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14. ABSTRACT
CL study of ammonothermal GaN crystals. Preliminary results on ammonothermal AlGaIn crystals show a clear prevalence of deep level luminescence. Study of the luminescence spectral characteristics. Optimization of the excitonic emission vs deep level emission. Relation between the CL data and the crystal growth parameters. Study of the surface properties, using variable e-beam kV excitation. Study of grain boundaries, influence of crystal defects on the Yellow luminescence. Incorporation of cations in different growth sectors of ammonothermal AlGaIn crystals. This study targets to supply the crystal growers the relevant parameters necessary to improve the crystalline quality of these crystals suitable for obtaining high quality substrates.
CL study of e- irradiated ZnO crystals previously indented, in order to determine the interaction between Frenkel pairs and the crystal defects. Thermal treatments in controlled atmospheres: influence of the treatments in the distribution of defects. Local studies around grain boundaries in melt grown crystals, identification of defects. This study targets the understanding of the intrinsic defects in ZnO in order to allow p-type doping by controlling the compensating levels.

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**Microscopic optical characterization of free standing
III-Nitride substrates, ZnO bulk crystals, and III-V
structures for non-linear optics**

(Part II)

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GaN 45 Top view (c^- facet).

The CL spectra change close to the top surface. In fact, the NBE part of the spectrum is greatly enhanced as one goes from the seed to the top c^- surface, Fig.17.

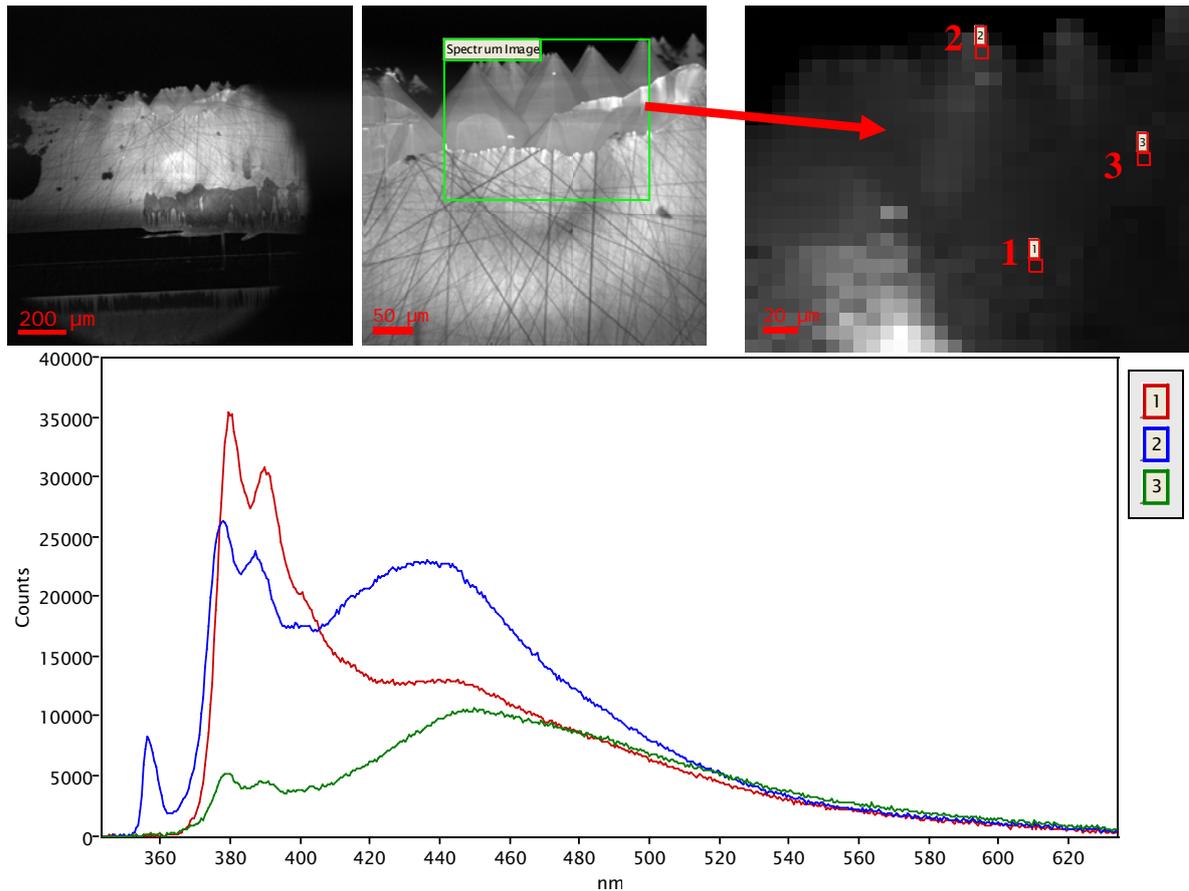


Fig.17

One observes the CL data in the upper region of the c^- growth sector. The spectrum on the top part of this sector, exhibits the NBE bands, contrarily to what was observed in zones closer to the seed, which points to an improved purity of the crystal in the regions far from the seed. One observes the excitonic region at 358 nm, and a very strong contribution of the oxygen related donor-acceptor pair (DAP) transition at 378 nm (3.27 eV), with its corresponding phonon replicas. Additionally, the BL band is also present; however, the Green-Yellow band is very weak, being observed as a shoulder in the low energy side of the BL band, contrarily to what is observed in regions closer to the seed. The differences between the three spectra represented in Fig. 17 are related to the different facets probed on those points; in fact, the spectra #2 and 3 are acquired on the top etched surface. We will analyse this surface in detail.

