Nanocrystalline ZnO by Cathodic Electrochemical Deposition

Santosh Singh and M. Arora
National Physical Laboratory, Dr. K.S. Krishnan Road, New Delhi - 110 012
santoshs@mail.nplindia.ernet.in

Abstract *Nanocrystalline zinc oxide thin films were deposited on conducting tin oxide coated glass plates by cathodic electrochemical deposition method at different electrode potential. These as deposited films were characterized by high resolution XRD, SEM, FTIR and PL spectroscopic techniques to reveal their structural, morphological and optical properties. The quality of these films was compared and deposition parameters were optimized. The structural details of different phases, bonding groups and microstructure were obtained from XRD, IR transmission and SEM measurements. These studies revealed the uniform preferrential growth of nanocrystalline ZnO films. X-ray diffractogram of the as-deposited ZnO exhibits the hexagonal wurtzite type structure with good crystallinity and no indication of amorphous components or other crystalline compounds. The average crystallite sizes were estimated by Scherrers formula. The variation in relative intensities of diffraction peaks (100), (002) and (101) indicates a preferential crystallite growth in the c-axis orientation, i.e. (002) plane. The spherical ZnO nanoparticles form a spatial homogenous film on the substrate without any discontinuities was exhibited from the SEM micrographs. The recombination of electrons in singly occupied oxygen vacancies with photo-excited holes in the valence band of these ZnO films was the origin of its photoluminescent behavior. The energy gap of these electrochemically deposited ZnO films lies in the range of 3.15 eV to 3.30 eV.*

Keywords Zinc oxide; Electrochemical deposition; II-IV semiconductor oxide; Nanocrystalline.

Introduction

Nanocrystalline transparent metal oxide semiconductors have drawn considerable attention due to their unique physical, chemical and optical properties. Recently, the promising application of nanocrystalline ZnO thin films in wide ultraviolet (UV) optoelectronic devices [1-6] such as UV light detectors, UV light emitting diodes, and semiconductor lasers has enhanced considerable interests in its studies. The photoluminescence of ZnO film at room temperature and the growth of p-type ZnO film and p–n homojunction has further encouraged the R&D work on this material. ZnO films can be grown on different substrates by various methods viz. as solid state reaction, sputtering, pulsed laser ablation, chemical vapor deposition, sol–gel, spray pyrolysis, spin coating electrochemical deposition [7-19] etc. An exhaustive work has been done on the structural, morphological and luminescent properties of ZnO bulk and its thin films while nanostructured ZnO films exhibit important optical properties which make them suitable candidate for electro-optic device applications has not yet been fully explored. In these studies nanocrystalline zinc oxide thin films were deposited on conducting tin oxide coated glass by cathodic electrochemical deposition process at different electrode potentials. This is a very simple and economic process through which the film composition can be easily controlled and deposited over large area with consistent properties. The aim of these studies was to grow nanostructured ZnO films and characterized their structural, morphological and photoluminecent properties by different spectroscopic techniques.

Experimental & Measurements

Nanocrystalline ZnO films were deposited on tin oxide coated glass plates with sheet resistance of 10Ω/cm, platinum as counter electrode and saturated calomel electrode (SCE) as reference electrode at -1.28 V, -1.30 V and -1.35 V electrode potentials at 0°C. Analytical grade zinc nitrate (0.01M $Zn(NO_3)_2$) and potassium nitrate (0.1M KNO_3) were used for electrolyte preparation of pH around 5. XRD patterns of these ZnO films were recorded on D8 Advanced Bruker Axs X-ray powder diffractometer by using CuKα radiation at 30kV, 30mA in 15 – 75° 2θ range. The surface morphology of the ZnO grains in these nanostructured zinc oxide thin films were studied by LEO 440 SEM spectrometer. Perkin Elmer FTIR spectrophotometer was used to characterize the various IR transmission bands obtained in these films spectra at ambient temperature in 4000 – 400 cm^{-1} region. Samples were taken in the form of KBr pellets. DTGS pyroelectric detector was used and each spectra was an average of 200 number of scans at 8 cm^{-1} resolution. Scratched powder of nanostructured ZnO film from glass substrate was used in KBr pellets for recording infrared transmission spectra. Photoluminescence (PL) spectra were measured using a indigenously developed system consisting of a two stage monochromator, a PMT photomultiplier tube with a lock-in amplifier for PL detection, and an Ar^+ ion laser operating at 488 nm and 5mW (corresponding to 0.125 Wcm^{-2}) for excitation in all the measurements.

