

Effect of Rapid Thermal Annealing on optical and electrical properties of undoped and N doped ZnO a-plane epilayers grown by molecular beam epitaxy (MBE) on r-plane oriented sapphire substrates

Mamadou. MBAYE, Ibrahima. NIANG, Bassirou. LO, Pape. M. WADE, Moustapha. BA, Mouhamed. B. GAYE, Alioune. A. DIOUF, B. DIOP. NGOM and Aboubaker. C. Beye

University Cheikh Anta Diop of Dakar/Senegal, Sciences and technologies Faculty, Physics Department, Solids Physics and Materials Science Group, B.P. 16899, Dakar-Fann Dakar, Senegal.

Received 2 April 2016; Accepted 28 April 2016; Published 2 May 2016

Address For Correspondence:

Bassirou. LO, University Cheikh Anta Diop of Dakar/Senegal, Sciences and technologies Faculty, Physics Department, Solids Physics and Materials Science Group, B.P. 16899, Dakar-Fann Dakar, Senegal.
E-mail: lobass57@gmail.com; Tel:+221 33 825 02 02-+221 33 82504 43 (poste 1141), Fax: +221 33 8256318

Copyright © 2016 by authors and American-Eurasian Network for Scientific Information (AENSI Publication).

This work is licensed under the Creative Commons Attribution International License (CC BY).

<http://creativecommons.org/licenses/by/4.0/>



Open Access

ABSTRACT

N-doped ZnO epilayers and also undoped ZnO epilayers have been grown by molecular beam epitaxy (MBE) on r-plane oriented sapphire substrate. After the growth of the ZnO thin film, the rapid thermal annealing (RTA) was performed at temperatures at 670°C. The effect of the post-annealing process on the electrical and the optical properties was investigated by using four-point probe technique, photoluminescence (PL) and reflectivity measurements. The electrical properties of as-deposited samples are considerably improved upon annealing at 670°C. The improvement is showed by the increase of the electrical intensity $I(V)$. The low-temperature (10 K) PL spectra showed that RTA induces a higher strength for near-band-edge emission. The reflectivity spectra also showed that the sample surface becomes significantly smoother after annealing. Accordingly, these results indicate that the RTA process effectively improves the electrical and optical properties of the N-doped and undoped ZnO a-plane oriented films.

KEYWORDS: Rapid thermal annealing, photoluminescence, Hall measurements, *p*-type ZnO, a- plane ZnO

INTRODUCTION

Zinc oxide (ZnO) is a versatile functional material. Its direct wide band gap (3.37 eV) at room temperature and high exciton binding energy (60 meV) had lead to extensive research on ZnO [1,2]. In the UV region laser devices operating at room temperature [3] have been studied. Several studies of bulk ZnO were published in the literature [4, 5] and layers were obtained by different growth method [6, 7]. Since the presence of an internal electric field parallel with the *c*-axis in the wurtzite structures, has been confirmed experimentally in ZnO/MgZnO quantum well structures [8], growth of quantum wells ZnO has attracted much more people [8,9]. In fact this inherent internal electric field acts to reduce the binding energy of the free excitons in ZnO-based

To Cite This Article: Mamadou. MBAYE, Ibrahima. NIANG, Bassirou. LO, Pape. M. WADE, Moustapha. BA, Mouhamed. B. GAYE, Alioune. A. DIOUF and Aboubaker. C. Beye., Effect of Rapid Thermal Annealing on optical and electrical properties of undoped and N doped ZnO a-plane epilayers grown by molecular beam epitaxy (MBE) on r-plane oriented sapphire substrates, 2016. **Journal of Applied Sciences Research**. 12(4); Pages: 1-5

quantum well structures which is detrimental to the performance of room temperature devices based in such a system. However the principal challenge for realizing ZnO optoelectronic devices is the lack of high-conductivity p-type. N-type is easy to realize because ZnO occurs naturally as n-type conduction due to the presence of intrinsic donor defects, such as oxygen vacancies (Vo) and zinc interstitials (Zni). There have been many reports for growth of high quality n-type ZnO using group-III elements such as B, Al, Ga, and In as dopants [10, 11]. However, the realization of p-type ZnO has been proven difficult and is thought to be the bottleneck due to high self-compensation, low solubility of the dopant and deep acceptor level [12]. P-type doping in ZnO may be possible by substituting either group-I elements (Li, Na, K) for Zn sites or group-V elements (N, P, As) for O sites. Theoretical studies have shown that while Nitrogen (N) is the most promising and commonly used p-type dopant among group-V elements (N, P, As and Sb), the N acceptor, which substitutes for O, has a high activation energy of 0.4 eV [13,14] with experimentally measured values in the range of 0.1 to 0.2 eV [15,16]. On the other hand, the P, As and Sb acceptors have been shown to have higher activation energies due to the large atomic radii and the high orbital energies [17, 18, 19]. Recently, some progress has been reported on the p-doping ZnO. [20, 21]

In this communication, we are studying the effect of Rapid Thermal Annealing (RTA) on optical and electrical properties of undoped and N doped ZnO a-plane epilayers grown by molecular beam epitaxy (MBE) on r-plane oriented sapphire substrates.

