

Materials characterization of n-ZnO/p-GaN:Mg/c-Al₂O₃ UV LEDs grown by pulsed laser deposition and metal–organic chemical vapor deposition

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Available online 27 June 2007

Abstract

n-ZnO/p-GaN:Mg hybrid heterojunctions grown on c-Al₂O₃ substrates showed 375 nm room temperature electroluminescence. It was suggested that the high materials and interface quality obtained using pulsed laser deposition for the n-ZnO growth and metal–organic chemical vapor deposition for the p-GaN:Mg were key factors enabling the injection of holes and the radiative near band edge recombination in the ZnO. In this paper we present the materials characterization of this structure using x-ray diffraction, scanning electron microscopy and atomic force microscopy.

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Keywords: Pulsed laser deposition; UV; ZnO; p–n; Heterojunction; LED

1. Introduction

ZnO ($E_g \sim 3.37$ eV) is considered a promising material for the development of next generation high brightness UltraViolet (UV) Light Emitting Diodes (LEDs) because of its

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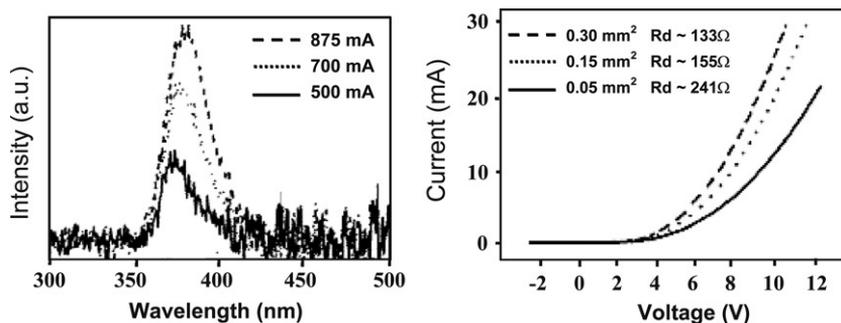


Fig. 1. RT EL spectra and I – V characteristics for the n-ZnO/p-GaN:Mg heterostructures (forward drive currents, mesa size and differential resistance, R_d , are indicated) [13].

relatively large exciton binding energy (~ 60 meV). For the moment, however, reproducible and stable p-type ZnO material with good conductivity and high carrier concentration is still under development and homostructural ZnO LEDs are not commercially available. In an alternative approach, there have been numerous attempts to develop hybrid p–n heterojunction LEDs with ZnO as the n-type layer [1–12]. These studies have employed a wide range of p-type materials deposited using a large variety of thin film growth tools. To date, however, there have been few publications reporting ElectroLuminescence (EL) and even fewer with a dominant UV emission.

We recently reported the fabrication of n-ZnO/p-GaN:Mg hybrid heterojunction LEDs on c -Al₂O₃ substrates using Pulsed Laser Deposition (PLD) for the ZnO and Metal–Organic Chemical Vapor Deposition (MOCVD) for the GaN:Mg [13]. The paper presented optical and electrical characterization data. In particular, I – V characteristics confirmed a rectifying diode behavior and Room Temperature (RT) EL spectra showed near band edge peak emission at about 375 nm (Fig. 1). A good correlation between the wavelength maxima for EL and PhotoLuminescence (PL) spectra suggested that recombination occurred in the ZnO layer and that it may be excitonic in origin. This also indicated that there was significant hole injection from the GaN:Mg into the ZnO. It was concluded that the high quality epitaxy and good interface at the p–n junction obtained using the PLD/MOCVD growth approach were key factors in obtaining the near band edge UV EL. In this paper, we present and discuss the results of the corresponding materials characterization.