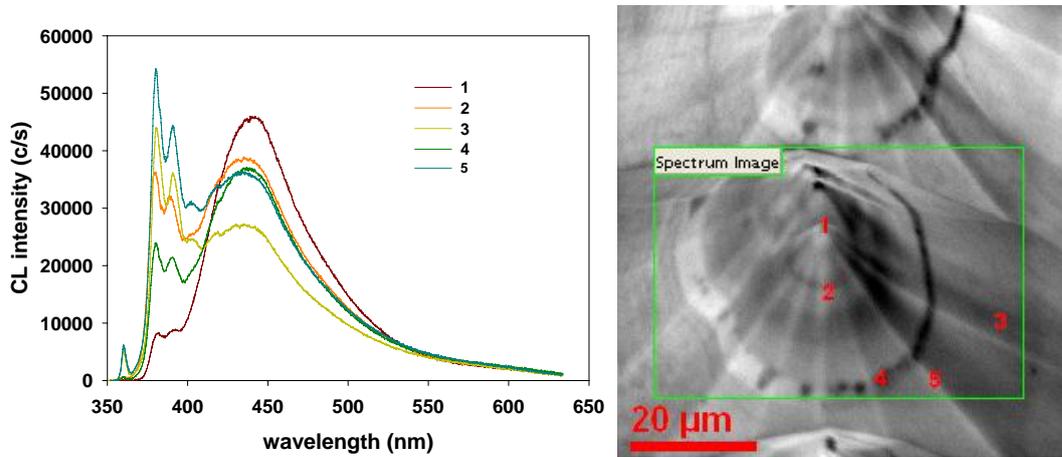


Fig.18

Fig.18 shows the CL image and the corresponding local spectra. The N surface presents the typical spiral dihexagonal pyramids, with marked CL contrast between the different edges, faces and summits, which accounts for differences in the incorporation of defects and impurities. The CL spectra present several. The excitonic transition (359 nm) is only observed in the regions with bright contrast, spectra #3 and 5, Fig.19, which correspond to the pyramid edges. The spectra also present the DAP transition at 3.25 eV (381 nm) and its phonon replicas. Also, a broad BL band is observed.

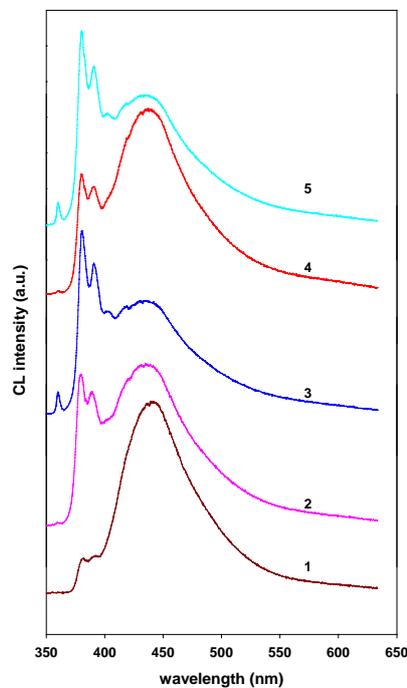


Fig.19

The BL band is dominant in the regions with dark contrast, in particular, the summit of the pyramid, point #1, and the dark rings observed around the pyramid, point #4, and in a minor extent point #2. It peaks around 2.83 eV (437 nm). This band has been related to different impurities, as Zn, Cd or Mg; being Zn the most probable candidate.

Nevertheless, the fact that it is mainly observed in the regions with dark CL contrast, could suggest its relation to some structural defect. Another important point is the low visible luminescence contribution. This makes different the upper part of the c- sector with respect to other growth sectors, and even with respect to the zone close to the seed of the c- sector.

A CL image obtained with low kV (5 kV) shows the pyramidal structure and some dark tiny defects, Fig. 20.

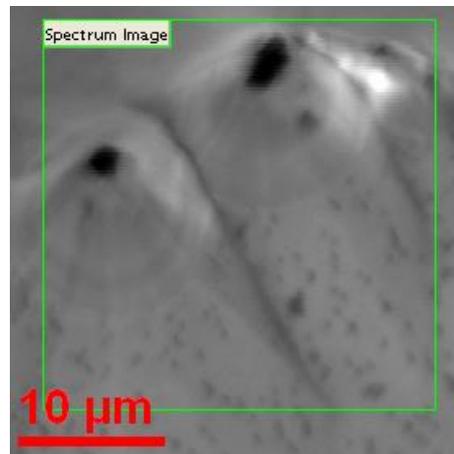


Fig.20

The spectral analysis of this region of interest is summarized in Figs. 21, and 22.

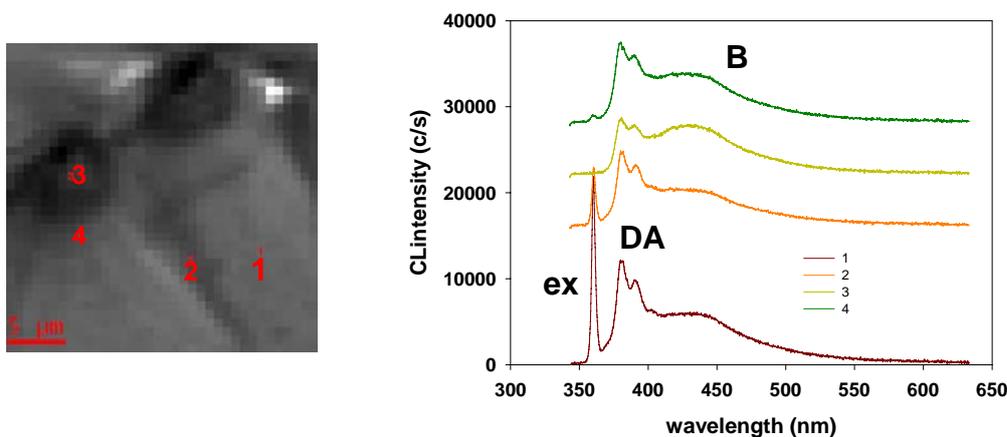


Fig.21

The local spectra showing the main spectral features are shown in Fig.21. One observes the excitonic band, the DAP band and its phonon replica, and the BL band, also a shoulder in the low energy side of the BL band is present, presumably corresponding to the visible band.

