Effect of laser irradiation on the luminescence of Mg and Si-doped GaN films

M. Herrera Zaldívar,[a] P. Fernández, and J. Piqueras
Departamento de Física de Materiales, Facultad de Físicas, Universidad Complutense, 28040 Madrid, Spain

J. Solís
Instituto de Optica "Dada de Valdés," C.S.I.C. Serrano 121, 28006 Madrid, Spain

(Received 18 August 1998; accepted for publication 14 October 1998)

Pulsed laser treatments have been performed in GaN samples of both *n*- and *p*-type conductivity. The laser induced changes have been monitored by emissive mode and cathodoluminescence (CL) in a scanning electron microscope. Emissive mode observations indicate a moderate laser induced recrystallization. The luminescent emission has been characterized in both types of samples, GaN:Si and GaN:Mg. Whereas the evolution of CL in the Si doped samples could be explained by the occurrence of laser induced annealing, the luminescent behavior of the Mg doped samples upon irradiation seems to be more complex and a strong relation with the compensation or Mg activation is suggested. Several luminescence bands with maxima ranging from 3.3 to 2.7 eV and their dependence on irradiation conditions have been studied. © *1999 American Institute of Physics.* [S0021-8979(99)04802-1]

INTRODUCTION

During the last years much effort has been devoted to the study of wide band gap semiconducting materials, which are very promising for optoelectronic applications. This property makes them very suitable for the fabrication of light emitting diodes (LED) and semiconductor lasers in the ultraviolet-blue region. The use of materials emitting in different regions would also offer the possibility to fabricate full color LED-based displays which allows to reach more extreme points in the chromaticity diagram than the standard television tubes.[1] Different materials may be used for these purposes. For instance II–VI compounds (mainly ZnSe based) are adequate for the blue-green spectral region and GaP would be usable in the red region.[2–4] In this context III–V nitrides have two main advantages. One is the large band gap associated to all the alloys from the system Al–Ga–In–N ranging from red (1.9 eV of InN) to ultraviolet (3.4 eV of GaN). The other advantage is the strength of chemical bonds in these compounds, which makes them very stable and resistant, diminishing the degradation problems encountered in other semiconductors.[1] However, these good properties are in many cases obscured by the difficulty to prepare the material with the desired conductivity due to the compensation phenomena widely observed in semiconductors.[5] In particular *p*-type GaN is difficult to prepare[6] and the compensation mechanism accounting for this difficulty is not still completely understood. Low resistivity *p*-type GaN samples have been obtained by doping with Mg atoms which should act as acceptor when occupying the Ga sites. However, there is no efficient compensation unless some treatments are performed. In particular Amano *et al.*[7] reported a resistivity as low as 35 Ω cm in Mg doped samples irradiated with low energy electrons. More recently, Nakamura[6,8] prepared *p*-type samples with even lower resistivity (2 Ω cm). In this case the postgrowth treatment consisted on thermal annealing in nitrogen atmosphere at temperatures above 700 °C.

An alternative to thermal treatment is laser annealing, that may be advantageous in many occasions.[9] However not much work has been done to study the influence of laser treatments on the defect structure of these materials of crucial importance in the fabrication of optoelectronic devices. In this work we have used cathodoluminescence (CL) microscopy to monitor the effect of pulsed ultraviolet laser irradiation on the defect structure and the emission properties, of *n*- and *p*-type GaN epitaxial layers.

EXPERIMENT

The samples used were GaN films grown on (0001) sapphire. The *n*-type films consisted of an 8-μm-thick GaN buffer layer grown by the hydride vapor phase epitaxy method and two 2-μm-thick epilayers, the upper of which was doped with Si. The carrier concentration was 10^{18} cm^{-3}. The *p*-type samples consisted of a 150 Å AlN buffer layer and two thin epilayers. The first one in contact with the buffer is undoped, 1 μm thick and with a resistivity about 10^5-10^6 Ω cm. The top epilayer is Mg doped, 2 μm thick and with carrier concentration around 7×10^{16} cm^{-3}. The samples were irradiated in air with 12 ns ArF excimer laser pulses at 193 nm. The use of a beam homogenizer allows to obtain a flat irradiance profile of 4×4 mm^2 at the sample site with a maximum deviation of 5%. In all cases a fresh surface was irradiated with a number of pulses ranging from 50 to 250 at a repetition rate of 1 Hz and an average fluence of 300 mJ/cm^2. The pulse to pulse energy fluctuation is lower than 5%. The reflectivity of the surface at 633 nm

[a]Permanent address: Instituto de Física, B. Universidad Autónoma de Puebla, 72570 Puebla, México.

