phys. stat. sol. (c) **5**, No. 9, 3095–3097 (2008) / **DOI** 10.1002/pssc.200779298

physica status solidi c
www.pss-c.com
current topics in solid state physics

Studies of optical emission in the high intensity pumping regime of top-down ZnO nanostructures and thin films grown on c-sapphire substrates by pulsed laser deposition

L. Divay[*,1], D. J. Rogers[,2], A. Lusson[3], S. Kostcheev[1], S. Mc Murtry[1], G. Lérondel[***,1], and F. Hosseini Téhérani[2]**

[1] Laboratoire de Nanotechnologie et d'Instrumentation Optique, ICD CNRS (FRE2848), Université de Technologie de Troyes, 10-12 rue Marie Curie, 10010 Troyes, France
[2] Nanovation SARL, 103 bis rue de Versailles, 91400 Orsay, France
[3] GEMaC, CNRS - Université de Versailles Saint-Quentin en Yvelines, 1 place Aristide Briand, 92190 Meudon CEDEX, France

Received 30 October 2007, accepted 10 December 2007
Published online 13 June 2008

PACS 78.55.Et, 78.67.–n, 81.05.Dz, 81.15.Fg

[*] Corresponding authors: e-mail laurent.divay@utt.fr, Phone: +33 (0)3 25 75 96 41, Fax: +33 (0)3 25 71 56 99
[**] e-mail d.j.rogers@nanovation.biz, Phone: +33 (0)6 68 23 43 98, Fax: +33 (0)1 64 46 29 49
[***] e-mail gilles.lerondel@utt.fr, Phone: +33 (0)3 25 71 58 74, Fax: +33 (0)3 25 71 56 99

We report on the emission of Zinc Oxide (ZnO) thin films obtained by Pulsed Laser Deposition (PLD) under high intensity excitation. In order to clarify the origin of the emission bands, we compared results for high quality thin films (75 nm) before and after "top-down" nanopatterning. A nanopattering technique was developed for this purpose. The technique combined Electron Beam Lithography (EBL) and lift-off techniques and Inductively Coupled Plasma Reactive Ion Etching (ICP RIE). The emission spectra of the two types of samples were found to have a difference in their fine structure that was attributed, in part, to the existence of guided emission in the thin films and exciton weak confinement effects in the nanostructures.

1 Introduction Zinc oxide (ZnO) is currently attracting considerable interest for use in blue and Ultra-Violet (UV) solid-state emitters and photonic devices. As a result of a relatively large exciton binding energy (60 meV), several research teams have reported optically pumped excitonic stimulated emission from ZnO thin films up to 550 K [1-4].

In this paper, we report on the emission from ZnO thin films obtained by Pulsed Laser Deposition (PLD) before and after top-down dry-etch nanostructuration.

2 Experimental

2.1 Thin films deposition 75 nm thick ZnO thin films were epitaxially grown on c-sapphire using PLD, as described elsewhere [5]. The films showed a Root Mean Square roughness of less than 2 nm in Atomic Force Microscope (AFM) studies and an X-Ray Diffraction (0002) peak omega rocking curve of under 100 arc.secs, indicating a relatively low crystallographic dispersion in the films. Low excitation intensity photoluminescence (PL) emission at room temperature showed a Free Exciton (FE) emission at 377.7 nm (3.28 eV), with a Full Width Half Maximum (FWHM) of 11 nm (98 meV) and negligible deep level emission.

2.2 Nanopatterning A standard Electron Beam Lithography (EBL) sequence, employing poly(Methyl Methacrylate) (PMMA) patterning, metallic thin film deposition and lift-off allowed the fabrication of nanoscale metallic disk-shaped mesas on the surface of the sample. The thin film was then selectively etched using ICP RIE (custom Plassys system) with C_2F_6 [6] with the metallic mesas acting as a mask. Parameters were adjusted so as to remove the metal and etch 65-70 nm down into the ZnO film. Observations of the etched sample (AFM and Scanning Electron Microscopy (SEM)) showed that 200 nm di-

ameter, 60 nm height ZnO nanoparticles were obtained. Figure 1 shows the resulting ZnO nanostructures arranged in a square 20 µm x 20 µm lattice, with a center-to-center spacing of 400 nm.

Room temperature Continuous Wave excitation PL (not shown) showed negligible defect emission, confirming that the technique did not significantly damage the ZnO luminescence properties.

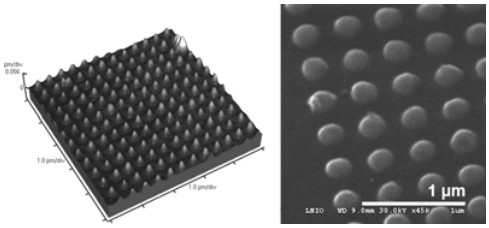

Figure 1 AFM and SEM images of the ZnO nanoparticle array. Disk-shaped ZnO nanostructures are 200 nm wide and 60 nm high.

