www.sphinxsai.com

ChemTech

International Journal of ChemTech Research
CODEN (USA): IJCRGG ISSN : 0974-4290
Vol.6, No.5, pp 2941-2945, Aug-Sept 2014

Effect of Annealing Temperature on Characterization of ZnO thin films by sol-gel method

M.Saravanakumar[1]*, S.Agilan[2], N.Muthukumarasamy[2]

[1] SVS College of Engineering, Coimbatore -642 109, India
[2]Coimbatore Institute of Technology, Coimbatore – 641 014, India.

***Corres.author: saranspectra@gmail.com**

Abstract: Zinc oxide (ZnO) thin films are deposited on glass substrates by sol–gel method. A homogeneous and stable solution is prepared by dissolving ZnAc in the solution of monoethanolamine (MEA). The films, after the deposition, are annealed in air at different temperatures.
The structural characteristics of the films and powder are studied using X-ray diffractometer (XRD). Scherer's formula is used to calculate crystalline size of prepared films. Scanning electron microscopy (SEM) is used to describe the surface morphology. Photoluminescence (PL) measurements are used to find the energy band gap of the films. Optical Characteristics were studied using Transmittance and Absorption Spectra. The result shows that we are successful to fabricate ZnO films in simple and low cost method with high quality.
Keywords: ZnO, Sol-gel, XRD, SEM, UV, PL.

Introduction

ZnO is a special characterized semiconductor with many potential applications[1-4]. The tetrahedral coordination indicates the covalent bonding of the Zn–O bond with a very strong ionic character. ZnO is used as conducting compounds in many opto electronic devices (solar cells, gas sensors, varistors, and light emitting diodes) [5]. Thin films made of ZnO has a high transmittance and conductivity which are used in solar cells and energy efficient window display. ZnO films are thermally and chemically stable with an wide band gap (3.37 eV at RT) and large excitation energy (60 meV), which is in the visible spectrum.

ZnO Films can be prepared by different methods, like chemical vapor deposition, sol–gel, spray-pyrolysis, molecular beam epitaxy, pulsed laser deposition, vacuum arc deposition, and magnetron sputtering. The sol–gel process is a simple and less expensive method with which coating can be obtained at room temperature.[6] There are some factors that effect microstructures and properties of thin films , such as concentration ,precursor, solvent the aging time of solution, temperature and heat treatment etc. [7,8]

In present work we used sol- gel method to obtain ZnO films and the studies have reported ZnO thin films using monoethanolamine (MEA) as a complexing agent. The thin film deposition was achieved by the dip coating method is obtaining ZnO thin films. The optical and structural properties of the thin films formed are analyzed by UV and XRD analysis.

Experimental Procedure

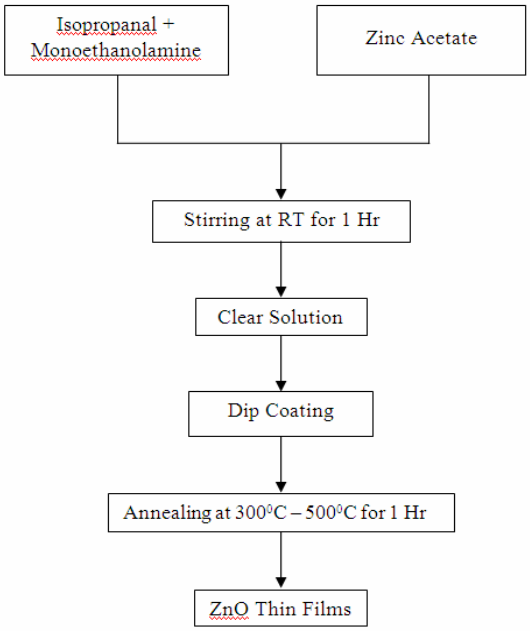
The preparation of ZnO films by sol gel technique and the characterization methods are introduced. The preparation of ZnO films consist of three steps

1. Preparation of solution
2. Film coating
3. Heat treatment

The solution was prepared using Zinc acetate dissolved in 10 ml of isopropyl alcohol (99.7 % sigma-aldrich, $CH_3CHOHCH_3$) and 5 ml Monoethanolamine (MEA) solution at room temperature.

The concentration of Zinc Acetate (ZnAc) was 1 M / 0.5 M of MEA. MEA was added drop by drop. The mixture was mixed well with stirrer at room temperature (30° C) until clear and transparent solution was formed.