2. Experiment

A 1 μm thick Mg doped GaN layer (GaN:Mg) was grown on c -Al₂O₃ by Metal–Organic Chemical Vapor Deposition (MOCVD) using a low-pressure horizontal-flow reactor. Trimethylgallium, NH₃ and bis(cyclopentadienyl)magnesium were used as the sources for Ga, N and Mg, respectively, as described elsewhere [14]. A ZnO layer was grown on top of the GaN:Mg layer using Pulsed Laser Deposition (PLD) in a molecular oxygen ambient with a Coherent KrF excimer laser (248 nm), as described elsewhere [15]. X-ray diffraction (XRD) studies were made with a four-circle Panalytical “X-Pert MRD Pro” system. Atomic Force Microscopy (AFM) was conducted using a Park Scientific Instruments “Autoprobe” system and Scanning Electron Microscopy (SEM) was performed in a Hitachi “S4500” system.

Circular LED mesas were fabricated from the heterostructure by masking the surface and chemically etching away the ZnO layer using a dilute acid. Six different masks were used to give

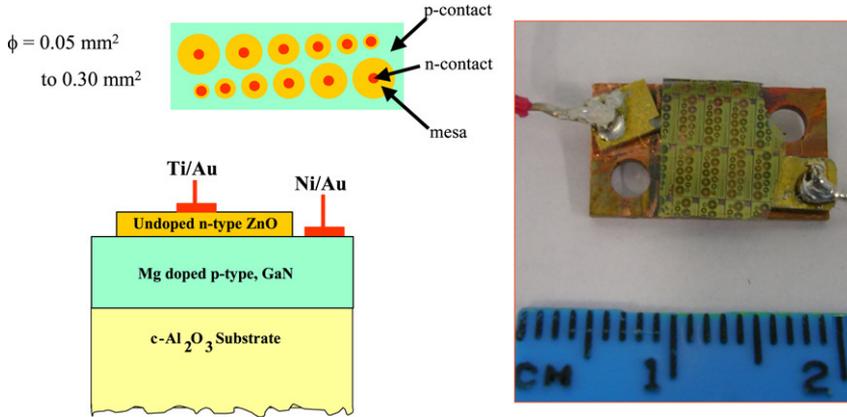


Fig. 2. Schematic and photograph of n-ZnO/p-GaN/c-sapphire ring mesa LEDs.

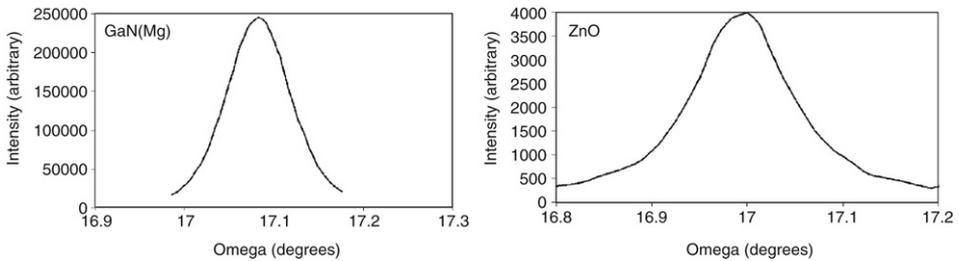


Fig. 3. XRD (0002) peak Ω scan rocking curves for the p-GaN and n-ZnO layers.

mesa areas ranging from 0.05 mm^2 up to 0.30 mm^2 in increments of 0.05 mm^2 . Semi-transparent Ni/Au contacts were evaporated onto the p-type GaN:Mg and Ti/Au contacts were evaporated onto the n-type ZnO (Fig. 2).

3. Results and discussion

Fig. 3 shows XRD omega scan rocking curves for the (0002) peaks in the p-GaN:Mg and n-ZnO layers. They show Full Widths at Half-Maxima (FWHM) of about 290 and 430 arcsec, respectively. This indicates that the dispersion in the crystallographic orientation about the crystallographic *c*-axis was relatively low for both films but that the ZnO top layer was not as highly oriented as the GaN:Mg underlayer. Fig. 4 shows a 2-theta/omega scan for the heterojunction with (0002) peaks for both the p-GaN:Mg and n-ZnO clearly visible. The p-GaN:Mg peak is about 60 times more intense than the n-ZnO peak which can be linked to the higher thickness of the p-GaN:Mg layer. The peak positions indicate *c* lattice parameters for relaxed wurtzite GaN:Mg and ZnO of about 5.19 and 5.21 Å, respectively. These are as expected for relaxed wurtzite GaN:Mg and ZnO. The peak FWHM are about 50 and 200 arcsec, respectively, for the p-GaN:Mg and n-ZnO. This suggests that the grain size in the p-GaN:Mg was larger than that in the n-ZnO, which is consistent with the omega rocking curve data. The 2-theta/omega spectrum also show thickness fringes. The presence of such fringes indicates that the film surface