2.3 Experimental setup for high intensity photoluminescence measurements High intensity excitation PL was conducted using a 337.1 nm N_2 laser with 4ns duration pulses at a 20 Hz repetition rate and an average power of 2.4 mW. Laser spot diameter was controlled by varying the distance between the sample and the focusing lens. The excitation density was defined using UV optical density attenuators. The size and position of the excitation spot were controlled using an optical microscope. Spectra were recorded using a triax-550 Jobin-Yvon spectrometer equipped with a 600 line/mm diffraction grating and a nitrogen cooled CCD array.

3 Results and discussion

3.1 Continuous thin film Figure 2 shows the PL side-emission spectra from the continuous thin film when excited by a 30 µm laser spot.

The side emission from the thin film exhibited a strong dependence on excitation density [1-4], and shows fine structures. For lower intensity excitation, three emission bands are seen and labelled FE, P_2 and P. The P_2 band is attributed to the exciton-exciton collision emission, in which an exciton is scattered into an n = 2 energy state, while the other emits a photon. The FE band can be seen as a shoulder in the P_2 band. The P band originates from the same phenomenon as the P_2 band, except that the exciton is scattered into an $n\rightarrow\infty$ energy state. The emissions are centered at 381.4nm for the P_2 band and 388.7nm for the P band, as would be expected for exciton-exciton inelastic collision [1-4, 7]. Above 50 MW/cm², N band stimulated emission dominates the spectrum. The position of the N band is progressively red-shifted with increasing excitation density. The emission is attributed to the recombination of carriers in an electron-hole plasma (EHP) [1].

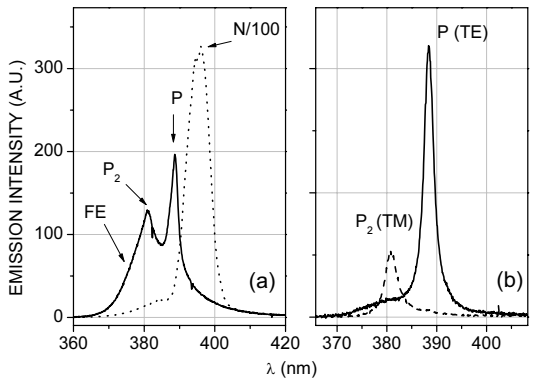

Figure 2 (a) Side emission from the continuous thin film. FE, P_2 and P bands are seen for a pumping intensity lower than 50 MW/cm². Pumping above this threshold induces the appearance of N band emission. (b) the P_2 band is TM polarised and the P band is TE polarised.

Polarization dependent measurements (Fig. 2(b)) showed that the P_2 band is mainly TM polarised while the P band is mainly TE polarised. This suggests that these emissions were supported by a guided mode in the thin film [8, 9].

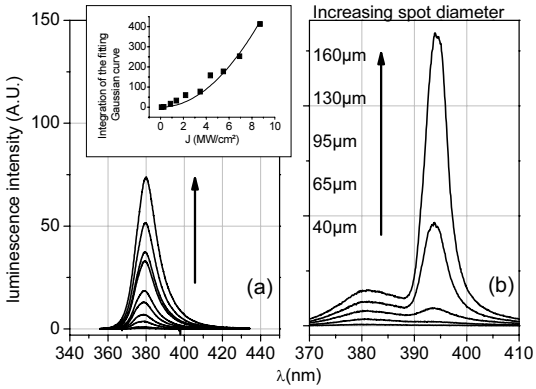

Figure 3 (a) PL spectra recorded from the surface of the film as a function of excitation density for a 60 µm excitation spot. The inset illustrates a quadratic evolution of the P_2 band emission intensity. (b) Evolution of the PL spectra as a function of the excitation spot diameter. The N band appears as the diameter is increased.

The peak visible in the surface emission spectrum (Fig. 3(a)) mainly corresponds to the P_2 band. No P or N band emission was detected in this geometry with a 60 µm spot. However, spot size dependent measurements showed that the N band emerged when a larger excitation spot was used (Fig. 3(b)), suggesting that the high intensity of the N band emission is due to stimulated emission. Therefore, EHP recombination emission is, in fact, present in the Fig. 3(a) spectra but remains weak compared to P_2 emission when there is no stimulated emission. Using a sufficiently large excitation spot diameter (140 µm), the threshold for N band stimulated emission was found to be about 5.5 MW/cm². The relatively high threshold values observed in this study can be explained as a result of employing much smaller excitation spots than those typically used in such investigations.

A least square fitting method was employed to calculate the integrated luminescence intensity of the P2 band. It revealed a quadratic dependence on J (optical pumping density) within the experimental and fitting errors (Fig. 3). This is as would be expected for a bi-excitonic process [1].

3.2 Nanostructure array The high intensity excitation PL spectra for the nanostructure array were recorded with surface collection, as no significant emission could be detected from the side of the sample. At low pumping intensity the results show similar behaviour to that for the continuous thin film. At high pumping density (above 25 MW/cm²), however, the behaviour is quite different. A new emission band emerges from the low energy side of the spectrum and becomes predominant as the pumping intensity increases. The new band is centered at 385.5 nm for a 50 MW/cm² pumping density. Moreover, no N band lasing was detected, as in the small excitation spot results for the continuous thin film. This could be attributed either to the small volume of the emissive material (too small to give sufficient gain) or to the lack of optical confinement (waveguiding).

