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CBD grown ZnO thin films: Optical and structural analysis

Rajni Seth[1] and Rubi[1]
[1]Department of Physics, Dyal Singh College, Karnal, Haryana, India

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Abstract
In the present investigations, CBD technique was used to deposit ZnO thin film with HMTA as a complexing agent and $Zn(NO_3)_2.6H_2O$ as a source of Zn ions on glass substrates. The XRD pattern confirmed the presence of nano crystalline thin film with a preferential (002)-orientation. The sample was characterized for surface morphology by scanning electron microscope (SEM). Elemental phase composition of as deposited film was analyzed using energy dispersive X-ray spectroscopy (EDX) which confirmed the presence of Zn and O_2 without impurities. Transmittance was observed to be 87% in the visible region. Optical parameters like absorption coefficient, extinction coefficient, refractive index and dielectric constant were calculated. The study of Photoluminescence spectra revealed a near band edge strong UV emission peak, centered at 385nm and a week broad band in visible region.

Keywords: ZnO, XRD, SEM, UV/VIS, CBD

Introduction

ZnO is a II-VI semiconductor possessing a wide band gap energy of 3.37 eV at room temperature [1] and hence become an important functional material with near UV-emission, optical transparency, electric conductivity and piezoelectricity [2, 3]. It is a stronger candidate for optoelectronic devices such as solar cell [4, 5], chemical sensor for some gases [6, 2], biosensors for detection of biomolecular interactions [8], luminescent and electrical devices, vacuum fluorescent displays(VFDS), solid state white light source [9], textiles [10], sun screen due to UV absorption property etc. The non-toxic, cost-effective zinc oxide nanostructures are being intensively investigated to replace very expensive materials in different applications. Thin polycrystalline films of ZnO can be prepared by different methods such as spray pyrolysis[11], sputtering [12], pulsed laser deposition [13], sol-gel [14], physical vapor deposition [15], chemical bath deposition (CBD) [16] etc. Among these various techniques, CBD is the simplest and most economical method. In the present study, attempts were made to deposit ZnO nano crystalline thin films using CBD. These films were investigated for the structural and optical properties.

Materials and Methods

ZnO thin film was deposited using CBD with Zinc nitrate, HMTA and nitric acid as precursors and investigated for its structural and optical properties. The deposition was carried out using a two-step process: coating of ZnO seeds on the substrate and further growth of thin films on the seeded substrate. The glass slide was thoroughly cleaned and finally dried in hot air at 100 °C for 3 hours. For deposition of seed layer on the substrate, 25mM of Zn $(CH3COO)_2$. H_2O in absolute ethanol solution was used [17]. For deposition of thin film, equal volume of equimolar (0.1M) of HMTA and Zn $(NO_3)_2$. $6H_2O$ were mixed with the help of an ultrasonicator for 15 min. The pH of chemical bath was adjusted at 5.0 using concentrated nitric acid. The seeded substrate was dipped in the solution bath at 90 ºC in slant position for two hours. After taking out the glass slide, it was rinsed with distilled water and dried at 100 °C in a hot air. Afterwards the thin Film thus deposited on glass substrates was further annealed at 400ºC for 15 minutes.

Results and Discussion

Tada H[18] proposed the protonated hexamine $[(CH_2)_6N_4H]^+$ undergoes hydrolytic decomposition in acidic media producing protonated ammonia through the following reaction in the chemical bath:

$$[(CH_2)_6N_4] + H^+ \longleftrightarrow [(CH_2)_6N_4H]^+$$
$$[(CH_2)_6N_4H]^+ + 3H^+ + 4\,No_3^- + 6\,H_2O \longleftrightarrow 4NH_4^+ + 4No_3^- + 6CH_2$$

Under weak acidic conditions ammonia combines with Zn^{2+} ions to produce a large number of Zn^{2+}-amino complexes in the solution. These complexes will be directly hydrolyzed and ZnO can be formed on the glass substrate and the vessel inter-surface through the decomposition reaction. Hence ammonia could stabilize Zn^{2+} through reversible reaction of consuming and decomposing of zinc ammonia complex. It was observed that in acidic bath (pH=5) the solution remained transparent indicating a slow chemical deposition process.

$$[Zn(NH_3)_4]^{2+} + 4H_2O \rightarrow Zn(OH)_2 + 4\,[NH_4]^{2+} + 2O\bar{H}$$

$Zn(OH)_2$ dehydrates into ZnO[19]

$$Zn(OH)_2 \rightarrow ZnO + H_2O$$

Structural and Morphological Analysis

In order to check the structural properties of CBD thin ZnO film, X-ray diffraction (XRD) was recorded by XPERT-PRO diffractometer (45 kV, 40 mA) equipped with a Gionometer PW3050/60 working with Cu K ALPHA radiation of wavelength 1.5406 A˚ in the 2θ range from 5 to 80. X-ray diagram for the sample corroborates the presence of more than one phase in the film (Fig.1). The sharp intense peaks of

ZnO confirm the good crystalline nature of ZnO nanocrystallites and can be indexed as the hexagonal wurzite structure (JCPDF data file No. 80-0074). It was observed that annealing enhanced the crystallinity of ZnO films, by reducing defects, modifying boundaries and increasing grain size [19].