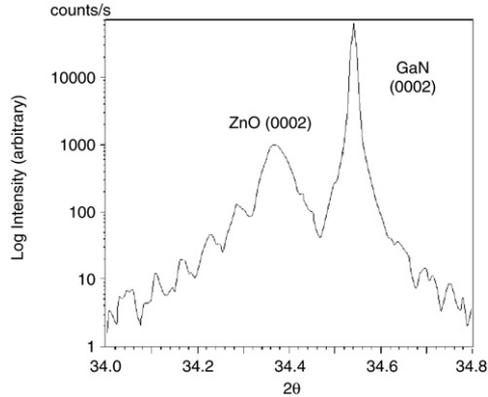


Fig. 4. XRD $2\theta/\Omega$ scan for the heterojunction showing the (0002) peak for both the p-GaN n-ZnO layers.

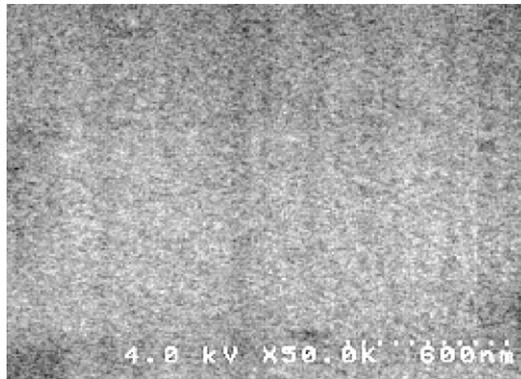


Fig. 5. SEM image of the surface of the n-ZnO layer grown by PLD.

is relatively smooth over a wide area. Their spacing gives an estimate of ZnO layer thickness at about 135 nm.

Fig. 5 shows a typical SEM image for the top of the n-ZnO/p-GaN:Mg/c-sapphire structure. The surface appears relatively smooth with no evidence of particulates. Fig. 6 shows contact mode AFM images of the surfaces for both the p-GaN:Mg and n-ZnO layers. The Root Mean Square (RMS) roughnesses (over an area $4\ \mu\text{m} \times 4\ \mu\text{m}$) are about 1.1 and 3.1 nm, respectively.

The corresponding peak-to-valley variations are 10.1 and 49 nm.

4. Conclusions

In this paper we presented the structural characterization of n-ZnO/p-GaN:Mg/c-sapphire UV heterojunction LEDs for which the optical and electrical data were reported elsewhere [13]. High crystal quality and good surface/interface morphology were confirmed by XRD, SEM and AFM studies. These results corroborate the high crystal quality and low defect/dislocation density inferred from the strong main peak and low green signal in RT PL data reported previously [13].