The spectra correspond to the positions numbered in the image. The excitonic band is quenched in the dark zones, points # 3 and 4, while the BL band is enhanced. The distribution of the different bands is shown in the spectral images of Fig. 22.

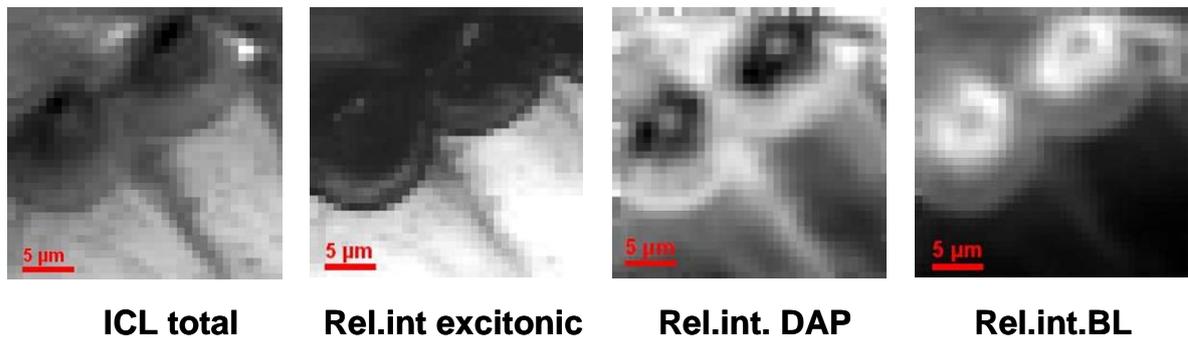


Fig.22

The images of Fig.22, represent the sum of the amplitudes of all the luminescence bands, and the intensities normalized to the total amplitude of the excitonic, DAP and BL bands. One observes a clear anticorrelation between the excitonic band distribution and the BL band. Also the DAP band is anticorrelated to the excitonic band, except around the pyramid summit. This accounts for the quenching of the excitonic band in regions with higher concentration of defects, which are witnessed by the presence of the extrinsic bands

Regarding the dark tiny structures revealed in the panchromatic images, one observes a clear anticorrelation between the excitonic band and the other bands, DAP and BL. Fig. 23 shows the typical spectra inside the tiny dark spots and out of them.

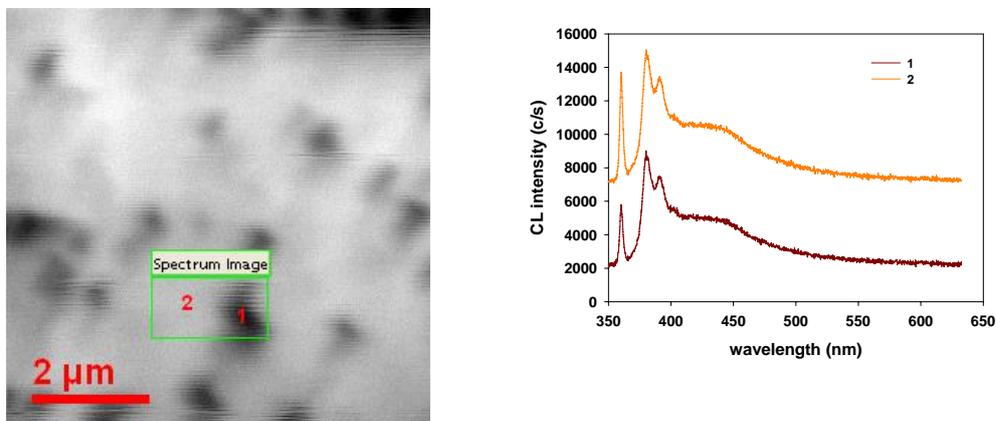


Fig.23

The relative weight of the defect related bands is enhanced in the dark tiny spots, accounting for the decoration with impurities, e.g. O and Zn, of the extended defects.

Sample AFRL_L20b

This sample presents mosaicity, which the structure is revealed in the CL image, Fig.24. The spectra in dark and bright points respectively are also shown in Fig.24.

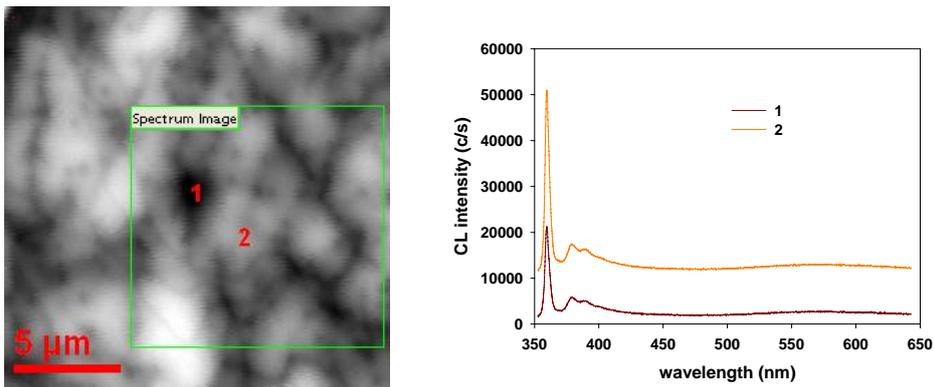
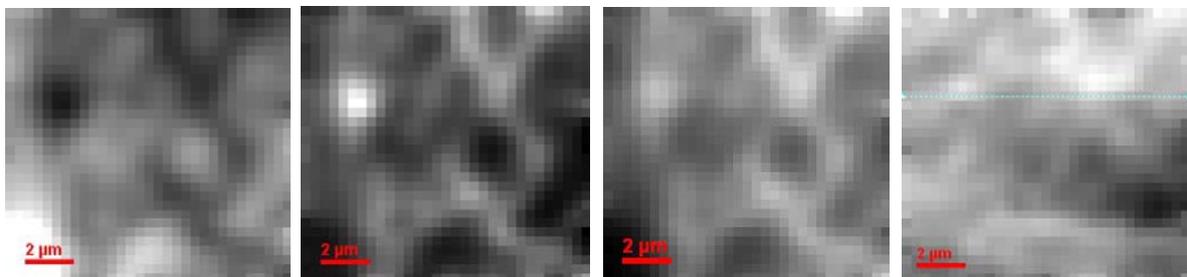