 © 1999 American Institute of Physics

Copyright © 1999. All rights reserved.

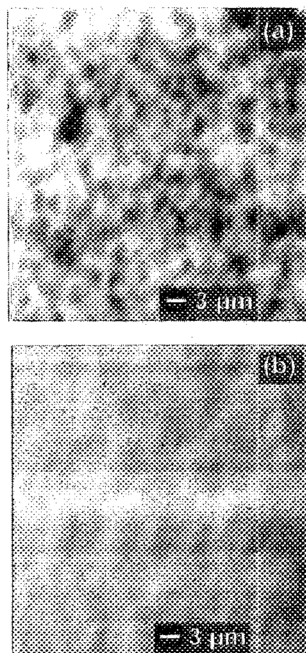

FIG. 1. CL images of the Si doped samples: (a) unirradiated sample, and (b) irradiated samples with 250 pulses.

before and after each laser exposure was monitored by means of a HeNe laser beam focused to the center of the irradiated region to a size of approximately 500 μm. The HeNe beam was chopped at a frequency of 130 Hz and the intensity of the reflected beam was measured by means of a Si photodiode connected to a lock-in amplifier. Before and after the irradiation the samples were investigated in the secondary electron and cathodoluminescence (CL) modes of scanning electron microscopy (SEM) by using a Hitachi S-2500 microscope with an electron beam energy of 15 keV. CL measurements were performed at temperatures between 77 and 300 K. For light detection in the visible range a Hamamatsu R928 photomuliplier was used.

RESULTS AND DISCUSSION

CL images from Si doped samples show that even for irradiation doses as low as 50 pulses, the contrast from the grains becomes blurred, though no changes are observed in the emission mode images even for the most severe irradiation conditions (250 pulses). These contrast changes which could be associated to the initial stages of a recrystallization process are shown in Fig. 1, and would be compatible with the observed increase in reflectivity at 633 nm, probably associated to a decrease of surface roughness.

Figure 2, curve a, shows the spectrum from unirradiated samples with three bands peaked at 3.54, 2.85, and 2.23 eV, respectively. The 3.45 eV band corresponds to the near band edge transitions while the 2.85 eV, whose origin has not been exactly determined, has been attributed to point defects.[10,11] The 2.73 eV band, often reported in the literature, e.g., Refs. 12, 13, and 10 is referred as the yellow band of GaN and is generally attributed to defects. Irradiation with 50 or 150 pulses does not cause changes in the spectrum of

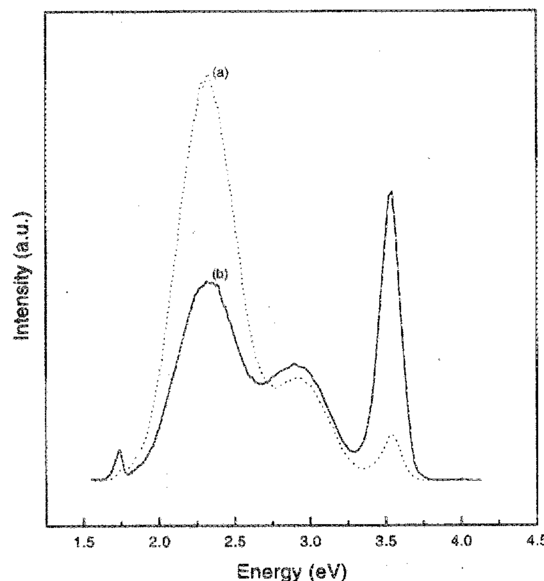

FIG. 2. CL spectra from n-type samples. (a) Unirradiated sample, and (b) 250 pulses irradiated sample.

the nonirradiated samples. After irradiation with 250 pulses a marked decrease of the relative intensity of the yellow band is observed (Fig. 2, curve b). These changes are similar to those observed after annealing in N_2 atmosphere[14] which are explained by a decrease in nitrogen vacancy concentration during the thermal treatment.