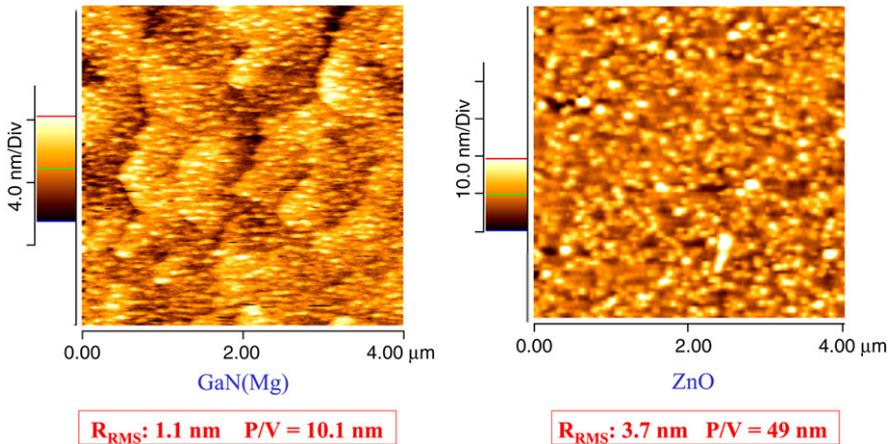


Fig. 6. Contact mode AFM images of p-GaN and n-ZnO surfaces.

Acknowledgements

The authors would like to thank C. Litton (USAF WPAFB), R. Triboulet (CNRS Meudon) and I. Ferguson (Georgia Institute of Technology) for useful discussions. Nanovation would also like to gratefully acknowledge the help of CRITT CCST, CRITT MECA, Varian Inc., Messer, Quanta Service, the Technopole de l'Aube, the Conseil Generale de l'Aube and 3A Conseil.

References

- [1] H. Ohta, M. Orita, M. Hirano, H. Hosono, *J. Appl. Phys.* 89 (2001) 5720.
- [2] H. Hosono, H. Ohta, K. Hayashi, M. Orita, M. Hirano, *J. Cryst. Growth* 237–239 (2002) 496.
- [3] H. Ohta, H. Mizoguchi, M. Hirano, S. Narushima, T. Kamiya, H. Hosono, *Appl. Phys. Lett.* 82 (2003) 823.
- [4] Y. Alivov, J.E. Van Nostrand, D.C. Look, M.V. Chukichev, B.M. Ataev, *Appl. Phys. Lett.* 83 (2003) 2943.
- [5] Y. Alivov, E.V. Kalinina, A.E. Cherenkov, D.C. Look, B.M. Ataev, A.K. Omaev, M.V. Chukichev, D.M. Bagnall, *Appl. Phys. Lett.* 83 (2003) 4719.
- [6] A. Kudo, H. Yanagi, K. Ueda, H. Hosono, K. Kawazoe, Y. Yano, *Appl. Phys. Lett.* 75 (1999) 2851.
- [7] H. Ohta, K. Kawamura, M. Orita, M. Hirano, N. Sarukura, H. Hosono, *Appl. Phys. Lett.* 77 (2000) 475.
- [8] Q.-X. Yu, Bo Xu, Qi-Hong Wu, Y. Liao, G.-Z. Wang, R.-C. Fang, H.-Y. Lee, C.-T. Lee, *Appl. Phys. Lett.* 83 (2003) 4713.
- [9] A.E. Tsurkan, N.D. Fedotova, L.V. Kicherman, P.G. Pas'ko, *Sov. Phys. Semicond.* 6 (1975) 1183.
- [10] I.T. Drapak, *Sov. Phys. Semicond.* 2 (1968) 624.
- [11] G. Xiong, J. Wilkinson, S. Tüzemen, K.B. Ucer, R.T. Williams, *Proc. SPIE* 256 (2002) 4644.
- [12] A. Osinsky, J.W. Dong, M.Z. Kausar, B. Hertog, A.M. Dabiran, P.P. Chow, S.J. Pearton, O. Lopatiuk, L. Chernyak, *Appl. Phys. Lett.* 85 (2004) 4272.
- [13] D.J. Rogers, F.H. Teherani, A. Yasan, K. Minder, P. Kung, M. Razeghi, *Appl. Phys. Lett.* 88 (1) (2006) 1.
- [14] A. Yasan, R. McClintock, S.R. Darvish, Z. Lin, K. Mi, P. Kung, M. Razeghi, *Appl. Phys. Lett.* 80 (2002) 2108.
- [15] D.J. Rogers, F.H. Teherani, A. Yasan, R. McClintock, K. Mayes, S.R. Darvish, P. Kung, M. Razeghi, G. Garry, *Proc. SPIE* 5732 (2005) 412.