2-Experimental works:

A 1 μm -thick undoped ZnO film was grown in the temperature range of 450-550°C. The growth was performed using solid source Zn and an RF activated plasma as the oxygen source. The growth rate was 0.35 $\mu\text{m}/\text{h}$, slightly lower than the optimal growth rate in a c-direction growth. Prior to growth, the r-plane (01-12) sapphire substrates were thermally cleaned and subsequently exposed to oxygen plasma. A streaky RHEED pattern was maintained throughout the growth, albeit with a slight modulation in the [1-100] azimuthal direction. The optical properties of the structures were studied using non-resonant photoluminescence excited with the 325nm line from He-Cd laser and. The emitted light was dispersed using a 0.6m monochromator and detected using silicon PMT with conventional lock-in techniques. The sample was mounted in an optical cryostat where the temperature could be varied from 6 to 300K. Reflectivity measurements were excited using a standard mercury bulb. While, N-doped ZnO was grown at temperature about 730°C and the thickness was 0.5 μm . Prior to the electrical measurement, the samples were successively immersed in three solvent Tri-ethyl, acetone, and isopropyl separately for 5min and then dried with nitrogen. A flash annealing was performed on a few samples. The samples were placed on a silicon substrate inside the furnace in N_2 ambient at the temperature of 670 °C for 16s. After the flash annealing, ozonation of all samples was made in a UV furnace at 20°C for two hours. Immediately brought out of the UV furnace, the samples were metalized. The metal contacts are small and large studs of Ti/Au. Successively a titanium (Ti) and gold (Au) flux was sent through the pores of the mask. The samples were subjected to electrical characterization by applying a voltage in reversed mode.

3-Results:

PL measurements were carrying out in the ELc and the spectra at low temperature of the as-grown and the annealed undoped ZnO sample are displayed in Fig.1. The PL spectra of as-grown samples show peaks corresponding to the bound excitons and consisting of a strong emission band and two weak emissions respectively labelled D_3X , D_2X and D_1X and respectively located at 3.382, 3.364 and 3.355eV. Another strong emission band observed at the lower energy of the bound exciton (DX) band, in the region of first longitudinal optical phonon replicas (LO), was identified as a defect line [22]. In the PL spectra of the annealing sample, the D_2X bound exciton were disappearing and the PL intensity is significantly enhanced leading to the increase in grain size and crystallinity. This indicates that at this annealing temperature, defects, such as Zn interstitials, Zn vacancies, oxygen interstitials, oxygen vacancies and other impurities regarded as the source of the broad bands, decrease. These results also imply that a thermal energy corresponding to at least 670°C is needed to deform and recover the crystal structure to improve the crystallinity of ZnO. The lack of Zinc atom and oxygen atom can explain the bound exciton emission D_2X , so it is expected to be related to interstitial defect or vacancies [11].

The effect of the RTA on the free excitons is difficult to reveal in ZnO films because these free excitons are not resolved in the PL spectrum measured at 10K. This is due to the pre-eminence of the bound excitons. Furthermore, in the ELc polarization, the allowed free excitons A and B have approximate energies and large non-radiative damping constants. For these reasons, it is necessary to study the excitonic emissions of ZnO films in detail by using reflectivity for the determination of the peak position. The reflectivity spectra of the as-grown (a) and the annealed samples (b), displayed in figure.2, allow distinguishing the free excitons peak positions and show the influence of the RTA on the free excitons emission.

Figure 3 represents the electrical intensity with voltage for as-grown N doped ZnO thin film. This intensity is found to be increasing after annealing. The observed increase can be correlated with the improved crystallinity which can reduce scattering processes and induces an increase in carrier concentration and mobility.

In fact defects, such as Zn interstitials, Zn vacancies, oxygen interstitials, oxygen vacancies and other impurities contribute to degrade the electrical and the optical properties, such as carrier mobility and PL. So annealing is supplied to suppress the presence of such defects [23] as displayed in figure 4. The electrical intensity is fourfold higher than the as-grown N doped ZnO sample after annealing but the evolution of the current-voltage characteristic is not a Schottky type. It is possible that they are completely a depletive zone. However, the principal challenge is to realize high-conductivity and reproducible p-type ZnO films. This is essential for tailoring the material for specific applications and for developing the devices.

