AIP | Applied Physics Letters

Time-resolved cathodoluminescence assessment of deep-level transitions in hydride-vapor-phase-epitaxy GaN

C. Díaz-Guerra, J. Piqueras, and A. Cavallini

Citation: Appl. Phys. Lett. **82**, 2050 (2003); doi: 10.1063/1.1565501
View online: http://dx.doi.org/10.1063/1.1565501
View Table of Contents: http://apl.aip.org/resource/1/APPLAB/v82/i13
Published by the AIP Publishing LLC.

Time-resolved cathodoluminescence assessment of deep-level transitions in hydride-vapor-phase-epitaxy GaN

C. Díaz-Guerra[a] and J. Piqueras
Departimento Física de Materiales, Facultad de Físicas, Universidad Complutense de Madrid, Ciudad Universitaria s/n, E-28040 Madrid, Spain

A. Cavallini
INFM and Dipartimento di Fisica, Universitá di Bologna, Viale Berti Pichat 6/2, I-40127 Bologna, Italy

(Received 9 December 2002; accepted 7 February 2003)

The temporal behavior of deep-level luminescence emissions in undoped hydride-vapor-phase-epitaxy GaN layers of different thicknesses has been investigated by time-resolved cathodoluminescence (TRCL). The complex nature of the yellow luminescence is revealed in the TRCL spectra by the presence of two bands peaked at 2.22 and 2.03 eV. A red band with a decay time of 700 μs, centered at about 1.85 eV, dominates spectra recorded for long delay times. Exponential transients with associated decay times of hundreds of μs were measured at 87 K for all the deep-level emissions found in the layers. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1565501]

Gallium nitride has been intensively investigated in the last years due to its application in optoelectronics and high-temperature microelectronics. Nevertheless, it is widely recognized that the role of deep levels controlling the electrical and luminescence properties of this material should be fully understood in order to achieve devices optimization. In particular, a broad emission centered at about 2.2 eV, known as the yellow band, is commonly observed in *n*-type layers. The origin of this luminescence remains unclear and different models[1–3] have been proposed to explain the emission. Variations in peak position, shape and decay times reported in different studies[3–5] suggest that several bands involving different defects could contribute to the mentioned luminescence.[6] On the contrary, deep-level-related emissions in the green and red ranges of the visible spectrum are less frequently observed in undoped GaN.[7–9] Cathodoluminescence (CL) in the scanning electron microscope (SEM) has been used to investigate the spatial distribution of GaN deep-level emissions and their association to extended and point defects.[6,10,11] Although electron beam excitation usually leads to light emission by all mechanisms of radiative recombination present in a semiconductor, several investigations concerning the recombination kinetics of GaN defect centers have been carried out by time-resolved photoluminescence (TRPL),[3–5,12] while time-resolved cathodoluminescence (TRCL) studies of GaN deep levels have not yet been undertaken. In this work, TRCL is used to investigate the temporal behavior of deep-level emissions in undoped GaN layers of different thicknesses grown by hydride-vapor-phase epitaxy (HVPE). Our results indicate that CL emissions observed in the yellow and red ranges of the visible spectrum are probably related to transitions from the conduction band to deep acceptor levels.

Two GaN films with thickness of 2.6 μm (LH1232) and 55 μm (LH1234) were investigated. Both layers were grown on sapphire substrates by HVPE following the procedure described in Ref. 13. Room-temperature capacitance–voltage and Hall measurements, respectively, indicate a free-carrier concentration of $n=8\times10^{16}$ cm^{-3} and a mobility of $\mu_n=260$ cm^2/V s for the LH1232 sample, while values of $n=2\times10^{16}$ cm^{-3} and $\mu_n=810$ cm^2/V s were obtained for the LH1234 layer.

CL observations were performed in a Hitachi S-2500 SEM at accelerating voltages from 5 to 20 kV and temperatures between 85 and 295 K. Steady-state spectra were acquired using a Hamamatsu PMA-11CCD camera with a built-in spectrograph. TRCL measurements were carried out using a pulsed electron beam. To record CL spectra at delay times ranging from 500 ns to 3 ms, the signal detected by a photomultiplier was collected trough a boxcar integrator triggered by a pulse generator and then fed to a computer.[14] The decay transients of the CL emissions were monitored with the aid of a digital oscilloscope.

