OPTOELECTRONICS AND ADVANCED MATERIALS – RAPID COMMUNICATIONS Vol. 4, No. 5, May 2010, p. 689 - 692

Hydrothermal synthesis and optoelectronic properties of spike-like ZnO nanostructures

R. S. YADAV[*], R. K. SRIVASTAVA[a], M. KUMAR, A. C. PANDEY, S. G. PRAKASH[a]
Nanophosphor Application Centre, Physics Department, University of Allahabad, Allahabad-211002, India
[a]Department of Electronics and Communications, University of Allahabad, Allahabad- 211002, India

In this paper, we report, spike-like ZnO nanostructures synthesized by hydrothermal process. The spike-like ZnO nanostructures with distinguishing feature with tip, suggest possible interesting optical and electrical properties of this novel nanostructure. The spike-like ZnO nanostructures were hexagonal and single crystal in nature. It is found that the Electro-luminescence (EL) emission intensity B depend on the applied voltage, $B = B_0 \exp(-b/\sqrt{V})$ and frequency $1/B = 1/\alpha + \beta/f$. It is interesting for nanostructured based device that EL brightness increases linearly with applied voltage and frequency.

(Received April 26, 2010; accepted May 20, 2010)

Keywords: Nanostructures, Hydrothermal method, ZnO, Semiconducing II-VI material, Electrical properties, Optical properties

1. Introduction

The fabrication of ZnO nanostructures is an issue in nanotechnology as they have potential to find applications in opto-electronic devices [1-3]. Different ZnO nanostructures such as nanowires, nanorods, nanotubes, nanobridges and nanonails, nanowalls, nanohelixes, seamless nanorings, mesoporous single-crystal nanowires, polyhedral cages, porous structures, needle-like, sisal-like, flower-like and disc-like etc. have been synthesized [4-11]. It is supposed that nanostructures would possess the high specific area on the surface of the particles and likely be an ideal host material for solar cells, nanolasers, other highly functional and effective devices.

ZnO is an excellent semiconductor for low-voltage and short-wavelength optoelectronics applications because of a direct wide band gap of 3.37 eV and a large exciton binding energy of ~ 60 meV [12-13]. The increase in surface area and the quantum confinement effects have made nanostructured materials quite distinct from their bulk form in both electrical and optical properties. ZnO nanostructures have potential applications for piezoelectric transduction, optical emission, catalysis, actuation, drug delivery, optical storage with promising photoelectronic, photochemical and catalytic properties [14].

In addition to the conventional vapour-phase methods of vapour transport and condensation, thermal evaporation, metal-organic chemical vapor deposition and solution phase methods have been developed as alternative ways to synthesize ZnO nanostructures with different shapes and dimensions. A hydrothermal method is a widely used technique that can control the shape and dimension of ZnO nanostructures among all-solution based approaches. Unlike conventional vapour-phase methods, the hydrothermal method can produce various ZnO nanostructures at a relatively low temperature (below 200 ^{0}C). A hydrothermal method has been recently investigated as a promising alternative technique for the fabrication of ZnO nanostructure under ambient conditions. The reason is that this method is simple, convenient, economical and environmental friendly.

2. Experimental section

2.1 Chemicals

The zinc acetate dihydrate ($Zn(CH_3COOH)_2 \cdot 2H_2O$), sodium hydroxide (Na OH) were from E. Merck Ltd. Mumbai,400018,India. These chemical were directly used without special treatment.

2.2 Sample preparation

The spike-like ZnO nanoparticles were prepared by the following process: 1g of zinc acetate dihydrate was put into 105 ml of double distilled water under vigorous stirring. After 10 minute stirring ,15 ml of 2N NaOH aqueous solution was introduced into the above aqueous solution, resulting in a white aqueous solution (pH value was maintained at 12), which was then transferred into stainless steal autoclaves, sealed and maintained at temperature 383K for 8h. The resulting white solid product was centrifuged, washed with distilled water and ethanol to remove the ions possibly remains in the final product. It was finally dried at 60° C in air.

2.3 Instrumentation

The crystal structure of spike-like ZnO nanostructures were characterized by X-Ray diffraction (XRD), Rigaku D/Max -2200 H/PC, Cu Kα radiation (λ=1.54056 Å). Transmission Electron Microscopy observation was performed with a Philips CM 12 microscope operated at 110 kV. Schematic diagram for experimental arrangement of Electro-luminescence study was shown in Fig. 1.