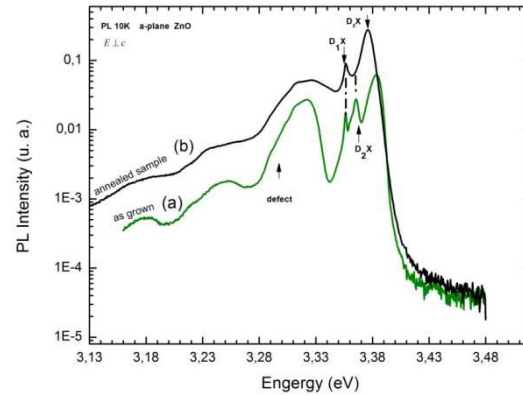


Fig. 1: PL spectra at low temperature (10K) of as-grown (a) and annealed (b) a-plane ZnO thin films. The spectra are shown in σ polarization ($E \perp c$). The D_2X bound exciton is disappearing in (b) ZnO sample. For clarity the spectra are vertically displaced.

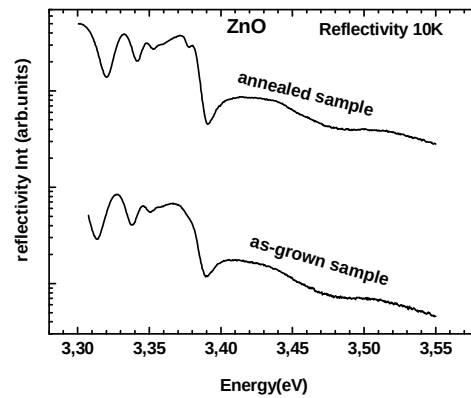


Fig. 2: Reflectivity spectra at low temperature (10K) of as-grown (a) and annealed (b) a-plane ZnO thin films. The spectra are shown in σ polarization ($E \perp c$). The A and B free excitons are clearly seen in the annealed ZnO sample (b). For clarity the spectra are vertically displaced.

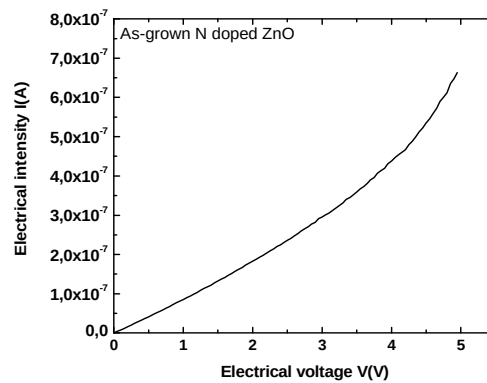


Fig. 3: Electrical intensity of N doped a-plane ZnO thin films before Rapid Thermal Annealing in N_2 ambient.

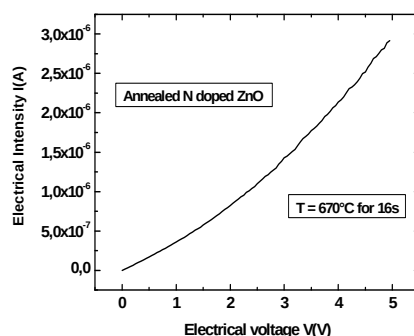


Fig. 3: Electrical intensity of N doped a-plane ZnO thin films after Rapid Thermal Annealing in N₂ ambient. The electrical intensity is fourfold higher after Rapid Thermal Annealing.

Conclusion:

We investigated the electrical and optical properties of undoped and N doped ZnO films. It was shown that the annealing at 670°C for 16s in nitrogen ambient results in the improvement of the electrical and optical properties of the samples. The annealed samples gave an electrical intensity and PL intensity higher than the as grown ones. The results suggest that the Rapid thermal annealing (RTA) process plays a critical role in improving the electrical and optical properties of the undoped and N doped a-plane oriented ZnO films.