Fig.24



Amplitude excitonic

Relative Amplitude
DAP

Relative Amplitude
YL

FWHM excitonic

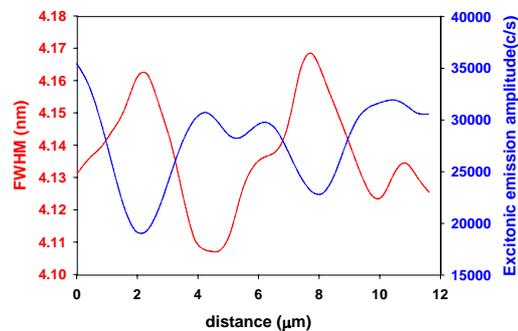


Fig.25

The spectra show the excitonic band, the DAP transition, the BL band is absent, and the visible emission is weak, but observable. If one looks at the mosaicity, the separation between dark zones is significantly larger than the usual submicrometric distance observed in epitaxial layers, Fig.4; which evidences a significant improvement in terms of crystal quality respect to the epitaxial layers. The spectrum images reveal the distribution of the different luminescence bands, Fig.25. One observes that the distribution of the extrinsic bands, DAP and YL, are anticorrelated to the excitonic band, and they are more relevant in the dark areas. Also the full width at half maximum (FWHM) of the excitonic emission is anticorrelated to the excitonic emission, this relation is better observed in the scan profiles shown in Fig. 25, where one observes than in the zones with higher concentration of defects, lower excitonic emission, the FWHM is broadened as expected for a lower crystalline quality.

Other sectors were studied, in particular the prismatic side, Fig. 26.

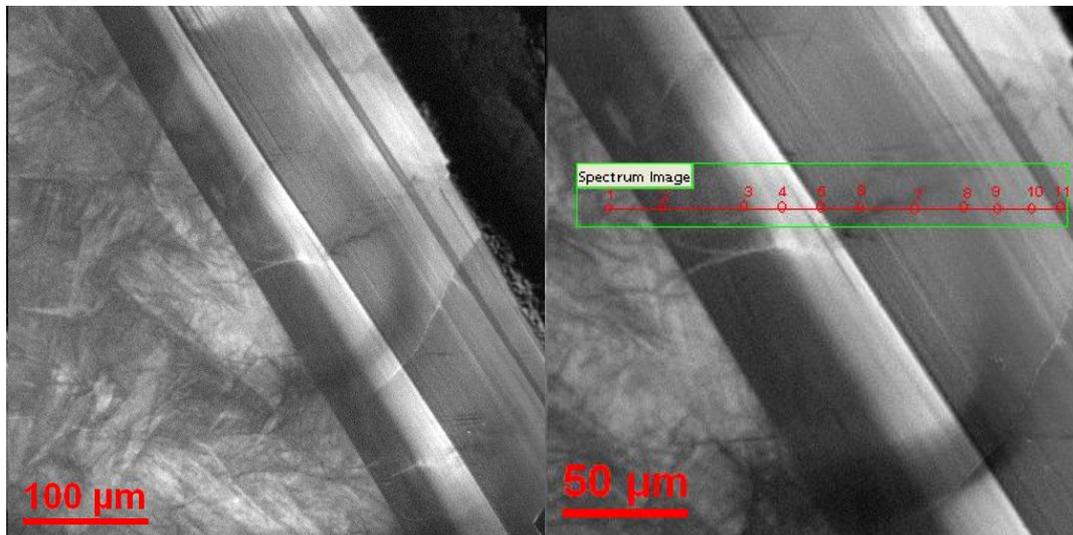


Fig.26

The panchromatic CL image shows a very homogeneous m sector, without dark defects or mosaicity as observed in the basal planes. Furthermore the m sector looks stratified, with the successive strata, presenting different luminescence signatures. Fig.27 presents the spectra corresponding to the number positions of Fig. 26. A relevant increase of the YL band is observed with respect to the seed. The successive strata present different contributions to the luminescence spectrum; the zone immediately adjacent to the seed only presents the YL band, spectrum #2. As the probed region goes away from the seed, one starts to observe the DAP transitions and the YL emission, #3 and 4. Beyond this zone, one observes a broad zone where the excitonic transition is present, #4-8. Beyond this point the excitonic transition is absent. Also the DAP band at 3.32 eV, with its phonon replicas is no more observed, being replaced by a broad band peaking at 3.08 eV (402 nm), which was already observed as a shoulder in spectra #4-8.

A band around this energy is usually associated with C impurities (S.M.Lee, et al; Phys.Rev.B 61, 16033 (2001); J.E. Northrup; Phys. Rev.B66, 045204 (2002)). The YL band shifts its peak position depending on the probed zone. Close to the seed it peaks at 543 nm (2.28 eV), and then it shifts to 574nm (2.16 eV).

