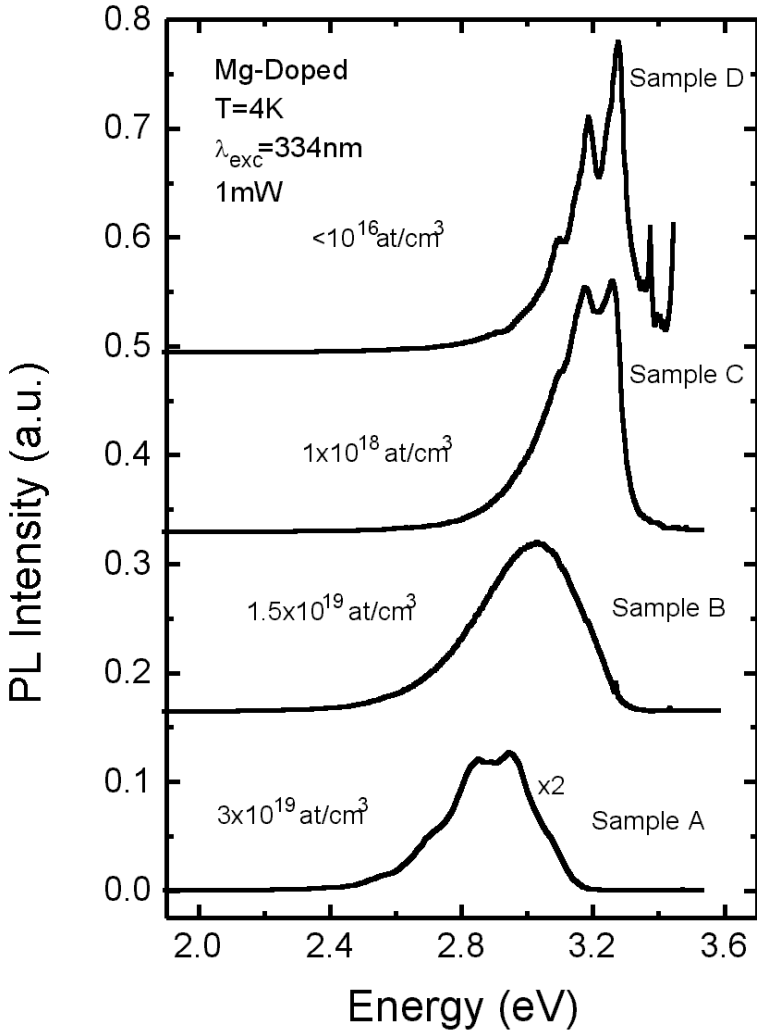

Figure 2. PL spectra of Mg-doped samples with increasing Mg concentration measured by SIMS.

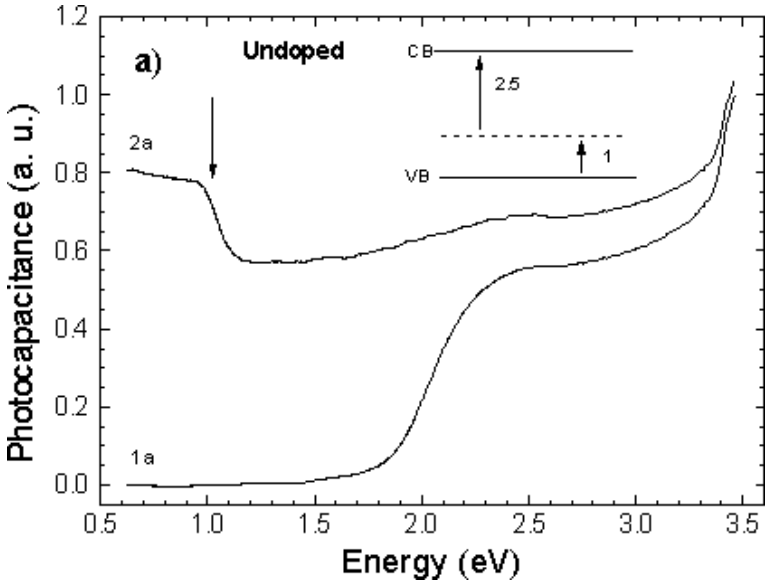

Figure 3a. Photocapacitance spectra of an undoped sample, after dark conditions (curve 1a) and after 3.5 eV illumination (curve 2a). Optical thresholds at 1 eV and 2.5 eV are related to a level located at 1 eV above the VB.

