OPTOELECTRONICS AND ADVANCED MATERIALS – RAPID COMMUNICATIONS Vol. 4, No. 5, May 2010, p. 662 - 664

Structural properties & photoluminescence of ZnO thin film and nanowires

NANDA SHAKTI, P. S. GUPTA
Indian School of Mines, Department of Applied Physics, 826004 Dhanbad, India

ZnO thin film was deposited using sol-gel spin coating method on Quartz substrate. Zinc acetatedihydrate was used as precursor. ZnO nanorods were grown in powder form by thermal evaporation of Zincacetatedihydrate. The structural study of the samples was done by X-ray diffraction.Charcteristic peaks and lattice constants were verified. SEM image confirm the synthesis of ZnO nanowires. Photoluminescence of ZnO nanowire showed strong UV emission as compared to ZnO film.

(Received March 19, 2010; accepted May 20, 2010)

Keywords: Sol-gel, Thin film, Nanorod, XRD, Photoluminescence

1. Introduction

Zinc Oxide is an inexpensive n-type semiconductor having direct band gap of 3.37 eV which crystallizes in hexagonal Wurtzite structure (c = 5.025 and a = 3.249) Due to large exciton binding energy of 60 meV , they have potential application in Optoelectronic devices such as in solar cells[1], Optical wave guide[2], Light emitting diodes (LED)[3]. Zinc Oxide thin films are applied in Thin Film Transistors (TFT) [4] and as gas, chemical and biological sensors [5]. Thin films of Zinc oxide can be prepared by various techniques; among them are Sputtering [6], Chemical Vapor Deposition (CVD) [7], Laser ablation [8], Sol-gel [9] and Spray pyrolysis [10].

Growth of 1-D nanostructures of ZnO such as wires, rods, tubes, belts etc has received increasing attention for its specific properties and for the fabrication of nanoscaled devices. Many different techniques have been employed for the growth of nanostructures. Primary synthesis methods include Vapour-liquid-solid (VLS) process [11], metal organic CVD [12] and Thermal evaporation [13].

In the present work we have prepared ZnO thin film and ZnO nanowire using sol-gel spin coating and Thermal evaporation techniques respectively. Both these methods are simple, cost effective and rapid synthesis methods. In both the methods Zinc acetate dihydrate served as the precursor. The structural study of ZnO thin film and nanowires was done by X- ray diffraction.

Scanning electron microscopy and Transmission electron microscopy was used for viewing the morphology of nanowire. The photoluminescence study of the ZnO film and nanowire revealed UV emission.

2. Experimental details

ZnO thin film was prepared on Quartz substrate (2.5 × 2.5 cm ^{2}) by sol-gel spin coating method. First the Quartz substrate was cleaned with soap solution followed by cleaning ultrasonically in acetone bath and finally in isopropanol vapours.For sol preparation 10% solution of Zinc acetate [Zn $(CH_3COO)_2.].2H_2O$ was prepared in boiling iso-proponal. This was followed by clearing the turbid solution by adding 10 drops of diethanolamine by a 5ml dropper. The sol was further boiled for 30 min. and then allowed to cool to room temperature. For film preparation, the silicon wafer was mounted on the spin coater (SCU 2005 Apex Inst.Co.) and 5-6 drops of sol was dropped over it while it was allowed to spin at the rate of 3000 rpm. This step was followed by drying the wet coated slide at 100^{o}C for 10 min and subsequent annealing at 400 ^{o}C for 1 hr. Multiple coating was done to obtain the workable thickness of the film.

ZnO nanowires were prepared using Zinc acetate dihydrate as the precursor. 2 gms of the precursor was placed in the Quartz crucible covered by Quartz lid and then placed in the furnace. The crucible was heated to 300°C for 12 h, producing ZnO nanowires in powder form.

The structural properties of the prepared samples were studied by X-ray diffraction measurements (Panalytical Xpert pro, with CuKα radiation (λ= 1.54059 Å)). The average crystallite size of film was determined by Scherrer formula from the broadening of the diffraction peaks. Scanning electron microscope (SEM) (Jeol; JSM-6390LV) was used for viewing the surface morphology of the samples. Photoluminescence of the samples was measured using fluorescence spectrophotometer (Hitachi).