REFERENCES

- [1] John Wiley and Sons, Ltd. 2011. Zinc Oxide Materials for Electronic and Optoelectronic Device Applications: Book Editor: Cole W. Litton, Donald C. Reynolds, Thomas C. Collins; Material sciences-Electronic material.
- [2] Ümit Özgür, Daniel Hofstetter Hadith Morkoç, 2010. ZnO Devices and Applications: A Review of Current Status and Future Prospects. Proceedings of the IEEE. 98(7): 1255-1268.
- [3] Liu, C.Y., H.Y. Xu, Y. Sun, J.G. Ma and Y.C. Liu, 2014. ZnO ultraviolet random laser diode on metal copper substrate, 22(14) OPTICS EXPRESS 16737.
- [4] Robert Triboulet, 2014. Growth of ZnO bulk crystals: A review. Progress in Crystal Growth and Characterization of Materials., 60(1): 1-14.
- [5] Klingshirn, C., 2007. ZnO: Material, Physics and Applications. ChemPhysChem., 8(6): 782-803.
- [6] Parka, S.H., H. Suzukia, T. Minegishia, G. Fujimoto, J.S. Parka, I.H. Ima, D.C. Oha, M.W. Choa, T. Yaaa, 2007. Low-temperature growth of high-quality ZnO layers by surfactant-mediated molecular-beam epitaxy. Journal of Crystal Growth., 309(2): 158-163.
- [7] Kyung Ho Kim, Kazuomi Utashiro, Yoshio Abe and Midori Kawamura, 2014. Growth of Zinc Oxide Nanorods Using Various Seed Layer Annealing Temperatures and Substrate Materials. Int. J. Electrochem. Sci., 9: 2080-2089.
- [8] Chauveau, J.M., Y. Xia, I. Ben Taazat-Belgacem, M. Teisseire, B. Roland, M. Nemoz, J. Brault, B. Damilano, M. Leroux and B. Vinter, 2013. Built-in electric field in ZnO based semipolar quantum wells grown on (101-2) ZnO substrates. Appl. Phys. Lett., 103: 262104.
- [9] Tabares, G., A. Hierro, M. Lopez-Ponce, E. Muñoz, B. Vinter and J.-M. Chauveau, 2015. Light polarization sensitive photodetectors with m and r-plane homoepitaxial ZnO/ZnMgO quantum wells. Appl. Phys. Lett., 106 061114.
- [10] Huang, J.Y., Z.Z. Ye, H.H. Chen, B.H. Zhao and L. Wang, J. Mater, 2003. Sci., 22: 249.
- [11] Ozgur, U., Y.I. Alivov, C. Liu, A. Teke, M.A. Reshchikov, S. Dogan, V. Avrutin, S.J. Cho and H. Morkoc, 2005. J. Appl. Phys, 98: 041301.
- [12] Ye, Z.Z., J.G. Lu, H.H. Chen, Y.Z. Zhang, L. Wang, B.H. Zhao and J.Y. Huang, J. Crystal Growth, 2003. 253-259.
- [13] Kobayashi, A., O.F. Sankey and J.D. Dow, 1983. Phys. Rev., B 28: 946.
- [14] Lee, W.-J., J. Kang and K.J. Chang, J. Korean, 2007. Phys. Soc. 50: 602.
- [15] Tsukazaki, A., A. Ohtomo, T. Onuma, M. Ohtani, T. Makino, M. Sumiya, K. Ohtani, S.F. Chichibu, S. Fuke, Y. Segawa, H. Ohno, H. Koinuma and M. Kawasaki, 2005. Nature Mater. 4: 42.
- [16] Look, D.C., D.C. Reynolds, C.W. Litton, R. L. Jones, D.B. Eason and G. Cantwell, 2002. Phys. Lett., 81: 1830.
- [17] Park, C.H., S.B. Zhang and S.-H. Wei, 2002. Phys. Rev., B 66: 073202.

- [18] Lee, W.-J., J. Kang and K.J. Chang, 2006. Phys. Rev. B 73: 024117.
- [19] Lee, W.-J., J. Kang and K.J. Chang, J. Korean, 2007. Phys. Soc., 50: 602.
- [20] Liping Yu, Qiqiang Zhu, Dayong Fan, Zili Lan. Development in *p*-type Doping of ZnO Journal of Wuhan University of Technology-Mater. Sci. Ed. 27(6): 1184-1187.
- [21] Sara Khosravi-Gandomani, Ramin Yousefi, Farid Jamali-Sheini, Nay Ming Huang. 2014. Optical and electrical properties of *p*-type Ag-doped ZnO nanostructures: Ceramics international, 40(6): 7957-7963.
- [22] Chauveau, J.M., C. Morhain, B. Lo, B. Vinter, P. Vennéguès, M. Laügt, D. Buell, M. Tesseire-Doninelli and G. Neu, 2007. Growth and characterization of A-plane ZnO and ZnCoO based heterostructures. Appl. Phys.A Materials Science & Processing, 88(1): 65-69.
- [23] Hooyoung Song, Jae-Hoon Kim and Eun Kyu Kim, 2008. Rapid Thermal Annealing of ZnO Thin Films Grown by Using Pulsed Laser Deposition. Journal of the Korean Physical Society, 53(1): 258-261.