CL spectra of the samples investigated were found to depend on beam excitation conditions. In particular, deep-level-related emissions could be better appreciated at 85 K in spectra obtained with a defocused electron beam, as Fig. 1 shows. Near-band-gap emission related to donor-bound excitons is centered at 3.472 eV in the LH1234 sample and at 3.492 eV in the LH1232 sample. This shift is caused by a compressive strain due to the thermal expansion coefficient mismatch between GaN and sapphire.[15] Other peaks corresponding to shallow donor–acceptor pair (DAP) transitions appear centered between 3.4 and 3.2 eV in spectra of both layers. Some of the deep-level-related emissions are common to the samples investigated, as the blue CL band peaked at 2.92 eV. A band centered at 2.88 eV has been previously observed in cross-sectional CL investigations of HVPE-grown GaN layers[11] and associated with point defects or impurities decorating grain boundaries and dislocations. Actually, oxygen donors seem to be involved in the mechanism responsible for this emission.[16] In addition, CL emission is also observed in the yellow and red ranges of the visible

[a]Electronic mail: cdiazgue@fis.ucm.es

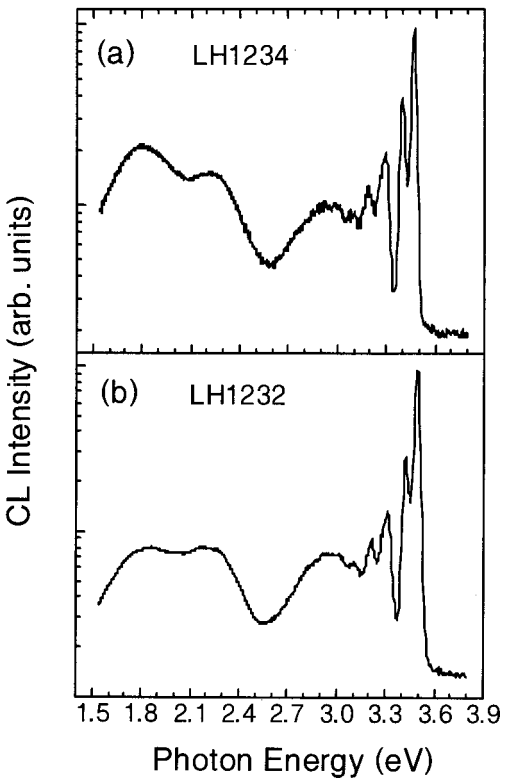

FIG. 1. CL spectra of the LH1234 layer (a) and the LH1232 film (b) recorded with a defocused electron beam (85 K, 15 kV).

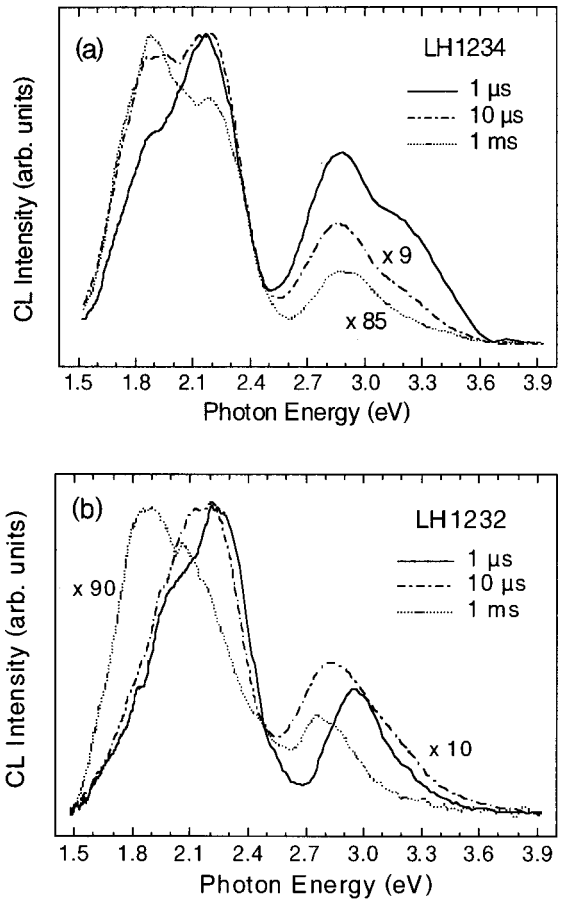

FIG. 2. Normalized TRCL spectra of the LH1234 layer (a) and the LH1232 layer (b) recorded at 85 K for different delay times using a defocused electron beam.