Optical transmission measurements were carried out on Shimadzu UN -3101 PC UV-VIS-NIR spectrophotometer.

Results & Discussion

The cathodic electrochemical deposition of nanocrystalline zinc oxide at different electrode potentials from was intiated by the reduction of nitrate ions. Nitrate ions at first reduced and form nitrite and hydroxide ions electrochemically. These hydroxide ions react with zinc ions and form zinc hydroxide at the cathode. This zinc hydroxide spontaneously dehydrates and form zinc oxide. XRD spectra of these nanocrystalline zinc oxide films (nc-ZnO) deposited at -1.30 V, -1.28 V and -1.35 V electrode potentials are presented in Fig. 1(a, b, c), respectively. All the three patterns showed three peaks of (100), (101) and (002) orientation planes with different intensity. This reveals that the grains of zinc oxide grow along different directions. All these peaks are attributed to the diffraction lines pertaining to the wurtzite structure. The weak preferential growth was observed in nc-ZnO films at -1.28 V electrode potential showed moderate perferential growth of (002) peak in comparison to the intensity of other two (100) and (101) peaks. But ZnO films deposited at -1.30 V electrode potential showed strongly oriented along c-axis i.e. (002) peak with very high intensity.

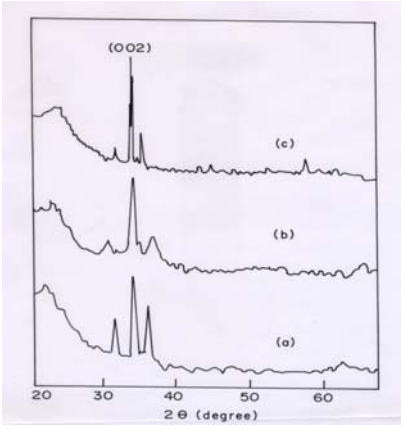

Figure 1(a, b, c) : XRD spectra of nc-ZnO films deposited at -1.30 V, -1.28 V and -1.35 V potentials

These studies showed that the structure of the deposited film was sensitive to the electrode potential used for the deposition of nc-ZnO films. The mean crystallite size was determined by using Scherrer's formula. For the (002) orientation line in these spectra, the crystallite size varies in the range of 10 - 25 nm.

Scanning electron micrographs (SEM) of these nc-ZnO films deposited at -1.30 V, -1.28 V and -1.35 V electrode potentials are shown in Fig. 2(a, b, c) . These micrographs exhibited the uniform distribution of microstructures without any cracks and voids with the variation in particle size and their packing density on different substrates. The size of the grains are regular and microstructure revealed many round shaped particles while in ZnO films at -1.30V electrode potential exhibited hexagonal shaped structures consistent with wurtzite structure. This confirmed that atoms in this film had sufficient activation lattice energy to align themselves in film network at correct crystal lattice sites and grains of small surface energy enhances in size. This resulted in oriented growth of the film in a preferrential direction of nanostructured ZnO films [16].

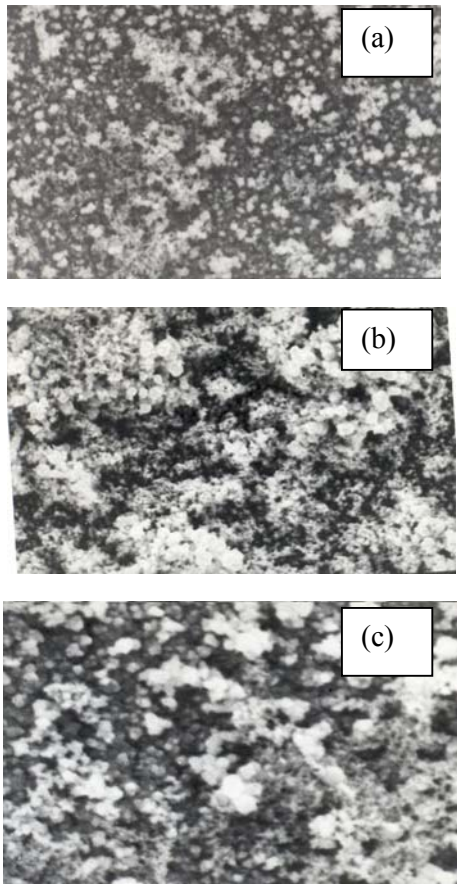

Figure 2(a, b, c) : SEM Micrographs of nc-ZnO films deposited at -1.30 V, -1. 28 V and -1. 35 V potentials

The packing density of film was increased in films deposited at -1.35V electrode potential was more in comparison to those at -1.30 V and -1.28V electrode potential. These variations are explained in terms of the disappearance of gap between the particles at higher electrode potential which may lead to the densification of film.