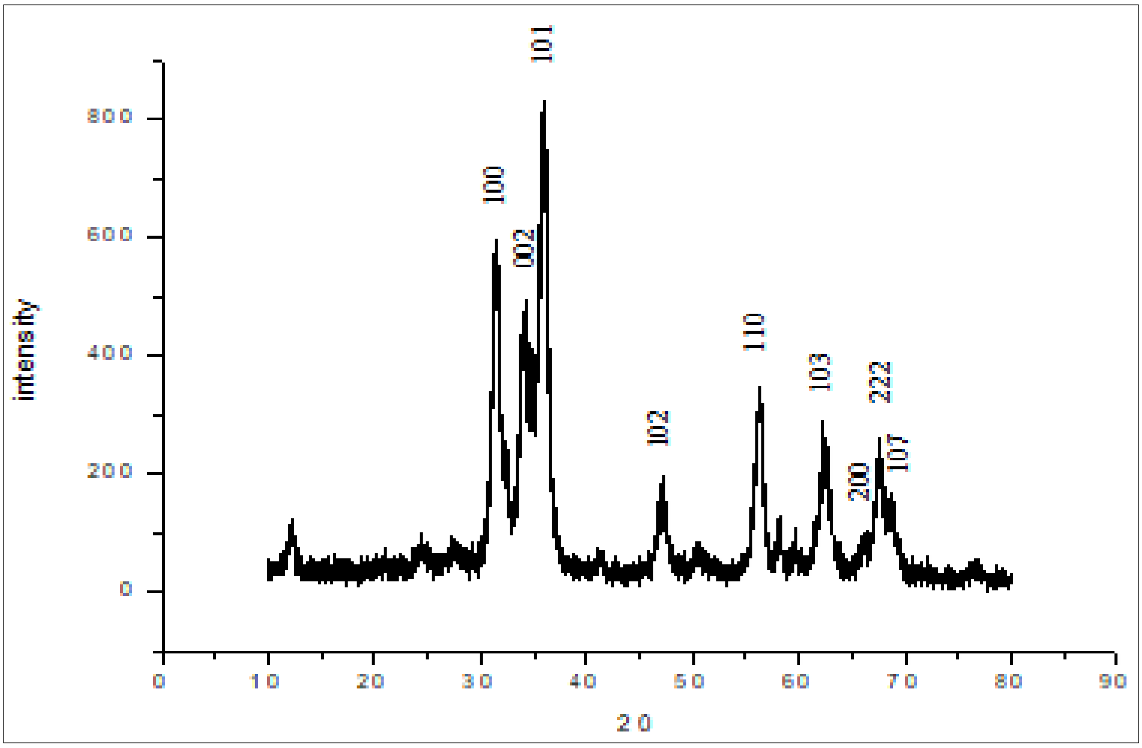

Fig1: XRD Spectra of ZnO Thin Film annealed at 400ºC

Scanning electron microscopy (SEM, HITACHI model S-3700N) was used to observe the morphology of the particles in the thin film. SEM micrograph (Fig.2) of the as prepared thin film showing sharp edges type structure of nano crystallite.

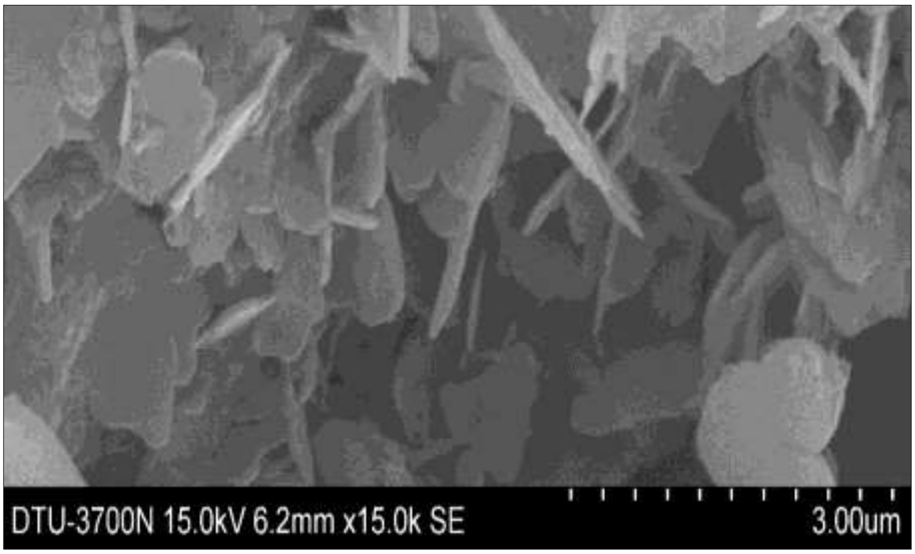

Fig 2: SEM image of ZnO Thin Film annealed at 400ºC

Elemental phase composition of as deposited film was analyzed using energy dispersive X-ray spectroscopy (EDX) (HITACHI model S-3700N). EDX spectrum (Fig.3) indicates that sample is pure ZnO with two small peaks of Mg and Ca which are due to the glass substrate.