https://doi.org/10.1557/S109257830000154X Published online by Cambridge University Press

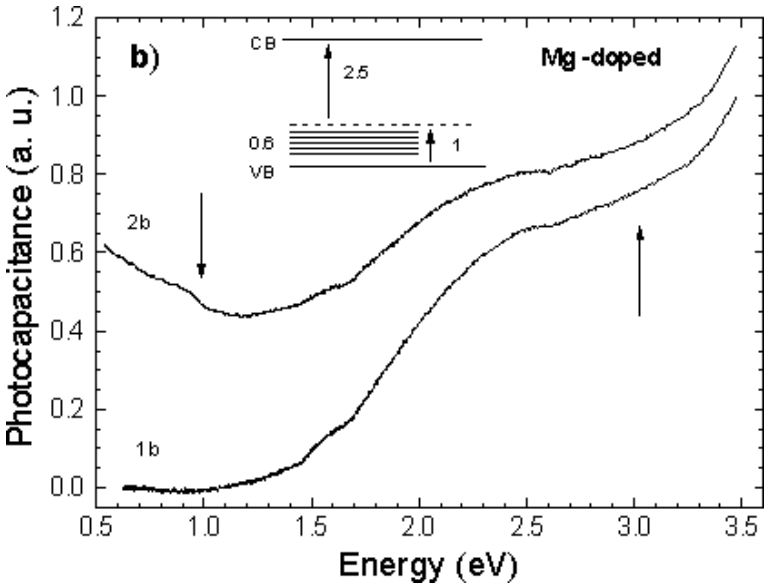

Figure 3b. Photocapacitance spectra of a Mg-doped sample, after dark conditions (curve 1b) and after 3.5 eV illumination (curve 2b). Optical thresholds at 1 eV and 2.5 eV are related to a level located at 1 eV above the VB. A continuous decrease in the capacitance is observed in the range of 0.5 to 1 eV in curve 2b.