The appearance of Zn-O stretching mode at 456 cm^{-1} in infrared transmission spectra of these films confirmed the formation of ZnO. Photoluminescence (PL) spectra of nc- ZnO films at -1.30V, -1.28V and -1.35 V electrode potential are presented in Fig. 3(a, b, c) which shows strong broad structureless band in the yellow green region with maximum at about 580 nm of linewidth approximately.

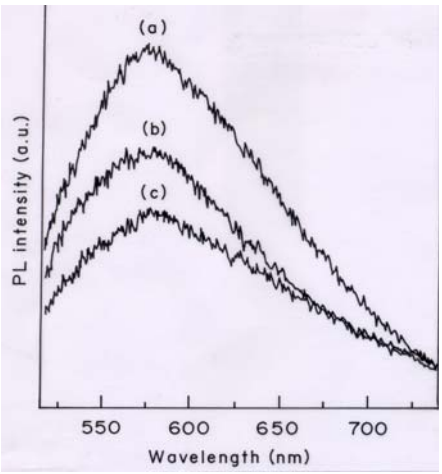

Figure 3(a,b,c): Photoluminescence spectra of nc-ZnO films deposited at -1.30 V,-1.28 V and -1.35 V potentials

The visible emission was discussed in terms of the electron transition induced by the defect levels in the band gap. These defects are oxygen vacancies or zinc interstitials in the nano film network which acts as radiative centres and traps electron from the valence band and contributes in the luminescent properties of the film [20-21]. So the luminescent behaviour of these nc-ZnO films at different electrode potential has confirmed the recombination of electron in singly occupied oxygen vacancies with photoexcited holes in the valence band.

The optical transmission spectra revealed that these films have optical transmittance more than 85% in the visible wavelength range. The absorption co-efficient confirmed
these nc-ZnO material as direct band gap material. The band gap energy is obtained by plotting a curve between $(\alpha h\nu)^2$ and $(h\nu)$ by using Tauc relation. Then straight line portion of the curve is extrapolatted to x-axis (i.e. $h\nu$) and get the energy band gap. In these films there value lie in 3.15 to 3.30 eV region.

Conclusion

Nanocrystalline ZnO thin films have been deposited on tin oxide coated conducting glass plates at different electrode potentials by cathodic electrochemical deposition process. The structural, morphological and photoluminescence properties revealed the formation of preferrentially oriented (002) uniform nanostructed ZnO films. The small variations in these nc-ZnO films structure, composition and morphology exhibited the role of electrode potential as controlling parameter to obtain good quality films with optimized stoichiometry. The recombination of electron in singly occupied oxygen vacancies with photoexcited holes in the valence band of ZnO film has confirmed the origin photoluminescence in these films. The good quality ZnO nanocrystalline films can be deposited at -1.30V electrode potential at 0°C temperature from 0.01M $Zn(NO_3)_2$ and 0.1M KNO_3 electrolyic bath solution on tin oxide coated glass plates.

Acknowledgement

The authors are greatful to Prof. Vikram Kumar, Director, National Physical Laboratory, New Delhi (India) and Dr.
S.T. Lakshmikumar for permitting to carry out this work and for their valuable suggestions during discussions.