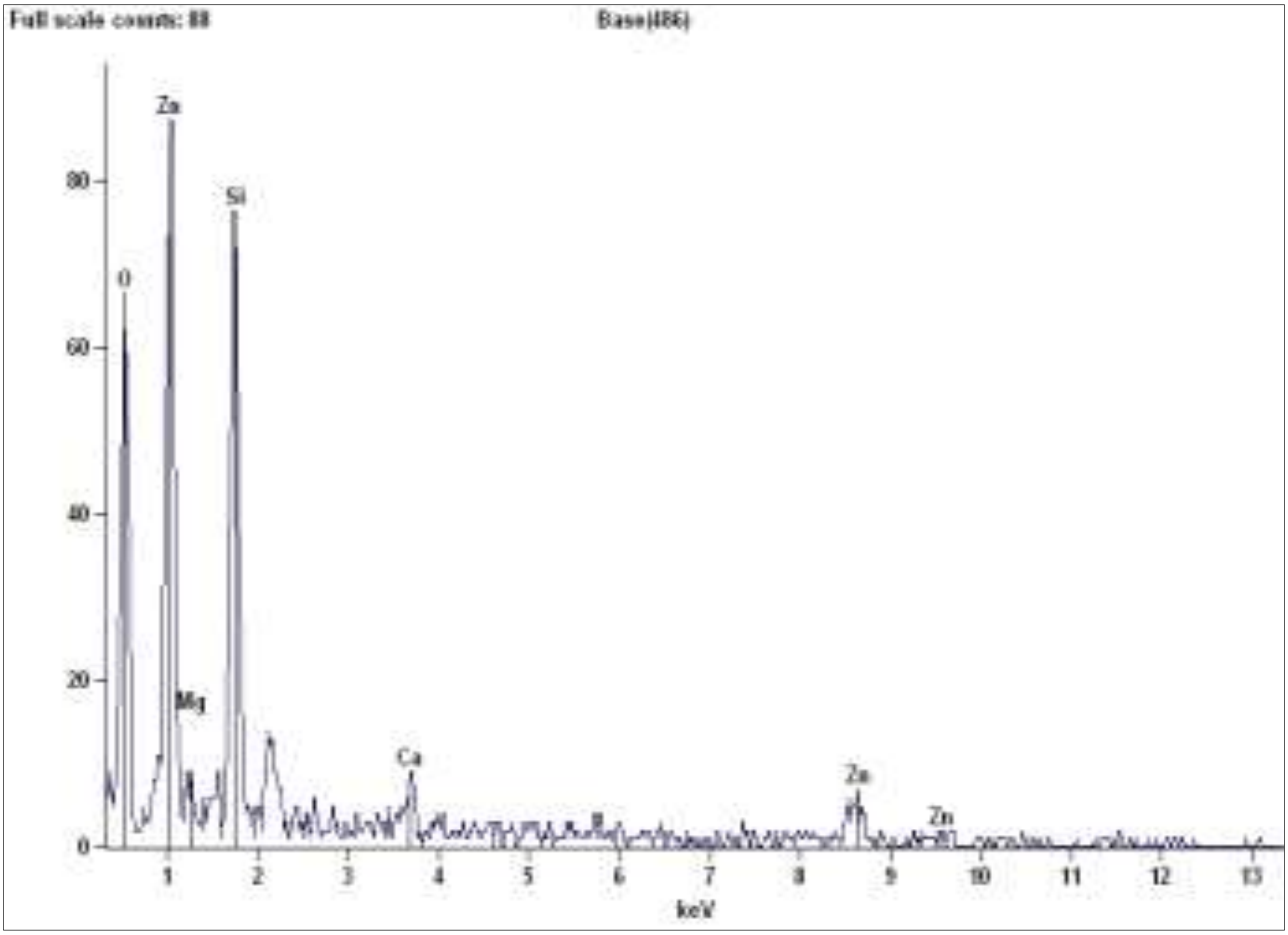

Fig 3: EDX spectrum of ZnO Thin Film annealed at 400°C

Optical Properties

UV Visible Spectroscopy

UV/VIS spectrophotometric scans were measured in the wavelength range 250-800 nm using UV Visible Spectrophotometer (UV-2550) with integrated sphere assembly ISR 240A with a resolution of 1 nm. The various optical parameters are reported in Table (1). It was observed that the optical parameters are also found to improve due to annealing of ZnO thin films. High temperatures and an oxygen-rich atmosphere are especially effective for improving optical properties by eliminating defects [20, 21].

The absorption coefficient α was calculated using transmittance data,

$$\alpha = \frac{1}{t} \ln \frac{1}{T}$$

t=thickness & T=transmittance and the extinction coefficient

[$\kappa = \frac{\alpha\lambda}{4\pi}$] is the imaginary part of the complex refractive index which relates to light absorption [22].