Emissive mode images of p-type samples show that even at the lowest irradiation doses some changes occur. As shown in Fig. 3 these changes consist mainly on the formation of a droplet-like structure inside the grains. The size of the droplets increases with the number of irradiation pulses, reaching about 2 μm for the samples irradiated with 250 pulses. Changes are also observed in CL images. The contrast from unirradiated sample is related to the grain structure while in the irradiated samples the luminescence emission seems to arise mainly from some of the droplets (Fig. 3). Ga rich droplet formation during laser irradiation has been reported by Wong *et al.*[9] and attributed to decomposition of the GaN surface. However for the lower irradiation doses an incipient recrystallization process would be rather likely to occur. Indeed for 50 pulses the background intensity seems to be higher than in the nonirradiated sample, but as observed in the Si-doped samples the contrast is more diffuse than before the irradiation, which reinforce the hypothesis of the recrystallization since the irradiation conditions are not so severe at this stage to expect a significant surface decomposition. The most severely irradiated sample (250 pulses) show that only a small fraction of the droplets are strongly luminescent, thus concentrating the major part of the emission observed.

CL results obtained from p-type samples are shown in Fig. 4. The spectra from p-type irradiated samples show a relatively complex behavior. In all cases the spectrum consists of a broad band centered in the violet-blue region. Deconvolution in the different cases shows the presence of several emissions peaked at about 3.3, 3.2, 3.0, 2.85, and 2.70 eV with relative weights dependent on the irradiation treat-

Copyright © 1999. All rights reserved.

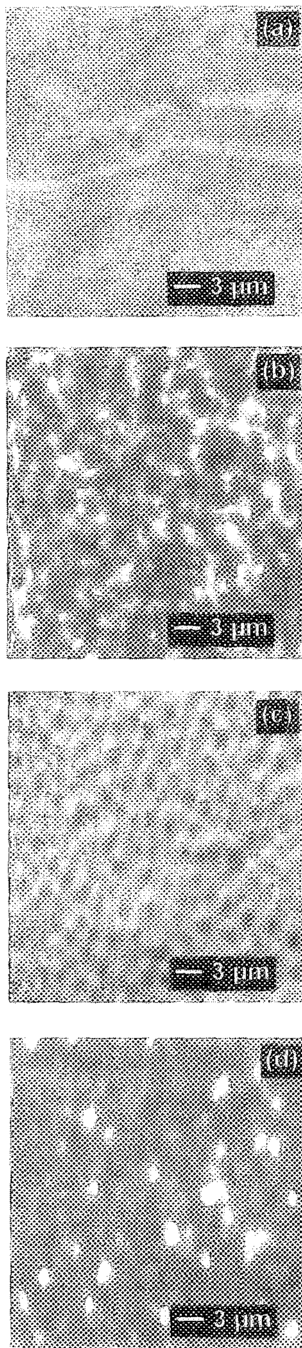

FIG. 3. Emissive mode and CL panchromatic images from *p*-type unirradiated sample [(a) and (b), respectively] and *p*-type irradiated sample with 250 pulses [(c) and (d), respectively].

ments. The spectra of unirradiated samples are peaked at 3.2 eV which is the most intense component of this band and is related to magnesium doping.[15] Additional components at 3.3 and 3 eV are also present [Fig. 4(a)]. The latter has been previously reported and related also to magnesium incorporation.[9,16] By decreasing the excitation conditions the deep level bands are revealed so that the components at 2.85 and 2.70 eV are the most intense [Fig. 4(b)]. This dependence of the spectra upon the excitation conditions has been already observed in many other semiconductors and attributed to a saturation effect due to the low concentration of the defects involved in these emissions.[11,17,18] The fact that emis-