The substrates of glass were cleaned with Distilled Water, NaOH and Acetone respectively. The substrates were cleaned ultrasonically with duration of 15 min. Film deposition was carried out in air at room temperature. The dipping was done mechanically into solution. Each deposition time 5cm /minute 5 dips. The deposited films were annealed at temperatures 300 ° C, 400 ° C and 500 ° C.



The samples were characterized by XRD, Morphology of the samples were examined by SEM and AFM. Optical absorption was studied by UV – Vis Absorption Spectrometer. PL and excitation spectra were measured at room temperature.

Results and Discussion

Structural Analysis

The crystal structure of Zno Films were studied using high resolution X- Ray Diffraction technique. The XRD pattern Zno films, annealed at different temperature is shown in figure (1,2,3).The diffraction peaks obtained for Zinc Oxide at 300° C are (100) ,(002), (101), (102), (110), (103), (112) respectively.

It was found that the quality of thin films prepared by sol gel- dip coating process and crystallization was influenced by annealing temperature. The orientation of crystallites is random which was clearly indicated by the several peaks obtained in XRD patterns of all the ZnO films. The XRD patterns were compared to powder diffraction data of zincite (wurzite) structure (JCPDS) 36-1451 the XRD patterns of all the films indicates intensities for the peaks corresponding to (100) (002) (101) (102) (110) (103) (112) respective planes which indicates orientation along z-axis. The highest peak (101) plane of all the tilus indicates, the structure is wurtzite. The intensities of the film increases with the increase in annealing temperature which is indicated by the increasing FWHM values.

Higher peak intensity is obtained due to annealing treatment of the film. Increasing the annealing temperature increases intensity and particle size. The particle size were calculated and are14nm, 28nm and 34 nm for 300°C, 400°C and 500°C respectively.

In order to attain the detailed structure information, grain size along z-axis was calculated by the Scherrer formula

$$D = \frac{0.9\,\lambda}{B\,\mathrm{Cos}\theta} \qquad (1)$$

where λ - wavelength of x-ray (0.154×10^{-9}m)