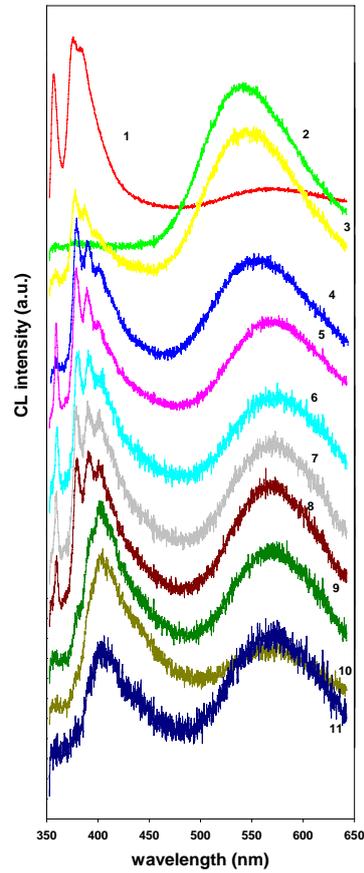


Fig.27

E-irradiated ZnO crystals

To achieve successful p-type doping, one needs to improve the knowledge about the native defects, which can complex with impurities and also form compensating levels precluding effective p-type conversion [M. D. McCluskey and S. J. Jokela, *J. Appl. Phys.* **106**, 071101 (2009)]. The role of the native point defects in ZnO is still controversial. High energy e-irradiation is an efficient method to create intrinsic defects, while luminescence techniques are very useful to study the signature of the defects [L. S. Vlasenko and G. D. Watkins, *Phys. Rev. B* **71**, 125210 (2005)]. However, the luminescence spectrum of e-irradiated ZnO has not reported dramatic spectral changes, which is consistent with the strong radiation hardness of ZnO. Positron annihilation studies have revealed the presence of Zn vacancies under high energy electron irradiation, as the main defects generated by the irradiation [F. Tuomisto, V. Ranki, K. Saarinen, and D. C. Look, *Phys. Rev. Lett.* **91**, 205502 (2003). C. Koscum, D. C. Look, G. C. Farlow, and J. R. Sizelove, *Semicond. Sci. Technol.* **19**, 752 (2004).]. Zinc vacancies are acceptors which can compensate the n-type nature of as grown ZnO. We have studied the cathodoluminescence (CL) ZnO crystals irradiated with high energy electrons. The e-irradiation mainly generates Zn sublattice primary defects, which interact with the previously existing defects and impurities in the crystal; therefore, the final defects shall depend on the growth conditions and the history of the samples.

ZnO wafers were irradiated at room temperature with high energy electrons (1 MeV) at fluences of 10^{17} cm⁻², in AFRL Hanscom. The wafers labelled as M were annealed at 650°C in 1,4 Torr O₂ atmosphere during 0.5 h. Then they were irradiated. The wafers labelled as TD were irradiated without previous annealing.

The CL measurements were carried out at 80 K. The acceleration voltage of the e-beam was varied between 2 and 30 kV, in order to modify the penetration depth of the probe beam. Some Vickers indentations were done on the samples, in order to compare the effects of the e-irradiation with the mechanically generated defects. Hall effect measurements were carried out on sample TD after irradiation.

The luminescence spectrum of ZnO crystals consists of three main spectral regions, the near band edge (NBE) emission with energies above 3.33 eV, the bands with energies below 3.33 eV, usually associated with donor acceptor pair (DAP) transitions and/or phonon replicas of the different excitonic bands, and the visible luminescence in the green–red spectral range. The relative importance of the different bands depends on the sample growth method and history. The CL spectra of the two samples studied herein, before irradiation, are shown in Fig.1. One observes significant difference between both samples, which reveals different defect compositions. First, the CL emission is significantly more intense for sample TD than for sample M, over one order of magnitude, which suggests a lower defect concentration in that sample with respect to the M sample. The nature of the non radiative recombination centers in ZnO is a matter of controversy, they have been related to extended defects and /or to native defects; in particular, V_{Zn} related complexes were associated with non radiative recombination centers [S. F. Chichibu, T. Onuma, M. Kubota, A. Uedono, T. Sota, A. Tsukazaki, A. Ohtomo, and M. Kawasaki, *J. Appl. Phys.* **99**, 093505 (2006)]. The CL spectrum of sample TD is characterized by a strong contribution of the phonon replicas, which can be even more intense than the excitonic bands, while sample M presents lower intensity phonon replicas; note that the NBE spectrum consists of several close lying free, FX, and bound, BX, excitonic transitions. This result is also compatible with a better crystalline quality of TD sample. In previous work we established a correlation

between the relative intensity of the phonon replicas with respect to the NBE band in terms of the crystal quality [J. Mass, M. Avella, J. Jiménez, A. Rodríguez, T. Rodríguez, M. Callahan, D. Bliss, and Buguo Wang, *J. Cryst. Growth* **310**, 1000 (2008)].

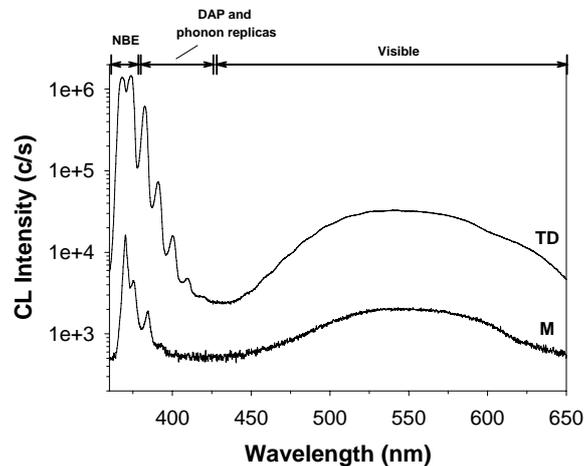


Figure1. CL spectra of both TD and M samples without irradiation ($E_b = 10$ kV).