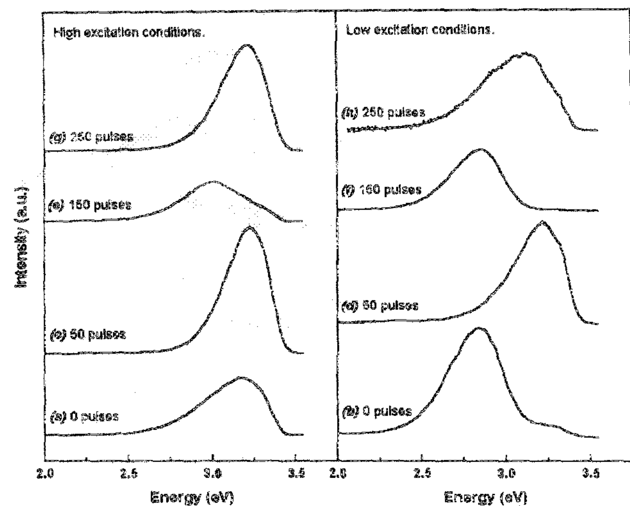

FIG. 4. CL spectra of *p*-type irradiated samples recorded for different excitation conditions.

sion usually observed after Mg activation[9] are present prior to any treatment would be explained on the basis that a small fraction of magnesium atoms are directly incorporated to the Ga sublattice in such a way that can participate in the compensation mechanism. Indeed Smith *et al.*[19] have performed time resolved measurements which reveal the presence of two close lines in the exciton region which they suggest could be associated to two different states of Mg atoms, one corresponding to activated centers, and the other to dopant atoms still inactivated. On the other hand similar bands have been reported in *n*-type samples and, as stated above, attributed to different kinds of defects and not directly related to doping, so that a contribution of them could be expected in Mg-doped samples.

After irradiation with 50 pulses a relative increase of the 3.2 eV band is observed for all excitation conditions [Figs. 4(c) and 4(d)]. This decrease of the intensity of deep level bands could be understood as an annealing effect. In the samples irradiated with 150 pulses the most intense emission corresponds to the 3 eV component [Fig. 4(e)] in agreement with the previous work of Wong *et al.*[9] This increase of the relative intensity of the blue bands is compatible with a Mg activation process induced by the laser treatment since one of the mechanisms involved in the activation is the displacement of Mg atoms to exact Ga sites.[7,8] The use of a low excitation density yields spectra with main components at 2.85 and 2.7 eV [Fig. 4(f)]. A similar dependence on excitation conditions have been observed by Kaufmann *et al.*[20] who reported photoluminescence spectra peaked at 2.8 or 3.2 eV depending on the excitation density. These authors attribute the high energy emission to a (Mg^0,e) recombination process, while the 2.8 eV band would be related to a distant donor–acceptor pair transition in which the defects involved are suggested to be Mg_{Ga} (shallow acceptor) and a complex $Mg_{Ga}V_N$ (deep donor). This model could be considered the counterpart of the model proposed by some authors to explain the yellow band.[21,22] Finally, for 250 pulses irradiation the initial situation is recovered in the sense that again for any excitation conditions the most intense component of the spectra is peaked at 3.2 eV [Fig. 4(g) and 4(h)]. This de-

Copyright © 1999. All rights reserved.

crease of the blue components could be related to the incorporation of N_2 during the irradiation, which is likely to occur since the irradiations are performed in air, thus a decrease of the V_N concentration could be expected. Consequently, the concentration of $Mg_{Ga}V_N$ complexes and the blue emission intensity would be lower. Nakamura *et al.*[8] have reported that a thermal annealing in N_2 atmosphere subsequent to Mg activation causes an important reduction of the blue components of the spectra, without a decrease in conductivity. On the other hand a surface decomposition as suggested by Wong *et al.*[9] and Nakamura *et al.*[8] would take along the existence of certain amount of magnesium atoms not surrounded by four nitrogen atoms so that no Mg_{Ga} centers are properly formed. Since these defects seem to be involved in the high energy component of the blue band, again a decrease of the relative intensity of the emission is expected.