References

1. J. P. Atanas, R. A. Asmar, A. Khoury, and A. Foucaran, "Optical and structural characterization of ZnO thin films and fabrication of bulk acoustic wave resonator (BAW) for the realization of gas sensors by stacking ZnO thin layers fabricated by e-beam evaporation and rf magnetron sputtering techniques",
Sensors and Actuators A: Physical, vol. 127, no1. , pp49-55, 2006.
2. H. Zhang, Y. Cui, Y. Men, and X. Liu , "Strong ultraviolet emission from zinc oxide thin films prepared by electrophoretic deposition ", Journal of Luminescence, In Press, Corrected Proof, Available online 9 March 2006.
3. P. Ahmet, Y.Z. Yoo, K. Yamada, K. Tsutsui, Y. Wada, and T. Chikyow, T. Nagata, "Schottky metal library for ZNO-based UV photodiode fabricated by the combinatorial ion beam-assisted deposition", Applied Surface Science, vol. 252, no. 7, pp. 2503-2506, 2006.
4. K. Ramamoorthy, C. Sanjeeviraja, M. Jayachandran, K. Sankaranarayanan, Pankaj Misra and L.M. Kukreja, "Development of a novel high optical quality ZnO thin films by PLD for III–V opto-electronic devices", Current Applied Physics, vol. 6, no. 1, pp. 103-108, 2006.
5. C. Yuen, S.F. Yu, S.P. Lau and George C.K. Chen, "Design and fabrication of ZnO light-emitting devices using filtered cathodic vacuum arc technique", Journal of Crystal Growth, vol. 287, no. 1, pp. 204-21, 2006.
6. J. Wood,"Bright future for p-type zinc oxide: Electronic materials", Materials Today, vol. 8, no. 2, pp. 9, 2005.
7. W. Wu, and Q. Jiang, "Preparation of nanocrystalline zinc carbonate and zinc oxide via solid-state reaction at room temperature", Materials Letters, vol. 60, no. 21-22, pp. 2791-2794, 2006.
8. A. Mosbah, A. Moustaghfir, S. Abed, N. Bouhssira, M.S. Aida, E. Tomasella, and M. Jacquet, "Comparison of the structural and optical properties of zinc oxide thin films deposited by d.c. and r.f. sputtering and spray pyrolysis ", Surface and Coatings Technology, vol. 200, no. 1-4, pp. 293-296, 2005.
9. P. Bilkova, J. Zemek, B. Mitu, V. Marotta and S. Orlando, "Deposition of zinc oxide thin films by reactive pulsed laser ablation", Applied Surface Science, vol. 252, no. 13, pp. 4604-4609, 2006.

10. C. L. Wu, Li. Chang, H. G. Chen, C. W. Lin, T. F. Chang, Y. C. Chao, and J. K. Yan, "Growth and characterization of chemical-vapor-deposited zinc oxide nanorods", Thin Solid Films, vol. 498, no. 1-2, pp. 137-141, 2006.
11. M. Ristić, S. Musić, M. Ivanda and S. Popović, "Sol–gel synthesis and characterization of nanocrystalline ZnO powders", Journal of Alloys and Compounds, vol. 397, no. 1-2, pp. L1-L4, 2005.
12. H. Li, J. Wang, H. Liu, H. Zhang and X. Li , "Zinc oxide films prepared by sol–gel method", Journal of Crystal Growth, vol. 275, no. 1-2, Pages e943-e946, 2005.
13. F. Paraguay D., W. Estrada L., D. R. Acosta N., E. Andrade and M. Miki-Yoshida, "Growth, structure and optical characterization of high quality ZnO thin films obtained by spray pyrolysis", Thin Solid Films, vol. 350, no. 1-2, pp. 192-202, 1999.
14. M. Berber, V. Bulto, R. Kliß and H. Hahn, "Transparent nanocrystalline ZnO films prepared by spin coating", Scripta Materialia, vol. 53, no. 5, pp. 547-551, 2005.
15. T. Yoshida, D. Komatsu, N. Shimokawa and H. Minoura , "Mechanism of cathodic electrodeposition of zinc oxide thin films from aqueous zinc nitrate baths", Thin Solid Films, vol. 451-452, pp. 166-169, 2004.
16. L. Zhang, Z. Chen, Y. Tang, and Z. Jia, "Low temperature cathodic electrodeposition of nanocrystalline zinc oxide thin films", Thin Solid Films, vol. 492, no. 1-2, pp. 24-29, 2005.
17. J. Weng, Y. Zhang, G. Han, Y. Zhang, L. Xu, J. Xu, X. Huang and K. Chen , "Electrochemical deposition and characterization of wide band semiconductor ZnO thin film", Thin Solid Films, vol. 478, no. 1-2, Pages 25-29 , 2005.
18. T. Mahalingam, V.S. John, M. Raja, Y.K. Su and P.J. Sebastian , "Electrodeposition and characterization of transparent ZnO thin films", Solar Energy Materials and Solar Cells, vol. 88, no. 2, Pages 227-235, 2005.
19. Q. Wang, G. Wang, J. Jie, X. Han, B. Xu and J.G. Hou., " Annealing effect on optical properties of ZnO films fabricated by cathodic electrodeposition", Thin Solid Films, vol. 492, no. 1-2, Pages 61-65, 2005.
20. S. A. Studenikin, N. Golego and M. Cocivera, "Fabrication of green and orange photoluminescent undoped ZnO films using spray pyrolysis", J. Appl. Phys., vol. 84, no. 4, pp. 2287-2294, 1998.
21. K. Vanheusden, W. L. warren, C. H. Seager, D. R. Tallant, J. A. Voigt and B. E. Gnade, Mechanisms behind green photoluminescence in ZnO phosphor powders, J. Appl. Phys., vol. 79, no. 10, pp. 7983-7990, 1996.