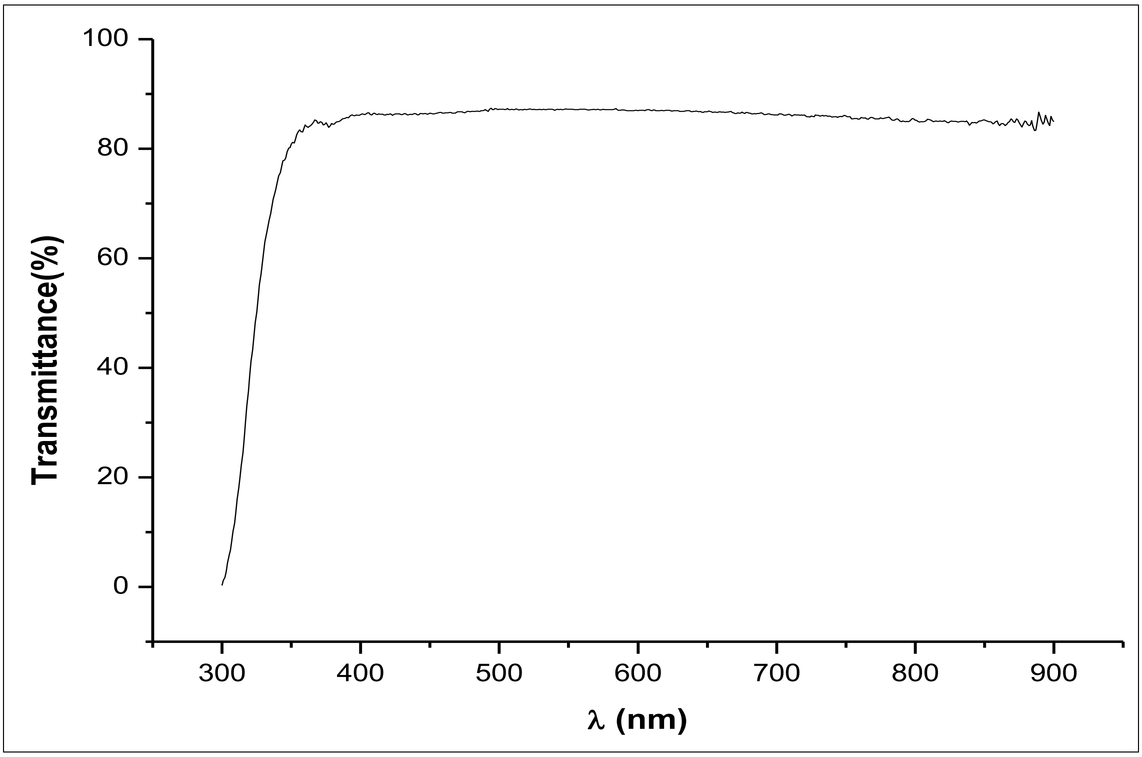

Fig 4: Transmittance of ZnO Thin Films

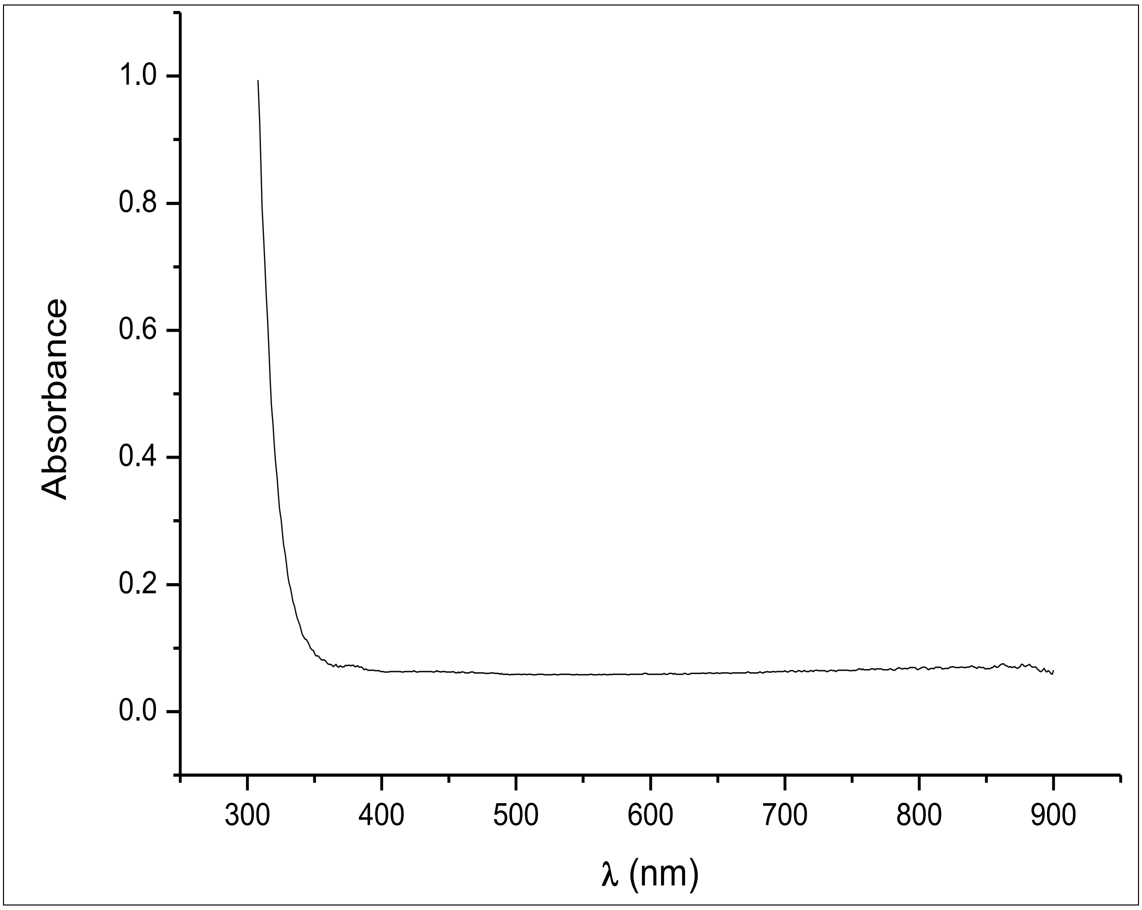

Fig. 5: Absorbance of ZnO Thin Films

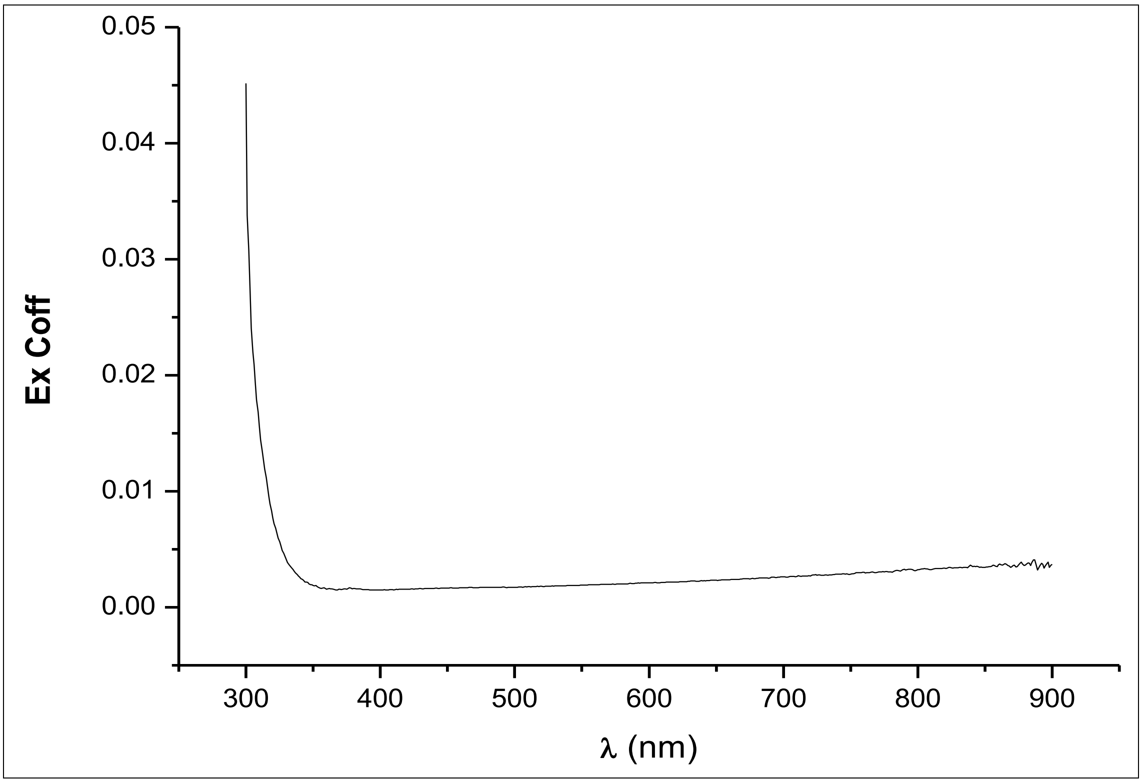

Fig 6: Ex. Coefficient. of ZnO Thin Films