θ - Bragg angle of peaks

B - FWHM value

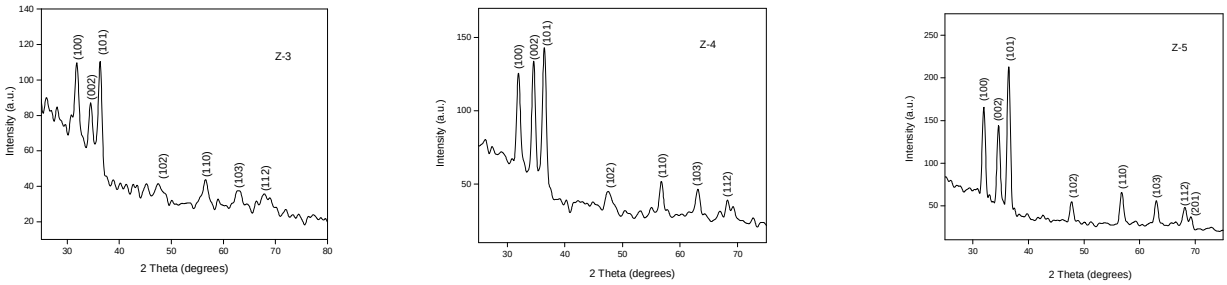


Fig. 1: XRD pattern of ZnO thin films annealed at (a) 300°C (b) 400°C (c) 500°C

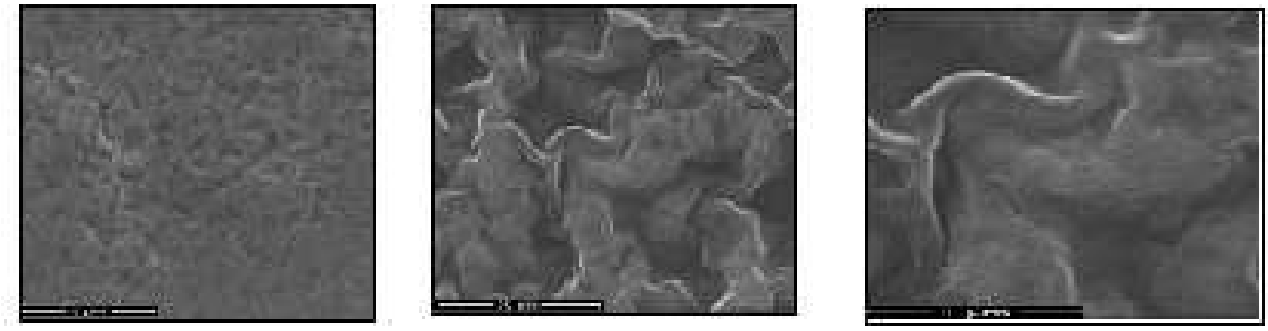


Fig. 2: SEM images of ZnO thin films annealed at (a) 300°C (b) 400°C (c) 500°C

Figure 2 shows the surface morphology of ZnO thin films annealed at different temperature. The SEM image shows a uniform compact surface. The ZnO thin films are porous and the average crystallite size of the films is about 14–34 nm, which matches with XRD data identified in that range. The crystallite size increases with increase in annealing temperature. The surface of the thin film, annealed at 300^0C, contained some cracks while no crack was observed after annealing at 400^0C, and 500^0C. The highest density thin film was achieved after annealing at 500^0C. As the annealing temperature of ZnO films increased from 300^0C to 500^0C, the crystallite size is increased and the films became denser.

The grain boundary decreased with increasing crystallization of thin films, and the electrical resistivity decreases with increase in crystallization and orientation with increasing heat-treatment temperature. Our results are in good agreement with other works. [9, 10, 11]

Optical Studies

The optical transmittance spectra of ZnO annealed at 400°C was shown in figure 3. The average transmittance in the visible range was measured to be approximately 60%.

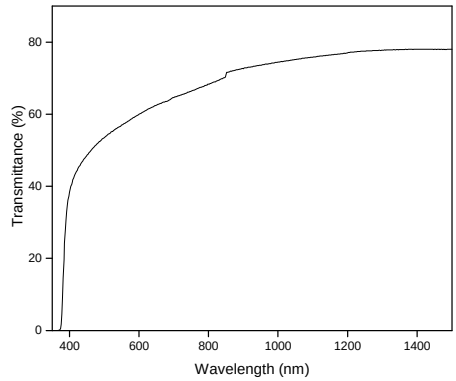


Fig. 3: Transmittance spectra of ZnO thin films annealed at 400°C

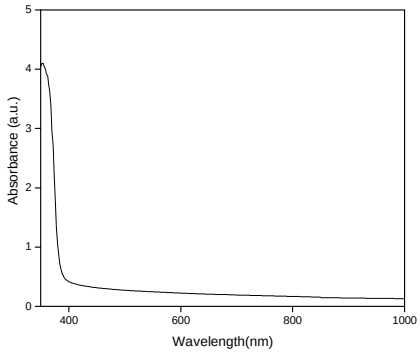


Figure. 4: Optical absorption spectra of ZnO thin films annealed at 400°C

The optical properties of synthesized differently shaped zinc oxide nanostructures were examined via UV vis spectroscopy at room temperature was demonstrated in Fig. 7. UV vis spectroscopy is the measurement of the absorption of near and visible ultraviolet light by using semiconductor zinc oxide nanostructures.

In our differently shaped nanostructures' sample such as needle, flowers composed with nanorods, pencil and microparticles give an electronic transition at a specific wavelength that is absorbed and the intensity of the absorption gives us an information about the electronic spectra of the sample. All the nanostructures wavelength were found in the range of 358-360 nm, which is a characteristic peak of wurtzite hexagonal phase ZnO, demonstrating that the synthesized products are pure ZnO [12-14]. The obtained band gap from the room temperature UVevis spectra is well matched with the standard bulk ZnO [12-14]. We found that the band gaps (3.27 eV) of our synthesized nanostructures are very near to the available band gap of bulk ZnO (3.37 eV) [12-14]. Due to the presence of a broad peak in the obtained UV vis spectra, one can conclude that the grown ZnO nanostructures exhibited good optical properties.