The spectral region below 3.33 eV consists of several bands separated each other by ≈ 70 meV, which is roughly the energy of the LO phonon (72 meV) in ZnO. There is a main band at ≈ 3.31 eV and several phonon replicas at 3.24, 3.17 and 3.1 eV. The nature of the 3.31 eV band is a matter of controversy. It has been associated with a donor-acceptor pair (DAP) transition [T. B. Hur, G. S. Jeon, Y. H. Hwang, and H. K. Kim; *J. Appl. Phys.* **94**, 5787 (2003)], the nature of the defects involved is unknown. It is also identified as the first phonon replica of the free exciton transition, FX-1LO band [B. K. Meyer, H. Alves, D. M. Hofmann, W. Kriegseis, D. Forster, F. Bertram, J. Christen, A. Hoffmann, M. Strasburg, M. Dworzak, U. Haboek, and A. V. Rodina, *Phys. Stat. Sol. (b)* **241**, 231 (2004)]. Also, a band related to structural defects was reported around such energy [B. K. Meyer, H. Alves, D. M. Hofmann, W. Kriegseis, D. Forster, F. Bertram, J. Christen, A. Hoffmann, M. Strasburg, M. Dworzak, U. Haboek, and A. V. Rodina, *Phys. Stat. Sol. (b)* **241**, 231 (2004), M. Schirra, R. Schneider, A. Reiser, G. M. Prinz, M. Feneberg, J. Biskupek, U. Kaiser, C. E. Krill, R. Sauer, and K. Thonke, *Physica B* **401-402**, 362 (2007), Y. Ohno, H. Koizumi, T. Taishi, I. Yonenaga, K. Fujii, H. Goto, and T. Yao, *Appl. Phys. Lett.* **92**, 011922 (2008)]. On the other hand, the broad visible band consists of at least three contributions, green (GL), yellow (YL), and orange-red (RL), which the origin is still a matter of controversy. GL is usually associated with defects related to oxygen deficiency (V_O and Zn_i), while the YL and RL bands have been rather associated with Zn deficiency (V_{Zn} , O_{Zn} , O_i) [H. C. Ong and G. T. Du, *J. Cryst. Growth* **265**, 471(2004)].

The CL spectra before and after irradiation are shown in Figures 2a and b. Sample M does not present significant changes in the CL spectrum after e-irradiation of the annealed sample, Figure 2a; the main effect is the relative quenching of the overall luminescence emission, because of the generation of non radiative recombination centers, but the spectral shape is very similar before and after irradiation; a slight increase in the relative intensity of the visible luminescence respect to the NBE emission could also be considered, but it is not very relevant. Note that the previous

annealing of this sample shifted the visible band to the yellow, and the subsequent irradiation did not shift anymore the band.

The situation is different for sample TD, for which the CL spectrum presents significant changes after irradiation, Figure 2b. The overall CL intensity is drastically reduced, which is due to the generation of non radiative recombination centers. The NBE spectral region is also modified, one observes changes in the bound exciton bands. The region of the phonon replicas presents noteworthy changes; a new band appears clearly differentiated from the FX-1LO band, the new band labelled P_D is observed in the high energy side of the FX-1LO band. The existence of a defect related band around 3.32 eV appearing as a shoulder of the FX-1LO band was previously reported [12], usually in the neighbourhood of crystal defects; in particular, we observed it in TD samples in the regions surrounding the dislocations generated by Vickers indentation [J. Mass, M. Avella, J. Jiménez, A. Rodríguez, T. Rodríguez, M. Callahan, D. Bliss, and Buguo Wang, *J. Cryst. Growth* **310**, 1000 (2008), J. Mass, M. Avella, J. Jiménez, M. Callahan, D. Bliss, and Buguo Wang, *J. Mater. Res.* **22**, 3526 (2007)]. A similar band (3.32 eV (≈ 373 nm)) was seen enhanced in e-irradiated ZnO [M. A. Hernández-Fenollosa, L. C. Damonte, and B. Marí, *Superlatt. and Microstr.* **38**, 336 (2005)].

The visible band shifts from the green to the yellow-red under electron irradiation; furthermore, its relative intensity with respect to the NBE emission is strongly enhanced. To resume, under irradiation the GL band is quenched, while the YL band is enhanced, becoming dominant. This behaviour suggests a strong generation of the deep levels responsible for the YL. The visible bands have been reported to undergoing changes under the effect of e-irradiation [L. S. Vlasenko and G. D. Watkins, *Phys. Rev. B* **71**, 125210 (2005)] and plastic deformation [V. Coleman, J. E. Bradby, C. Jagadish, and M. R. Phillips, *Appl. Phys. Lett.* **89**, 082102 (2006)].

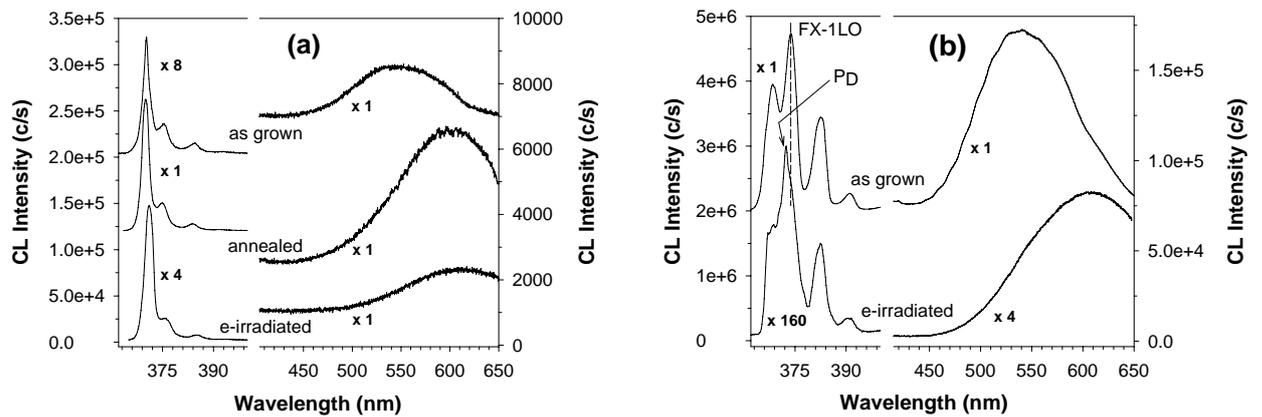


Figure 2. a) CL spectra of sample M before irradiation, annealed and e-irradiated ($E_b = 15$ kV); b) CL spectra of sample TD before and after e-irradiation ($E_b = 30$ kV).