spectrum. Gaussian deconvolution of spectra recorded under different excitation conditions in the thick layer indicate that the bands observed in Fig. 1(a) are centered at 1.81 and 2.23 eV. These bands are also observed peaked at 1.85 and 2.22 eV in CL spectra from the thin layer [Fig. 1(b)], but deconvolution reveals the existence of an additional emission, centered at 2.02 eV, in this sample. Such observation suggests that the latter peak could be related to structural defects located at the GaN–sapphire interface. In fact, an increase of the threading dislocation density with decreasing layer thickness has been found[17] in HVPE layers similar to those here investigated, while an enhanced yellow emission was observed[11] near the substrate interface in CL investigations of thin HVPE GaN films. In order to evidence a possible thickness dependence of the distribution of the radiative centers involved in the CL bands, depth-resolved measurements were performed by varying the beam voltage while keeping a constant injection rate (i.e., keeping a constant beam power). The intensities of the 1.81 and 2.23 eV bands were found to decrease by increasing the accelerating voltage, which suggests that the concentration of deep levels responsible for such emissions is higher near the surface of the samples. This result supports previous PL works[1,18] revealing a significant concentration of yellow-luminescence-related centers at the surface of different GaN layers.

The temporal behavior of the deep-level bands and their decay times were assessed by TRCL spectroscopy. Figure 2(a) shows TRCL spectra from the LH1234 sample recorded at 85 K for different delay times after excitation with a 20 μs pulse. A progressive delay time increase favors the red 1.81 eV emission, while the relative intensity of the yellow 2.23 eV band decreases in comparison. The 2.92 eV CL can be still observed for delays longer than 1 ms. Similar results were obtained in the LH1232 layer, as Fig. 2(b) shows. The 2.22 eV band dominates the spectrum recorded for a delay time of 1 μs, but the 2.03 eV CL band—previously found by deconvolution procedures—can be now clearly appreciated as a shoulder of the main emission. Present day views generally agree in the acceptor character of the deep levels involved in the GaN yellow luminescence, being Ga vacancies and its complexes with oxygen or carbon often suggested candidates.[1,2] The relative weights of the 2.03 and 1.85 eV bands increase by further increasing delay time, shifting the CL emission maximum towards higher energies. As in the case of the thick layer, the 1.85 eV band is dominant for delay times above 100 μs. The intensity of this CL band is almost independent of temperature between 85 and 295 K, which differs from the intensity change of more than an order of magnitude observed in the same interval for other GaN red PL bands[8,19] attributed to deep DAP transitions. Moreover, no peak shift of the 1.85 eV band is observed in our spectra by increasing delay time, which suggests that deep donors are not involved in the mechanism giving rise to this emission.[20] It should be mentioned that the temperature behavior of our red band is similar to that observed for the PL band peaked at 1.92 eV associated by Reshchikov *et al.*[21] to Ga vacancies—related defects bound to structural imperfections in HVPE GaN layers.

The decay times of the observed emissions obtained from CL transients recorded at 87 K are summarized in Table

TABLE I. Deep-level CL emissions decay times measured at 87 K in the GaN layers investigated after excitation with a 20 μs beam pulse.

Peak energy (eV)	Sample LH1234 (μs)	Sample LH1232 (μs)
2.92	430±10	420±10
2.23	260± 5	250± 5
2.02	···	340±10
1.81–1.85	700±20	670±20

I. Such transients are well fitted by single exponential decays. The shorter decay time (~250 μs) corresponds in both layers to the 2.23 eV band, while long decay times of about 430 and 700 μs were respectively found for the 2.92 and 1.81 eV emissions. An intermediate decay time of 340 μs was measured for the 2.03 eV band observed in the thin layer, in good agreement with TRCL spectra. Previous TRPL investigations show a clear controversy between decay times measured for the yellow emission.[3–5] In particular, nonexponential transients with decay times in the 10^{-1}–10^{3} μs range have been reported[3,4] and explained in the frame of the Thomas–Hopfield model[20] for DAP recombination. In principle, our exponential transients with associated decay times of hundreds of μs do not agree with the DAP recombination theory, which predicts a wide distribution of instantaneous decay times extending from the ns to the ms range.[3,4] This discrepancy can be explained considering both the different nature of the excitation source and the different experimental conditions used in PL and CL experiments. In particular, electron pulses of 20 μs were used in this work while in PL experiments the sample is commonly excited with ns light pulses.[3,4,7] Moreover, our CL transients were recorded at 87 K, while the mentioned PL investigations were carried out at liquid He temperature. A change in the recombination mechanism by increasing temperature has been recently reported for GaN deep-level PL.[7] While a DAP-type recombination was observed at 15 K, PL decay curves were found to approach an exponential behavior by increasing temperature due to an increase of the free-electron concentration and a decrease of the number of neutral donors. A similar process could account for the present CL results. Actually, the exponential character of our transients suggests that above 87 K, GaN yellow and red CL emissions observed in this work could be related to transitions from the conduction band to deep acceptors.