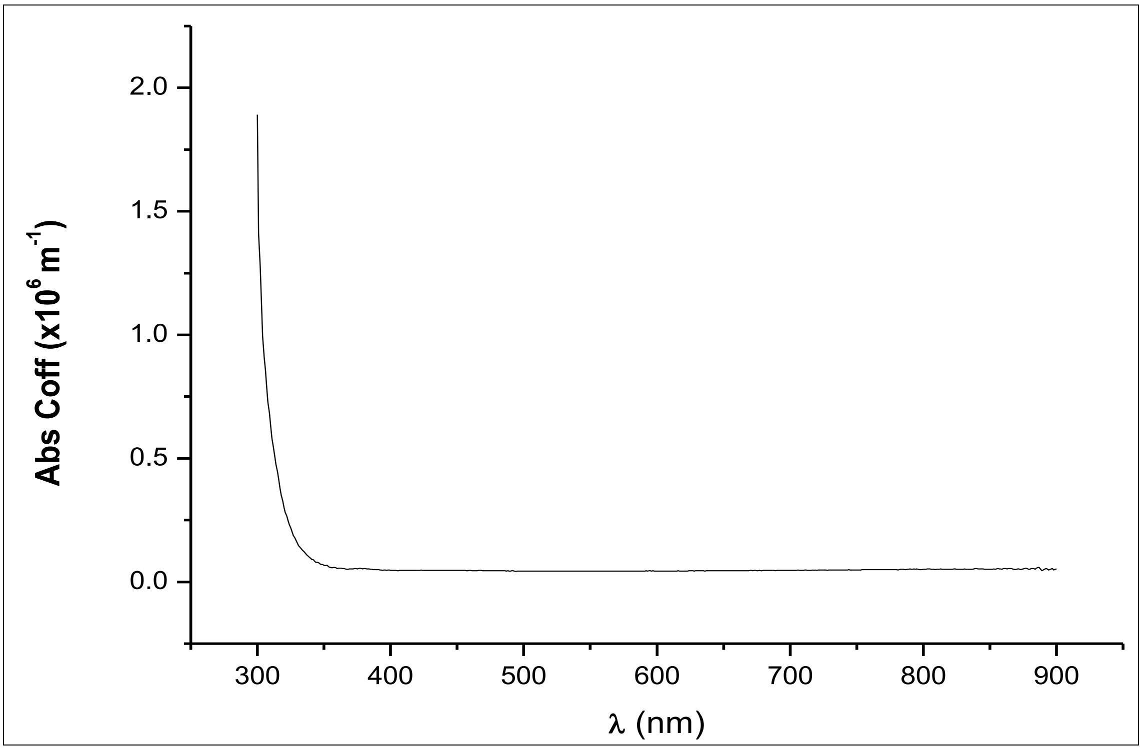

Fig 7: Abs. Coefficient of ZnO Thin Films

The refractive index of a material is a fundamental intrinsic material property and was calculated using the relation:

$$n = \frac{(1+R^{1/2})}{(1-R^{1/2})}.$$

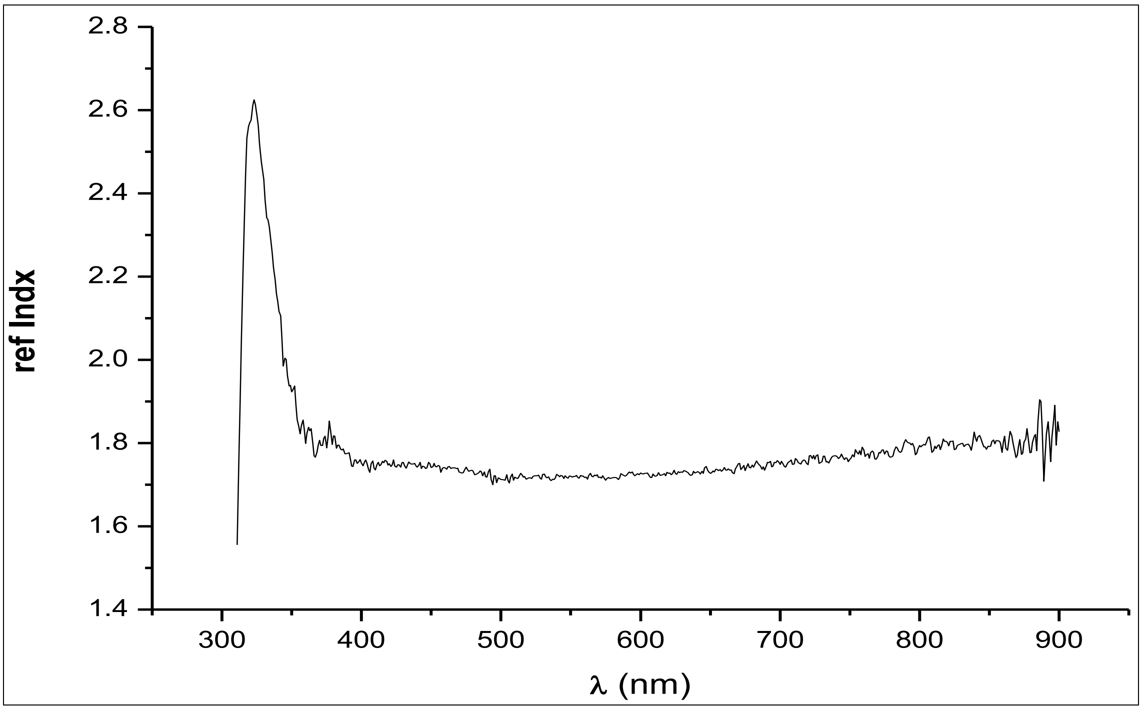

Fig 8: Refractive Index of ZnO Thin Films

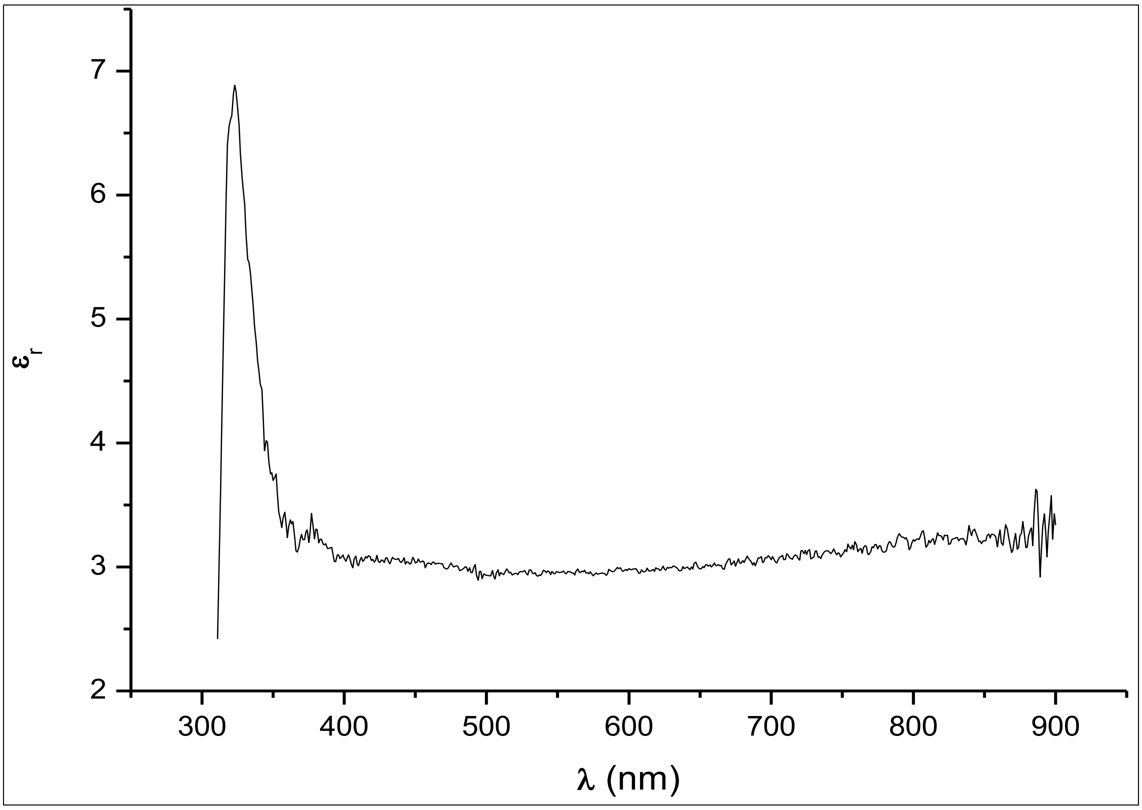

Fig 9: Dielectric Constant of ZnO Thin Films

The real part of dielectric constant is a measure of how much it will slow down the speed of light in the material and is related to refractive index by [23]:

$\varepsilon_r = n^2 - \kappa^2$

Annealing often improves crystallinity by reducing grain boundaries and defects (like oxygen vacancies), which typically increases the dielectric constant of ZnO films.

Table 1: Values of Various Optical Parameters

Transmittance	87%
Absorbance	0.054%
Abs Coff (αx10^6(m^{-1}))	0.042
Ref Index (n)	1.69
Ex. Coff. (κ)	0.002
Real D.Const (ε_r)	3.02

Photoluminescence Study: Room temperature PL spectrum (Fig.10) of the nanocystalline ZnO film is measured with an excitation wavelength of 350 nm. The near band edge strong UV emission peak, centered at 385nm, correspond to exciton recombination of ZnO [24, 25, 26] and a weak but broad band centered around 560nm