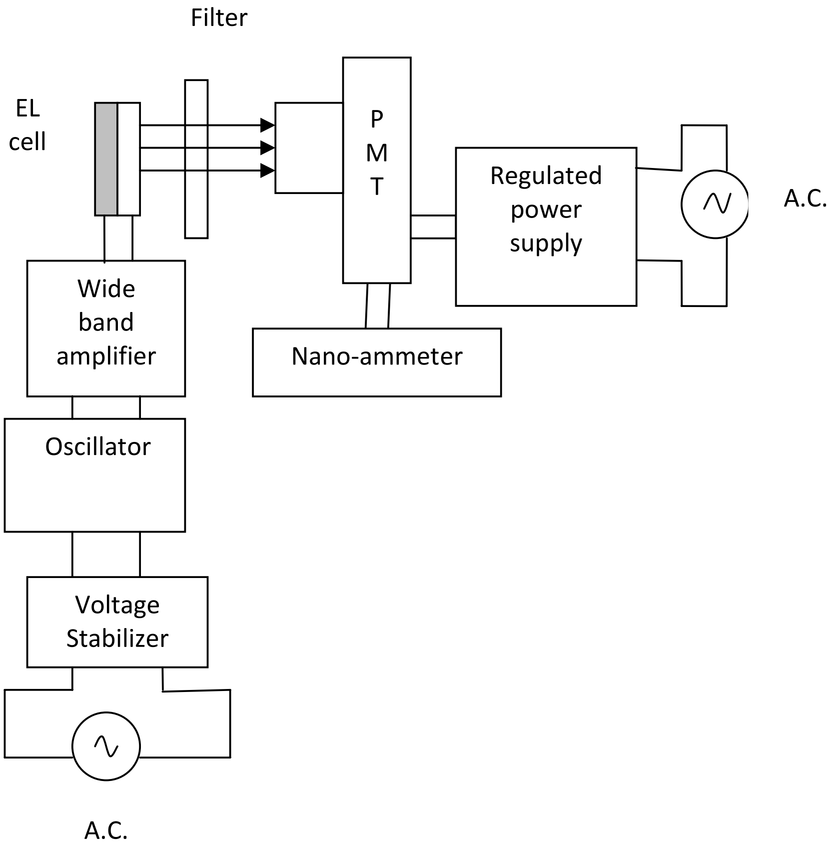

Fig. 1. Schematic diagram for experimental arrangement of electro-luminescence study.

3. Result and discussion

3.1 Structural study

A typical XRD pattern of spike-like ZnO nanostructures synthesized by hydrothermal process is shown in Fig. 2. The positions of diffraction peaks are quite similar to those of a bulk ZnO, which can be indexed as those from the known wurtzite-structured ZnO (a= 3.249 Å, c=5.026 Å, space group : P_63mc (186)) and the diffraction data are in agreement with the JCPDS card for ZnO (JCPDS 36-1451). The sharpness of the peaks implies a high crystallinity of the synthesized ZnO nanostructure. No characteristic peak of impurities such as those of $Zn(CH_3COO)_2.2H_2O$ and $Zn(OH)_2$ are observed.

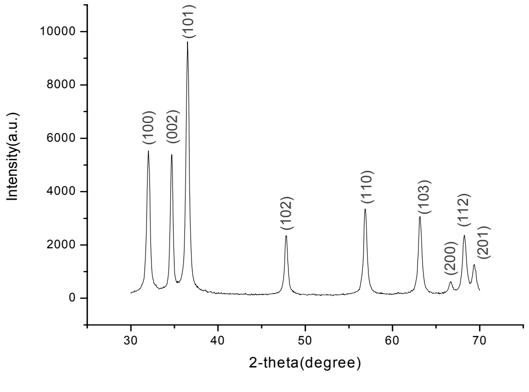

Fig. 2. XRD pattern of spike-like ZnO nanostructures synthesized by hydrothermal process.

3.2 Morphology study

TEM was employed to study morphology of hydrothermally synthesized ZnO nanostructures. Typical TEM image of hydrothermally synthesized ZnO nanostructures are shown in Fig. 3.

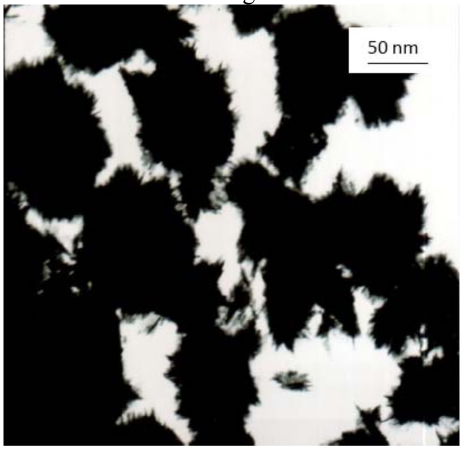

Fig. 3. TEM image of spike-like ZnO nanostructures synthesized by hydrothermal process.