Photoluminescence

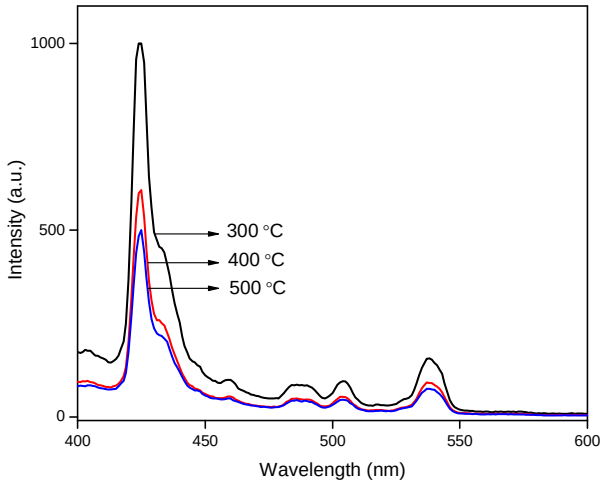


Fig 5 : Photoluminescence of ZnO thin films annealed at temperatures (300°C, 400°C, 500°C)

Fig.5 shows the temperature dependence of the PL spectrum of a sol–gel ZnO film. The main peak was positioned at 425 nm with a FWHM of 14 – 34 nm. These values were comparable to those of the ZnO film fabricated by laser ablation. [15, 16] No visible emission bands related to defects of ZnO crystal were observed. With the increase of annealing temperature the intensity of the peak were found decreasing.

Conclusion

In summary, nanocrystalline ZnO thin films on microscopic glass substrate has been deposited with the help of simple dip coating method. These thin films were annealed in different temperature (in air) region of 300–500°C. Obtained XRD pattern of ZnO thin films has polycrystalline wurtzite structure with a (101) orientation. Increasing annealing temperature increased the grain size of the thin film. The annealed ZnO thin films are highly transparent in the visible region (385nm) and have a sharp absorption edge in the ultraviolet region. The optical band gap energy (Eg), of ZnO thin films were between 3.27 eV-3.34eV through UV studies. SEM analysis has given a completely different surface morphology for different annealed ZnO thin films. PL studies proved that increase in annealing temperature decreases the intensity of the peak. These results suggest that the nano-crystalline ZnO thin films prepared by this sol–gel process have good c-axis orientation and optical properties.

References

[1] D.C. Look (2001), Mater. Sci. Eng. 80B: 383-389.
[2] K. Ellmer (2001), J. Phys. D: Appl. Phys. 34: 3097 -3103.
[3] A.B. Djurisic, Y. Chan, E.H. Li (2002), Mater. Sci. Eng. 38R: 237-240.
[4] Y.F. Chen, D. Bagnall, T. Yao (2000), Mater. Sci. Eng. 75B: 190-196.
[5] Ü. Özgür, Ya.I. Alivov, C. Liu, A. Teke, M.A. Reshchikov, S. Doğan, V. Avrutin, S.-J. Cho, H. Morkoç (2005), J. Appl. Phys. 98: 041301.
[6] S. Bethke, H. Pan, B.W. Wessels (1988), Appl. Phys. Lett. 52: 138-142.
[7] A.J.C. Fiddes, K. Durose, A.W. Brinkman, J. Woods, P.D. Coates, A.J. Banister (1996), J. Cryst. Growth 159: 210-213
[8] D.M. Bagnall, Y.F. Chen, Z. Zhu, T. Yao, S. Koyama, M.Y. Shen, T. Goto (1997), Appl. Phys. Lett. 70: 2230-2232.
[9] D. Bao, H. Gu, A. Kuang (1998), Thin Solid Films 312: 37-39.
[10] A. Ashour, M.A. Kaid, N.Z. El-Sayed, A.A. Ibrahim (2006), Appl. Surf. Sci. 252: 7844-7848.
[11] Davood Raoufi, Taha Raoufi (2009) Applied Surface Science 255: 5812-5817.
[12] R. Wahab, S.G. Ansari, Y.S. Kim, H.K. Seo, H.S. Shin (2007), Appl. Surf. Sci. 253 (18): 7622-7625.
[13] R. Wahab, S.G. Ansari, Y.S. Kim, H.K. Seo, G.S. Kim, G. Khang, H.S. Shin (2007), Mater. Res. Bull. 42 (9): 1640-1648.
[14] Rizwan Wahab, Young-Soon Kim, Hyung-Shik Shin(2011), Current Applied Physics 11: 334-340.
[15] S. Komuro, T. Katumata, T. Morikawa,X. Zhao, H. Isshiki, Y. Aoyagi (2000), J. Appl. Phys. 88: 7132-7136.
[16] T. Fukudome, A. Kaminaka,H. Isshiki,R. Saito,S. Yugo,T. Kimura, (2003) Nuclear Instruments and Methods in Physics Research B206: 287 -291.

*****