is due to deep level emission, probably due to the presence of a few intrinsic defects in ZnO nanocrystalline films. Different intrinsic defects correspond to various excited energy states in deep level emission [27, 28]. Van-Heusen *et al.* have also shown that singly ionized oxygen vacancies result in visible emission, producing a wide PL band in the range 500-650 nm [29].

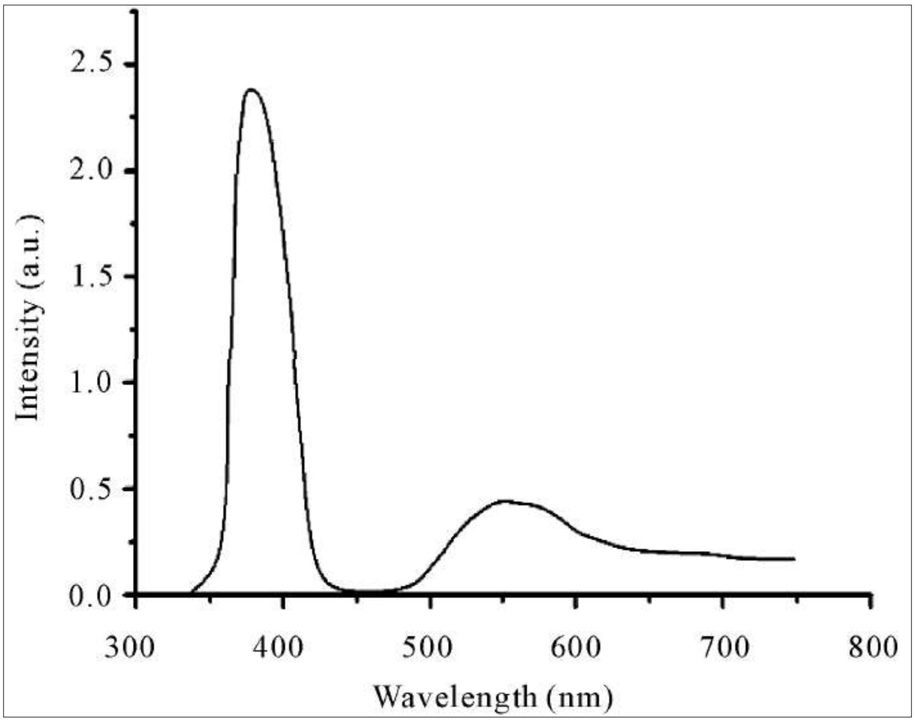

Fig 10: Photoluminescence Spectra of ZnO thin films

Conclusion

We successfully deposited ZnO thin films using chemical bath deposition in an acidic bath. The crystalline nature of thin films was found to be improved after annealing. The optical properties were found to be improved as compared to bulk values proving that chemical bath deposition is a good technique to deposit nanocrystalline ZnO thin films with flower like morphology. The coverage of thin film is very good on the substrate, so it is concluded that as such deposited and afterwards annealed films with improved structural and optical qualities can be utilized in solar cells.