3. Results and discussion

3.1 Structural properties

The crystal structure of ZnO film and nanowire was investigated through X-ray diffraction (XRD). The X-ray diffraction spectrum of ZnO film and ZnO nanowire is shown in Fig. 1.

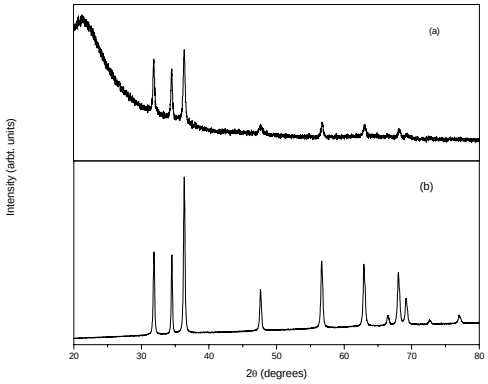

Fig. 1. XRD spectrum of ZnO thin film (a) and ZnO nanorod (b).

The peaks of the XRD spectrum correspond to those of the ZnO patterns from the JCPDS data [14], having hexagonal wurtzite structure of the bulk with lattice constants a=3.24982Å, c=5.20661Å. Due to the presence of all the prominent peaks the nanowires have more polycrystalline nature than thin film.

The crystallite size of the film for prominent diffraction planes (100), (002) and (101) was calculated using the Debye-Scherrer formula [15]

$$D=\frac{0.9\lambda}{\beta\cos\theta} \qquad (1)$$

Where D is the crystallite size, λ (=1.54059Å) is the wavelength of the X-ray used, β is the broadening of diffraction line measured at the half of its maximum intensity in radians and θ is the angle of diffraction. The average crystallite size was found to be 39 nm.

Fig. 2 and Fig. 3 shows the Scanning electron microscope image of the ZnO thin film and ZnO nanowires respectively.

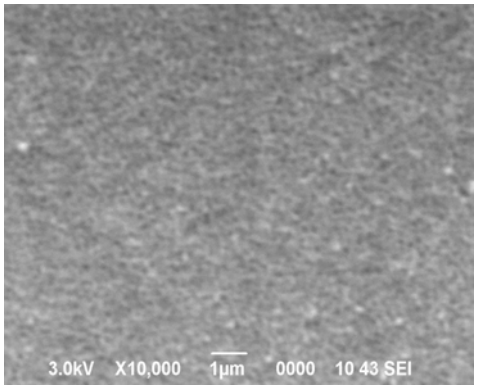

Fig. 2. SEM micrograph of ZnO thin film prepared on Quartz substrate.

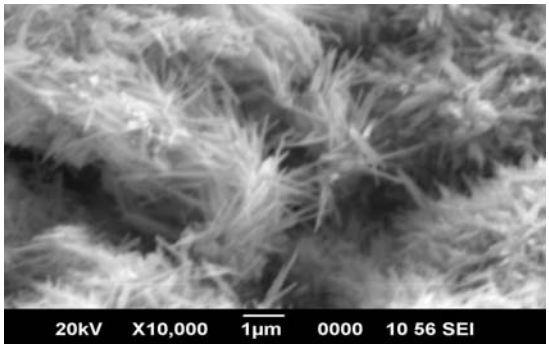

Fig. 3. SEM micrograph of ZnO nanowires.

From Fig. 2 we notice that surface of the ZnO film is granular in nature with grain size of the order of nanometers. Fig. 3 shows the growth of nanowires of ZnO in random directions. The length of the naowires is of the order of few microns while diameter is of the order of hundreds of nanometers.

3.2 Photoluminescence study

Photoluminescence (PL) is a widely used technique to investigate structural disorder in nanostructured materials prior to fabrication of optoelectronic devices. Fig. 4 shows the room temperature emission spectrum of ZnO nanowires and ZnO thin film excited at 315 nm.

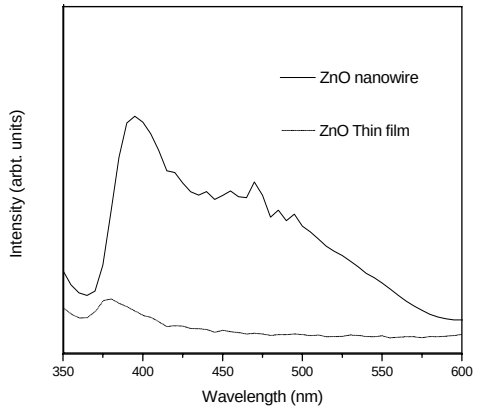

Fig. 4. PL spectrum of ZnO nanowire and ZnO thin film.