From TEM image, it is clear that ZnO nanostructures are spike-like, similar as reported by Lu-Ping Zhu et al. [15] for Fe_2O_3. The surface of ZnO nanostructures are very rough and contain sharp tips. It is also clear that after long ultrasonic treatment during the preparation of the TEM specimens, the sharp-tips were not destroyed.

3.3 Electroluminescence study

In Electroluminescence (EL), a direct conversion of electric energy into visible light takes place without the generation of heat. Electro-luminescence study was performed by preparing cell by suspending the ZnO nanomaterial powder in castor oil in form of parallel plate capacitor with one electrode being Aluminium plate and other a transparent mica sheet as shown in Fig. 4. When an ac field is applied across the EL cell, the ZnO are excited and emit blue visible light.

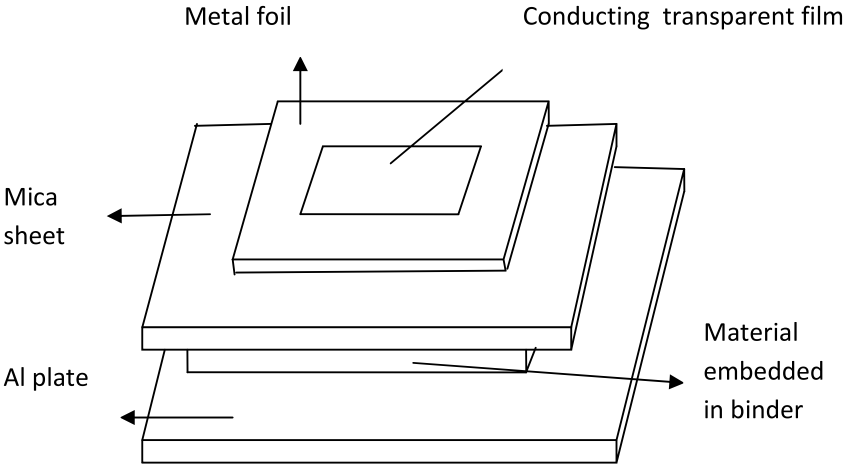

Fig. 4. Schematic diagram of Electro-luminescent cell.

The EL emission emitted by the phosphors may be emphasized or suppressed by controlling the conditions of excitation, the factors under control being the voltage and the frequency of the applied field. A large number of literature are available on EL study of phosphor materials, but not much attention seems to have been devoted to a systematic study of variation of EL intensity over a wide range of frequencies and voltages of the applied field. In order to obtain information on the voltage dependence of the brightness, intensities were measured by varying voltage applied to the electrodes of the EL-cell, at a fixed frequency.

For our spike-like ZnO nanostructures, the dependence of the electroluminescent light intensity B versus the applied voltage V is given by the following universal law, while keeping excitation frequency constant [16]:

$$B = B_0 \exp(-b/\sqrt{V})$$

where B is the brightness, V is the applied voltage, B_0 and b are constants, which are determined by the phosphor material, device structure and exciting condition. Fig. 7 shows the the plot log B versus $100/\sqrt{V}$. From figure 5, it is clear that electroluminescence brightness has linear dependence on applied voltage at different frequency 5000 c/s and 1500 c/s.

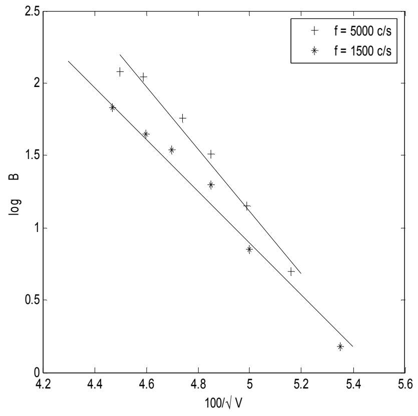

Fig. 5. The electroluminescence brightness and voltage curve at different f requencies (: f = 5000 c/s, +: f = 1500 c/s) of spike-like ZnO nanostructures synthesized by hydrothermal process.*

When the driving voltage increases, electrons in the insulator and in the interface of the emission layer and the insulator will have more probabilities to become hot electrons, which will impact excite the luminescence centres and then promote the entire luminance of EL cell.