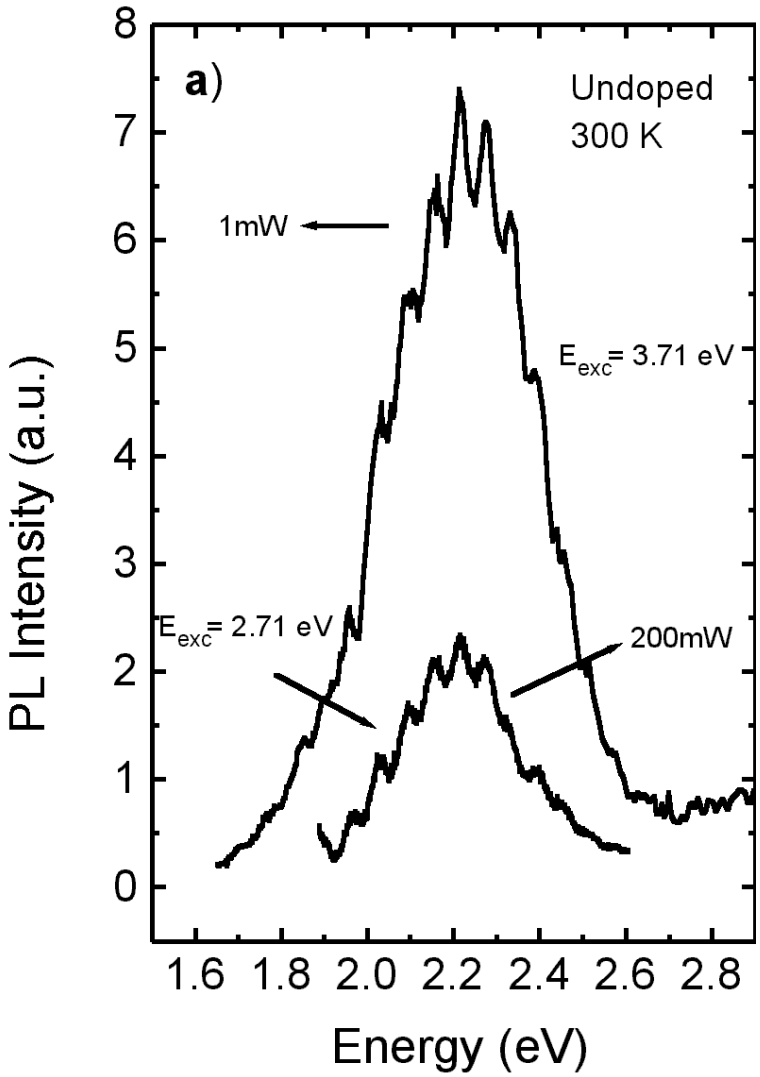

Figure 4a. PL spectra under above and below-bandgap excitation of an undoped sample.

https://doi.org/10.1557/S109257830000154X Published online by Cambridge University Press

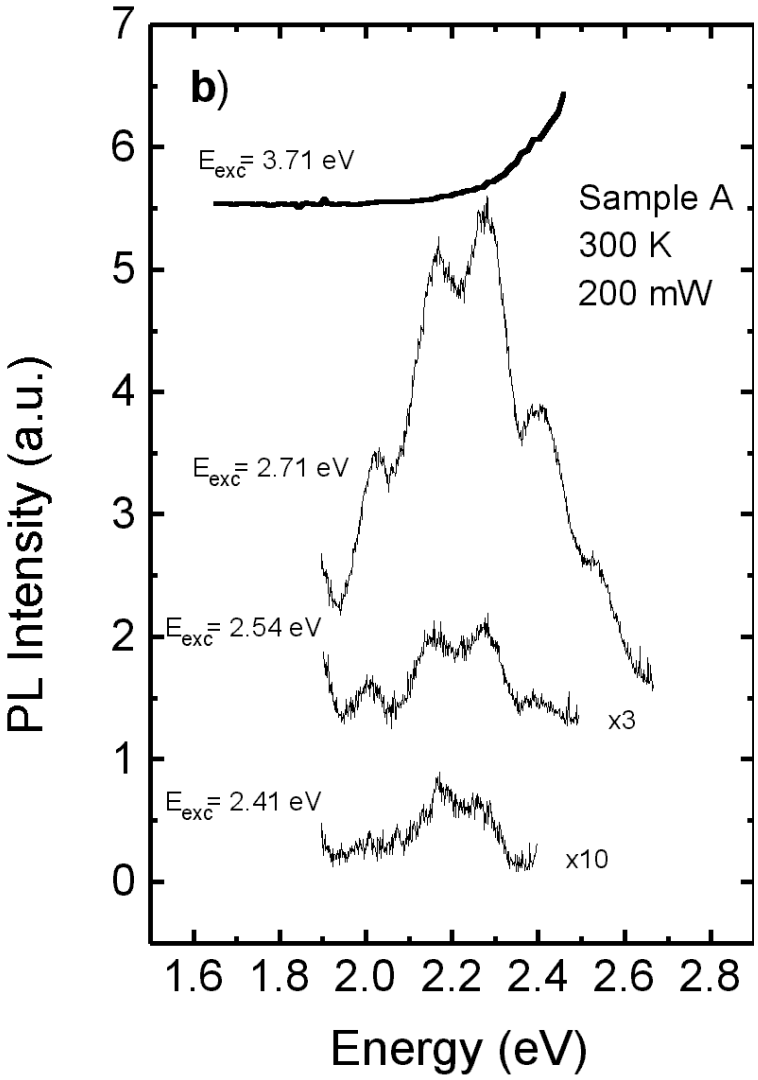

Figure 4b. PL spectra under above and below-bandgap excitation for a Mg-doped sample. The yellow emission is only observed for excitation energies below the Mg-related band energy (2.9-3 eV). (The spectra are shifted vertically for clarity).

https://doi.org/10.1557/S109257830000154X Published online by Cambridge University Press