Conclusion

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References

1. Huang MH, Wu Y, Feick H, Tran N, Weber E, Yang P. Catalytic growth of zinc oxide nanowires by vapor transport. J Am Chem Soc. 2001 Jan;13(2):113-116.
2. Nunes P, Fernandes B, Fortunato E, Vilarinho P, Martins R. Performance presented by ZnO thin films deposited by spray pyrolysis. Thin Solid Films. 1999 Jan;337(1-2):176-179.
3. Chen Y, Bagnall D, Yao T. ZnO as a novel photonic material for the UV region. Mater Sci Eng B. 2000 Jun;75(2-3):190-198.
4. Ramamoorthy K, Sanjeeviraja C, Jayachandran M, Sankaranarayanan K, Bhattacharya P, Kukreja LM. Preparation and characterization of ZnO thin films on InP by laser-molecular beam epitaxy technique for solar cells. J Cryst Growth. 2001 Mar;226:281-286.
5. Zhang Q, Dandeneau CS, Zhou X, Cao G. ZnO nanostructures for dye-sensitized solar cells. Adv Mater.

2009 Nov;21(41):4087-4108.
6. Chou SM, Teoh LG, Lai WH, Su YH, Hon MS. ZnO:Al thin film gas sensor for detection of ethanol vapor. Sensors. 2006 Oct;6(10):1420-1427.
7. Wongka W, Yata S, Gardchareon A, Mangkorntong P, Mangkorntong N, Choopun S. Zinc oxide nanowires impregnated with platinum and gold nanoparticle for ethanol sensor. CMUJ Nat Sci. Special Issue on Nanotechnology, 2008;7(1):185-190.
8. Choi AH, Kim K, Jung HI, Lee SY. ZnO nanowire biosensors for detection of biomolecular interactions in enhancement mode. Sensors Actuators B: Chem. 2010 Jul;148(2):577-582.
9. Nanda KK. Direct white light nanophosphors. Key Eng Mater. 2010 Nov;444:219-228.
10. Vigneshwaran N, Kumar S, Kathe AA, Varadrajan PV, Prasad V. Functional finishing of cotton fabrics using zinc oxide–soluble starch nanocomposites. Nanotechnology. 2006 Sep;17(20):5087-5095.
11. Lehraki N, Aida MS, Abed S, Attal N, Attaf A, Poulain M. ZnO thin films deposition by spray pyrolysis: Influence of precursor solution properties. Curr Appl Phys. 2012 Sep;12(5):1283-1287.
12. Dang WL, Fu YQ, Luo JK, Flewitt AJ, Milne WI. Deposition and characterization of sputtered ZnO films. Superlattices Microstruct. 2007 Jul-Dec;42(1-6):89-93.
13. Tsoutsouva MG, Panagopoulos CN, Papadimitriou D, Fasaki I, Kompitsas M. ZnO thin films prepared by pulsed laser deposition. Mater Sci Eng B. 2011 Apr;176(6):480-483.
14. Xu LH, Li XY, Chen YL, Xie F. Structural and optical properties of ZnO thin films prepared by sol–gel method with different thickness. Appl Surf Sci. 2011 Dec;257(9):4031-4037.
15. Fouad OA, Ismail AA, Zaki ZI, Mohamed RM. Zinc oxide thin films prepared by thermal evaporation deposition and its photocatalytic activity. Appl Catal B: Environ. 2006 Jan;62(1-2):144-149.
16. Mane RS, Lokhande CD. Chemical deposition method for metal chalcogenide thin films. J Mater Chem Phys. 2000;65:1-31.
17. Byrne D, Glyn INC, Cullen J, Henry MD. Nanoscale. 2011;3:1675.
18. Tada H. Decomposition reaction of hexamine by acid. J Am Chem Soc. 1960;82(2):255-263.
19. Look DC, Reynolds DC, Hemsky JW, Sizelove JR, Jones RL, Litton CW. Production and annealing of electron irradiation damage in ZnO. Appl Phys Lett. 1999;75(6):811-813.
20. Ahn KS, Yan Y, Li J, Perkins CL, Zhu K. Effect of annealing on the properties of ZnO thin films deposited by radio frequency magnetron sputtering. J Appl Phys. 2009;105(11):113533.
21. Bhosale CH, Rajpure KY, Uplane MD. Effect of annealing on the properties of chemically sprayed ZnO thin films. Mater Sci Eng B. 2003;98(3):250-255.
22. Swanepoel R. Determination of the thickness and optical constants of amorphous silicon. J Phys E Sci Instrum. 1983;16(12):1214.
23. Suresh Kumar. Thesis. 2014. Available from: http://hdl.handle.net/10603/251.
24. Srikant V, Clarke DR. Optical absorption edge of ZnO thin films: the effect of substrate. J Appl Phys. 1997;81(9):6357-6364.
25. Lyu SC, Zhang Y, Ruh H, Lee H, Shim H, Suh E, Lee CJ. Low temperature growth and photoluminescence of well-aligned zinc oxide nanowires. Chem Phys Lett. 2002;363(1-2):134-138.
26. Bergman L, Chen XB, Morrison JL, Huso J, Purdy AP. Photoluminescence dynamics in ensembles of wide band gap nanocrystallites and powders. J Appl Phys. 2004;96:675-682.
27. Lin B, Fu Z, Jia Y. Green luminescent center in undoped zinc oxide films deposited on silicon substrates. Appl Phys Lett. 2001;79:943-945.
28. Zhao L, Lian J, Liu Y, Jiang Q. Structural and optical properties of ZnO thin films deposited on quartz glass by pulsed laser deposition. Appl Surf Sci. 2006;252(24):8451-8455.
29. Vanheusden K, Seager CH, Warren WL, Tallant DR, Voigt JA. Correlation between photoluminescence and oxygen vacancies in ZnO phosphors. Appl Phys Lett. 1996;68:403-405.