From the PL spectrum of Fig. 4 we notice that the Ultra Violet (UV) emission (~ 380 nm) of ZnO nano wires has much higher intensity than ZnO thin film. Aweak Blue band (440-475 nm) and a negligible green band (510 nm) are also observed in case of ZnO nanowires. The UV emission must be contributing to the near band edge of the wide band gap ZnO. The green emission corresponds to the singly ionized oxygen vacancy in ZnO and results from the recombination of a photogenerated hole with the singly ionized charge state of this defect. Thus, the almost

negligible green band in Fig. 4 suggests that there is very low concentration of Oxygen vacancy in ZnO nanowires

4. Conclusions

ZnO thin film was deposited on Quartz substrate by sol-gel spin coating process. ZnO nanowires were synthesized in powder form by thermal evaporation. The structural characterization of the samples was done by X-Ray Diffraction (XRD). From XRD spectrum of the film and nanowires the characteristic reflection planes of ZnO was verified. The average grain size of the film was found to be 39 nm using Debye-Scherrer formula. SEM images of the ZnO film showed granular nature and nanowires of ZnO was confirmed. Photoluminescence spectrum of ZnO nanowires showed strong UV emission in comparison to ZnO film. Weak blue and green emission were also observed from ZnO nanowires. Thus ZnO nanowires are more efficient UV emitters than ZnO thin film which adds to its applications in optoelectronics in UV range.

References

[1] E. Fortunato, A. Goncalves, A. Marques, A. Viana, H. Aguas, L. Pereira, I. Ferreira, P. Vilarinho, R. Martins, Surf. Coat. Technol. **180**, 20 (2004).
[2] P. Yu, Z. K. Tang, G. K. L. Wong, M. Kawasaki, A. Ohtomo, H. Koinuma, Y. Segawa, J. Cryst. Growth **184-185**, 601 (1998).
[3]A. Tsukazaki, M. Kubota, A. Ohtomo, T. Onuma, K. Ohtani, H. Ohno, S. F. Chichibu, M. Kawasaki, Jpn. J. Appl. Phys. **44**, L643 (2005).
[4] Y. Ohya, T. Niwa, T. Ban, Y. Takahashi, Jpn. J. Appl. Phys. Part1 **40**, 297 (2001).
[5] W. P. Kang, C. K. Kim, Sens. Acutuat. B **13-14**, 682 (1993).
[6] A. Moustaghfir, E. Tomasella, S. Ben Amor, M. Jcquet, J. Cellier, T. Sauvage, Surf, Coat. Technol. **174-175**, 193 (2003).
[7] K. Haga, M. Kamidaira, Y. Kashiwaba, T. Sekiguchi, H. Watanabe, J. Cryst. Growth **214**, 77 (2000).
[8] K. L. Narasimhan, S. P. Pai, V. R. Palkar, R. Pinto, Thin Solid Films **295**, 104 (1997).
[9] Dinguha Bao, Haoshuang Gu, Anxiang Kuang, Thin Solid Films **132**, 37 (1998).
[10] F. D. Paraguay, W. L. Estrada, D. R. N. Acosta, E. Andrade, M. Mikiyoshida, Thin Solid Films **350**, 192 (1999).
[11] M. H. Huang, Y. Y. Wu, H. Feick, N. Tran, E. Weber, P. D. Yang, Adv. Mater. (Weinheim,Ger.) **13**, 113 (2001).
[12] J. Y. Park, D. J. Lee, Y. S. Yun, J. H. Moon, B. T. Lee, S. S. Kim, J. Cryst. Growth **276**, 158 (2005).
[13] Y. S. Zhang, L. S. Wang, X. H. Liu, Y. J. Yan, C. Q. Chen, J. Zhu, J. Phys. Chem. B **109**, 13091 (2005).
[14] Joint Committee on Powder Diffraction Standards, Powder Diffraction File, Card no: 36-1451.
[15] C. Suryanarayana, M. Grant Norton, X-Ray Diffraction A practical approach, Plenum Press, New York (1998).

*Corresponding author: nash_cbsa@yahoo.co.in