In summary, deep-level transitions in GaN layers of different thicknesses have been assessed by TRCL. The complex nature of the yellow emission observed in the thinner sample is evidenced by TRCL spectra revealing two bands peaked at 2.22 and 2.03 eV. A red emission, centered at about 1.85 eV, shows a higher intensity near the surface of the samples and dominates spectra recorded for long delay times. Exponential transients with associated decay times of hundreds of μs suggest that, above 87 K, emissions in the yellow and red ranges of the visible spectrum could be related to transitions from the conduction band to deep acceptor levels.

This work was supported by MCYT (Project No. MAT2000-2119). R. Molnar and D. C. Look are gratefully acknowledged for providing the samples.

[1] H. Morkoc, Mater. Sci. Eng., R. **33**, 135 (2001), and references therein.
[2] J. Neugebauer and C. G. Van de Walle, Appl. Phys. Lett. **69**, 503 (1996).
[3] D. M. Hofmann, D. Kovalev, G. Steude, B. K. Meyer, A. Hoffmann, L. Eckey, R. Heitz, T. Detchprom, A. Amano, and I. Akasaki, Phys. Rev. B **52**, 16702 (1995).
[4] R. Y. Korotkov, M. A. Reshchikov, and B. W. Wessels, Physica B **273-274**, 80 (1999).
[5] H. Haag, B. Hönerlage, O. Briot, and R. L. Aulombard, Phys. Rev. B **60**, 11624 (1999).
[6] M. Herrera Zaldívar, P. Fernández, and J. Piqueras, Semicond. Sci. Technol. **13**, 900 (1998).
[7] M. A. Reshchikov, H. Morkoç, S. S. Park, and K. Y. Lee, Appl. Phys. Lett. **78**, 2882 (2001).
[8] W. Götz, N. M. Johnson, C. Chen, H. Liu, C. Kuo, and W. Imler, Appl. Phys. Lett. **68**, 3144 (1996).
[9] D. M. Hofmann, B. K. Meyer, H. Alves F.leiter, W. Burkhard, N. Romanov, Y. Kim, J. Krüger, and E. R. Weber, Phys. Status Solidi A **180**, 261 (2000).
[10] F. A. Ponce, D. P. Bour, W. Götz, and P. J. Wright, Appl. Phys. Lett. **68**, 57 (1996).
[11] M. Herrera Zaldívar, P. Fernández, and J. Piqueras, J. Appl. Phys. **83**, 2796 (1998).
[12] Yong-Hwan Kwon, S. K. Shee, G. H. Gainer, G. H. Park, S. J. Hwang, and J. J. Song, Appl. Phys. Lett. **76**, 840 (2000).
[13] R. J. Molnar, W. Götz, L. T. Romano, and N. M. Johnson, J. Cryst. Growth **178**, 147 (1997).
[14] A. Urbieta, P. Fernández, J. Piqueras, Ch. Hardalov, and T. Sekiguchi, J. Phys. D **34**, 2945 (2001).
[15] D. C. Reynolds, D. C. Look, B. Jogai, J. E. Hoelscher, R. E. Sherriff, and R. J. Molnar, J. Appl. Phys. **88**, 1460 (2000).
[16] H. C. Yang, T. Y. Lin, and Y. F. Chen, Phys. Rev. B **62**, 12593 (2000).
[17] Z.-Q. Fang, D. C. Look, J. Jasinski, M. Benamara, Z. Liliental-Weber, and R. J. Molnar, Appl. Phys. Lett. **78**, 332 (2001).
[18] I. Shalish, L. Kronik, G. Segal, Y. Rosenwaks, Y. Shapira, U. Tisch, and J. Salzman, Phys. Rev. B **59**, 9748 (1999).
[19] M. A. Reshchikov, M. H. Zhang, J. Cui, P. Visconti, F. Yun, and H. Morkoç, Mater. Res. Soc. Symp. Proc. **639**, G6.7 (2001).
[20] G. Thomas, J. J. Hopfield, and W. M. Augustyniak, Phys. Rev. **140**, A202 (1965).
[21] M. A. Reshchikov, R. J. Molnar, and H. Morkoç, Mater. Res. Soc. Symp. Proc. **680E**, E5.6.1 (2001).