CONCLUSIONS

CL has been used to investigate the effect of pulsed laser irradiation on GaN films. Irradiation of Si doped *n*-type films causes an effect similar to thermal annealing which can be explained by changes in the defect structure. In Mg doped *p*-type samples irradiation at low doses induces activation of Mg as acceptor while at high doses an annealing effect takes place which degrades the luminescence properties in the blue spectral region.

ACKNOWLEDGMENTS

This work was supported by DGES (Project PB96-0639). M.H.Z. thanks AECI and CoNaCyT for a research grant.

[1] F. Ponce and D. B. Bour, Nature (London) **386**, 351 (1997).
[2] A. V. Nurmikko and R. L. Gunshor, Solid State Commun. **92**, 113 (1994).
[3] H. Morkoç, S. Strite, B. Gao, M. E. Li, B. Sverdlov, and M. Burns, J. Appl. Phys. **76**, 1363 (1994).
[4] S. Nakamura, Mater. Res. Bull. **22**, 29 (1997).
[5] Y. Marfaing, J. Cryst. Growth **161**, 205 (1996).
[6] S. Nakamura, Diamond Relat. Mater. **5**, 496 (1996).
[7] H. Amano, M. Kito, K. Hiramatsu, and I. Akasaki, Jpn. J. Appl. Phys., Part 2 **28**, L2112 (1989).
[8] S. Nakamura, N. Iwasa, M. Senoh, and T. Mukai, Jpn. J. Appl. Phys., Part 1 **31**, 1259 (1992).
[9] W. S. Wong, L. F. Schloss, G. S. Sudhir, B. P. Linder, K. M. Yu, E. R. Weber, T. Sands, and N. W. Cheung, Mater. Res. Soc. Symp. Proc. **449**, 1011 (1997).
[10] A. Cremades, J. Piqueras, C. Xavier, T. Monteiro, E. Pereira, B. K. Meyer, D. M. Hofmann, and S. Fischer, Mater. Res. Bull. **42**, 230 (1996).
[11] M. Herrera Zaldívar, P. Fernández, and J. Piqueras, J. Appl. Phys. **83**, 462 (1998).
[12] F. Ponce, D. P. Bour, W. Götz, and P. J. Wright, Appl. Phys. Lett. **68**, 57 (1996).
[13] S. Christiansen, M. Albrecth, W. Dorsch, H. P. Strunk, A. Pelzmann, M. Mayer, M. Kamp, K. J. Ebeling, C. Zanotti-Fragonara, and G. Salviatti, Mater. Sci. Eng., B **43**, 296 (1997).
[14] M. Herrera Zaldívar, P. Fernández, and J. Piqueras, Semicond. Sci. Technol. (in press).
[15] J. I. Pankove and J. A. Hutchby, J. Appl. Phys. **47**, 5387 (1976).
[16] M. Ilegems and R. Dingle, J. Appl. Phys. **44**, 4234 (1973).
[17] A. Castaldini, A. Cavallini, B. Fraboni, L. Polenta, P. Fernández, and J. Piqueras, Phys. Rev. B **54**, 7622 (1996).
[18] P. Fernández, J. Piqueras, J. A. García, A. Remón, and Muñoz, Semicond. Sci. Technol. **13**, 410 (1998).
[19] M. Smith, G. D. Chen, J. Y. Lin, H. X. Jiang, M. Asif Khan, and C. J. Sun, Appl. Phys. Lett. **67**, 3295 (1995).
[20] U. Kaufmann, M. Kunzer, M. Maier, H. Obloh, A. Ramakrishnan, B. Santic, and P. Schlotter, Appl. Phys. Lett. **72**, 1326 (1998).
[21] T. Ogino and M. Aoki, Jpn. J. Appl. Phys. **19**, 2395 (1980).
[22] J. Neugebauer and C. G. van de Walle, Appl. Phys. Lett. **69**, 503 (1996).

Copyright © 1999. All rights reserved.