On the other hand, Hall effect measurements showed a conversion from n-type to p-type after e-irradiation. Electric isolation was reported under O⁺ implantation and it was associated with the formation of Zn vacancies [A. Zubiaga, F. Tuomisto, V. A. Coleman, H. H. Tan, C. Jagadish, K. Koike, S. Sasa, M. Inoue, and M. Yano, *Phys. Rev. B* **78**, 035125 (2008)]. The conversion to p-type suggests that in addition to the

deep levels, the electron irradiation generates acceptor levels, shallow enough to supply holes to the valence band at room temperature. The defects responsible for the P_D band can be adequate candidates. The P_D band presents well defined phonon replicas, which supports the acceptor nature of the defects responsible for that emission.

One of the advantages of the excitation with an e-beam in the CL measurements is the large penetration depth range with respect to photoluminescence (PL), which is excited with an UV laser beam. The conventionally used He-Cd laser (325 nm) penetrates around 100 nm, while the penetration of the e-beam can be varied from a few nanometers to 3 μm [K.Kanaya, and S.Okayama; *J. Phys. D Appl. Phys.* **5**, 43 (1972)] using the 2 to 30 kV range. This allows observing the effect of the e-irradiation far from the surface where surface defects could interact with the primary defects generated by the e-irradiation. The CL signature depends on penetration depth, see the CL spectra of irradiated TD sample for two different e-beam acceleration voltages in Figure 3. The two spectra present different features. The structure of the visible band is different for the two e-beam voltages: while for 30 kV the GL is quenched and the YL is strongly enhanced, in the spectrum acquired at 10 kV, the visible band presents a relative lower intensity and appears as the convolution of both GL and YL bands. On the other hand, the P_D peak is observed in both cases but with different contribution. Note that at 10 kV the subsurface damage is still influencing the spectrum, while at 30 kV the subsurface damage does not play a major role.

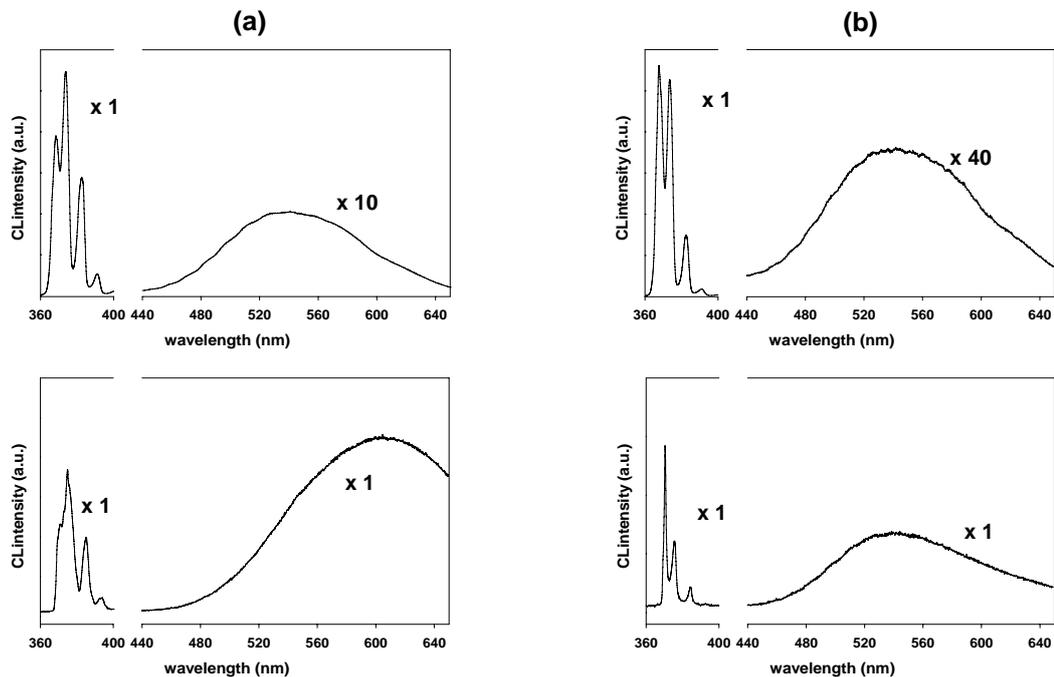


Figure 3. CL spectra of sample TD before (top) and after (bottom) e-irradiation. a) $E_b = 30$ kV; b) $E_b = 10$ kV.

The primary defects produced by electron irradiation are vacancies and interstitials. The atomic displacement rate can be estimated from the Macinley-Feshbach formula [F. Agulló-López et al, *Point defects in materials*, Academic Press, New York, 1988], using the displacement energy, E_d . The E_d values for ZnO, 41.4 eV for O and 18.5 eV for Zn, were estimated by Van Vechten [J. A. Van Vechten, in *Handbook on semiconductors*, ed. by T.S.Moss and S.P.Keller (North Holland, Amsterdam 1988) ch.1]. According to

this, the displacement rate is higher for Zn; therefore, Zn sublattice defects are expected in a higher concentration respect to O sublattice defects. Tuomisto *et al.* [F. Tuomisto, V. Ranki, K. Saarinen, and D. C. Look, *Phys. Rev. Lett.* **91**, 205502 (2003)] estimated a very low displacement rate of 0.03 cm^{-1} , which means that the defects should recombine at low temperature [L. S. Vlasenko and G. D. Watkins, *Phys. Rev. B* **71**, 125210 (2005), F. Tuomisto, V. Ranki, K. Saarinen, and D. C. Look, *Phys. Rev. Lett.* **91**, 205502 (2003), C. Koscum, D. C. Look, G. C. Farlow, and J. R. Sizelove, *Semicond. Sci. Technol.* **19**, 752 (2004)]. Frenkel pairs are formed as primary defects, but due to the high mobility of the interstitials they recombine at relatively low temperature, therefore, the concentration of defects at room temperature must be low. The recombination of the Frenkel pairs on one side, and the complex formed by the primary defects on the other side, must be influenced by the background defects and impurities present in the samples.