When the driving voltage is fixed at 400 V, the frequency dependence of EL brightness is plotted in Fig. 6.

The 1/B and 1/f curve for the spike-like ZnO nanostructure drawn in figure 6 which is linear and follows following Universal Law:

$$1/B = 1/\alpha + \beta/f$$

where B is EL brightness and α and β are constants.

From Fig. 6, it is clear that the EL brightness increases with increasing frequency. This can be explained by the increasing chances of excitation of ZnO nanomaterials.

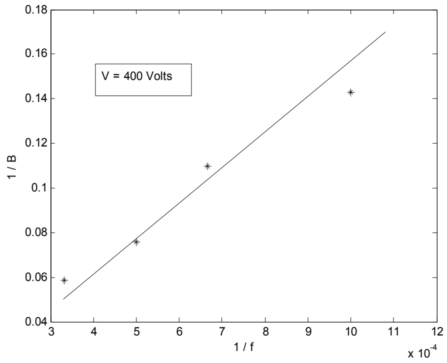

Fig. 6.The electroluminescence brightness and frequency curve of spike-like ZnO nanostructure synthesized by hydrothermal process.

4. Conclusions

In summary, spike-like ZnO nanostructures have been synthesized by hydrothermal method. The XRD pattern indicates that the synthesized ZnO nanostructures are of hexagonal phase. EL study of spike-like ZnO was also carried out, it is found that the EL emission intensity B depends on the applied voltage, $B = B_0 \exp(-b/\sqrt{V})$ and frequency $1/B = 1/\alpha + \beta/f$. It is seen that EL brightness increases linearly with applied voltage and frequency. It can be anticipated that the spike-like ZnO nanostructures will find applications in opto-electronic devices.

Acknowledgements

The authors are very grateful and also wish to express their gratitude to all the scientific members of Nanophosphor Application Centre, University of Allahabad, Allahabad, India. They also want to thank to Department of Science and Technology, India for funding the project under IRHPA in collobaration with Nanocrystal Technology, New York.

References

[1] M. H. Huang, S. Mao, H. Feick, H. Q. Yan, Y. Y. Wu, H. Kind, E. Weber, R. Russo, P. Yang, Science **292**, 1897 (2001).
[2] M. H. Huang, Y. Wu, H. Feick, N. Tran, E. Weber, P. Yang, Adv. Mater. **13**, 113 (2001).
[3] J. T. Hu, T. W. Odom, C. M. Lieber, Acc. Chem. Res. **32**, 435 (1999).
[4] Z. L. Wang, Mater. Today **7**, 26 (2004).
[5] J. H. Park, H. J. Choi, Y. J. Choi, S. H. Sohn, J. G. Park, J. Mater. Chem. **14**, 35 (2004).
[6] J. H. Park, H. J. Choi, J. G. Park, J. Cryst. Growth **263**, 237 (2004).
[7] Yunyan Zhang, Jin Mu, Nanotechnology **18**, 075606 (2007).
[8] Jiechao Ge, Bo Tang, Linhai Zhuo, Zhiqiang Shi, Nanotechnology **17**, 1316 (2006).
[9]Yujin Chen, C. L. Zhu, G. Xiao, Nanotechnology **17**, 4537 (2006).
[10] R. S. Yadav, A. C. Pandey, Physica E **40**, 660 (2008).
[11] R. S. Yadav, A. C. Pandey, S. S. Sanjay, Struct. Chem. **18**, 1001 (2007).
[12] R. Wu, Y. Yang, S. Cong, Z. Wu, C. Xie, U. Hiroyuki, K. Kawaguchi, N. Koshizaki, Chem. Phys. Lett. **406**, 457 (2005).
[13] W. Zhang, H. Wang, K. S. Wong, Z. K. Tang, G. K. L. Wong, Appl. Phys. Lett. **75**, 3321 (1999).
[14] Z. R. Tian, J. A. Voigt, J. Liu, B. Mckenzie, M. J. McDermott, M. A. Rodriguez, H. Kngishi, H. Xu, Nat. Mater. **2**, 821 (2003).
[15] Lu-Ping Zhu, Hong-Mei Xiao, Xian-Ming Liu, Shao-Yun Fu, J. Mater. Chem. **16**, 1794 (2006).
[16] P. Zalm, G. Diemer, H. A. Klasens, Phil. Res. Repts. **9**, 81 (1954).

---

[*] Corresponding author: raghvendra_nac@yahoo.co.in