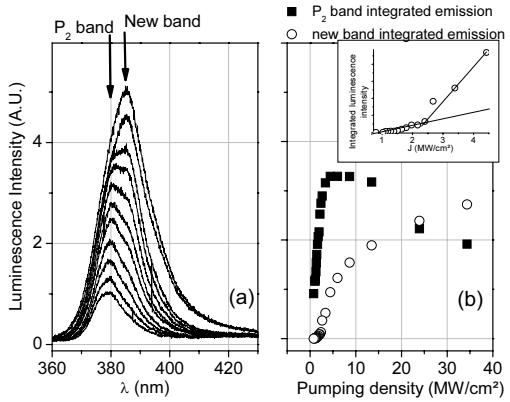

Figure 4 (a) Surface emission spectra for the nanostructure array. A new, distinctive emission band is observed. It is attributed to an emission specific to the nanostructures. (b) The new emission band is more intense than the P_2 band in spectra recorded with an excitation density over 25 MW/cm². Inset shows the emission threshold for the new band (2.5 MW/cm²)

A least square fitting was conducted on the emission spectra in the same way as for the thin film. The results of the fitting allowed us to determine the intensity and the spectral position variation of the new emission band. The new band blue-shifted as the excitation density was increased, confirming that it originates from a different recombination process than the P bands. The emission had a non-linear dependence on the pumping density. As shown in Fig. 4(b), the P_2 band has a maximum emission intensity around 5 MW/cm². At higher pumping densities the new emission band is significantly more intense than the P_2 band. At lower densities, the new band shows an emission threshold at 2.5 MW/cm² (Fig. 4). These results suggest either a concentration effect or a stimulated emission effect, although the process underlying this specific emission is unclear. Additional results are needed, especially the spectral position dependence of the band against the temperature.

4 Conclusion PL of ZnO thin films and nanostructures was studied under high intensity excitation. An EBL top-down process was developed for this purpose. It allowed nanostructuration without significantly damaging the luminescence properties of the ZnO. Emission spectra were found to be different for the two kinds of samples. The luminescence from the thin film depended on the pumping intensity, excitation spot diameter and collection angle. This combination of dependences is coherent with the presence of guided mode stimulated emission in the thin film. The nanostructure array showed a different behaviour. No P or N bands were detected. At high pumping intensities, a new emission band was recorded, which seemed to originate from a process other than exciton scattering (P band). The non-linear dependence of this emission on pumping intensity suggests a carrier concentration effect. A temperature dependent study will be conducted in the near future to clarify the origin of this emission.

In conclusion, these results indicate that photonic, rather than excitonic confinement is necessary to observe P band stimulated emission. We will, therefore, concentrate our efforts in the design and fabrication of thin film based photonic structures. It is projected that the high quality of the ZnO epilayers and the etching process that has been developed should allow us to obtain UV lasing structures.

Acknowledgements The authors would like to acknowledge the financial support of the CRCA (Champagne-Ardennes Council) for L.D. postdoctoral position, the NANODEF project grant and the Agence National de la Recherche SUMO programme.

References

[1] P. Zu, Z. K. Tang, G. K. L. Wong, M. Kawasaki, A. Ohtomo, H. Koinuma, and Y. Segawa, Solid State Commun. **103**(8), 459-463 (1997).
[2] D. M. Bagnall, Y. F. Chen, Z. Zhu, T. Yao, M. Y. Chen, and T. Goto, Appl. Phys. Lett. **73**(8), 1038-1040 (1998).
[3] T. Shimomura, D. Kim, and M. Nakayama. J. Lumin. **112** 191-195 (2005).
[4] G. Tobin, E. McGlynn, M. O. Henry, J. P. Mosnier, J. G. Lunney, D. O'Mahony, and E. dePosada, Pysica B **340-342**, 245-249 (2003).
[5] D. J. Rogers, F. Hosseini Téhérani, A. Yasan, R. McClintock, K. Mayes, S. R. Darvish, P. Kung, M. Razeghi, and G. Garry, Proc. SPIE **5732**, 412 (2005).
[6] G.-K. Lee, J.-H. Moon, and B.-T. Lee, Semicond. Sci. Technol. **21**, 971–974 (2006).
[7] C. Klingshirn, phys. stat. sol. (b) **71**, 547-556 (1975).
[8] Z. K. Tang, G. K. L. Wong, P. Yu, M. Kawasaki, A. Ohtomo, H. Koinuma, and Y. Segawa. App. Phys. Lett. **72**(25), 3270-3272 (1998)
[9] Z. K. Tang, M. Kawasaki, A. Ohtomo, H. Koinuma, and Y. Segawa, J. Cryst. Growth **287**, 169-179 (2006).