The P_D band observed under electron irradiation at 3.32 eV seems to be similar to the one induced by plastic deformation, Figure 4. It is probably associated with V_{Zn} defects. A relation between V_{Zn} and a luminescence band at 3.34 eV was reported [19]; note that that measurement was carried out at 10 K; therefore, it can be related to our band at 3.32 eV, which was measured at 80 K.

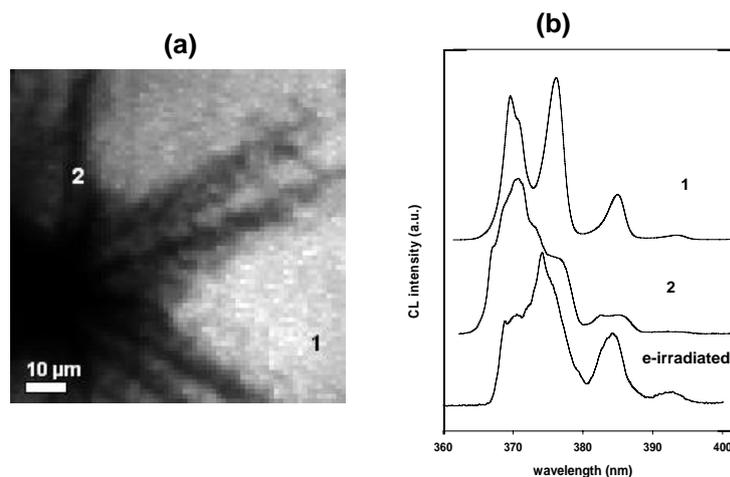


Figure 4. a) CL image of an indentation in as-grown TD sample; b) CL spectra in a defect free area (1), in an indented area (2) and after e-irradiation (3) ($E_b = 30$).

The presence of dominant Zn sublattice defects induced by the e-irradiation is consistent with our CL data, which reveal a prevalence of V_{Zn} related defects; in particular, the formation of a shallow acceptor related to V_{Zn} and responsible for the P_D band, the enhancement of the YL, which is usually associated with V_{Zn} complexes [H. C. Ong and G. T. Du, *J. Cryst. Growth* **265**, 471(2004)], and the formation of non radiative recombination centers, also associated with V_{Zn} complexes [S. F. Chichibu, T. Onuma, M. Kubota, A. Uedono, T. Sota, A. Tsukazaki, A. Ohtomo, and M. Kawasaki, *J. Appl. Phys.* **99**, 093505 (2006)]. Is the ability of V_{Zn} to form different complexes that could explain the differences observed among the different samples and the depth dependence of the e-irradiation effect. At the present time, one cannot account for other observations as the quenching of the GL band under e-irradiation. Tentatively, one can associate the

GL band to complexes involving V_O , which might be restructured under the e-irradiation. The quenching of this band under O_2 annealing suggests that the V_O defects are involved in the GL emission.

Conclusion

The characterization of the OP-crystals allowed to advancing some possible causes of optical losses. The main factors that can be considered are:

- i. The absorption by free electrons. This mainly affects the signal.
- ii. The absorption of the pumping light when the Fermi level is below the 0/+ level of EL2.
- iii. The light scattering by extended defects, rather probably situated on the domain walls, complementary experiments will be carried out shortly.
- iv. Furthermore, the stress induced around the domain walls can change the refractive index and can be the cause of internal reflections, which result in additional losses.

The GaN ammonothermal crystals have been characterized. Several samples and growth sectors have been studied; the crystal quality is substantially improved in samples 45 and L20. The incorporation of defects seems still high, however, an improvement is observed in some sectors of the last two crystals, which is established in terms of the observation of the excitonic emission.

In the regions free of dark defects, mainly inversion domains, the homogeneity of the luminescence emission is good, suggesting a low presence of extended defects, as compared to the epitaxial layers. The CL response of the GaN crystals, does not seem to be strongly influenced by the seed, but it seems rather influenced by the growth process itself, in terms of the incorporation of impurities and other defects. The properties of the crystals seem to change along the growth process, see the stratification, and the evolution of the spectral response with the distance to the seed.

The electron irradiated ZnO crystals have allowed to give some interpretations about the intrinsic defects in ZnO. E-irradiation has been demonstrated to generate defects related to Zn vacancies. Actually we are doing some analysis of the depth distribution of the defects generated during the irradiation, in order to understand the role of the surface defects on CL response of ZnO.

Publications:

- 1) Cathodoluminescence study of orientation patterned GaAs crystals for nonlinear optical frequency conversion by quasi-phase-matching; H. Angulo, M. Avella, O. Martínez, J. Jiménez, C. Lynch, and D. Bliss; MRS Symp.Proc.1108, A11-07 (2009)
- 2) A Luminescence Study of Electron-Irradiated ZnO Crystals; M.Avella, O.Martínez, J. Jiménez, B.Wang, P. Drevinsky, and D. Bliss; MRS Symp.Proc.1201, H05-09 (2010)



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- 3) Cathodoluminescence study of orientation patterned GaAs crystals for non-linear optics; O. Martínez, M. Avella, V. Hortelano, J. Jiménez, C.Lynch, D. Bliss J.Electron. Mater. 29, 805 (2010)

Actually, other articles are in preparation.