



STUDIES OF PROPERTIES OF MULTIFUNCTIONAL ZnO THIN FILMS FOR SOLAR CELLS

¹S. S. Kawar, ²V. S. Kalyamwar, ³D. R. Bijwe

¹Assistant Professor, ²Assistant Professor, ³Assistant Professor

¹Department of Physics,

¹Shri. Dr. R. G. Rathod Arts & Science College, Murtizapur, Dist. Akola, India

Abstract : Metal oxides possess a broad range of electronic, chemical, and physical properties that are often highly sensitive to changes in their chemical environment. Many scientists and engineers have studied metal oxide thin films as electronic materials due to their semiconducting behavior, structural simplicity and low cost. Many researchers in the world synthesize the Metal Oxides by different methods like Chemical Vapour deposition, Electrochemical Deposition, Pulsed Laser Deposition, Spray Pyrolysis, Sputtering, Chemical Bath Deposition Technique, etc. The material exhibits different properties depending upon the method utilized for the synthesis. Variety of morphologies, complex structure has been developed by physical or chemical methods. However the work on controlled growth of these films is still in developing state. Therefore in present work we deposited ZnO metal oxide thin films on different substrates by Chemical Bath Deposition Technique and the influence of Microwave annealing on its Structural, Surface Morphology and Optical properties of as deposited films by XRD, SEM, FTIR and UV-VIS Spectrophotometer has been studied. The properties of the materials are determined by the grain size in the materials, the substrate on which the materials are grown, the Band Gap of the materials, the crystal structure of the materials, thickness of the films, stoichiometry of the materials, growth parameters, etc. The band gap indicates the film is transmitting within the visible range and the band gaps changes because of the grain size of the films. We also observed that, the change in preparative parameters affects the deposition rate of thin films. From the observation, it is clear that the growth rate increases as the deposition temperature, deposition time, molarities of the solution increases. It is also clear that the growth rate increases as the film thickness and grain sizes increases while band gap decreases.

Keywords: Metal Oxides; Nanostructures; Photovoltaic Devices; Thin films;

1. Introduction:

Electronic semiconductor devices and Photovoltaic devices are the main applications resulted in a tremendous increase of innovative thin film processing technology. For the improvement of the technology, the materials of different properties and qualities are needed. The synthesis and characterization of various wide band gap metal oxide nanostructures such as nanowires, nanorods, nanobelts, nanobridges and nanowalls has attracted great interest due to their size, morphology-related properties, and their emerging applications in novel functional nanodevices [1,4]. Recently, research and development of alternative energy technologies, such as low cost flat-panel solar cells thin film devices, and many other innovative concepts have increased. Metal Oxides such as ZnO, TiO₂ is an important multifunctional materials which has received great attention during the last few years due to their unique applications in microelectronic and optoelectronic devices, and for self-assembled growth of three-dimensional nanoscale systems [5, 6].

Metal oxide nanostructures have the potential to significantly improve the performance and durability of certain devices used in areas of importance: energy production and homeland security. A key challenge in this research is to deposit nanostructured metal oxide thin films with consistent morphology and reproducible properties with a long-term stability [7-9].

In recent years, various research groups worldwide have devoted its efforts to a variety of synthesis techniques of Metal Oxide thin films viz. Sputtering, Screen Printing, Photochemical Deposition, Spray Pyrolysis, Electrochemical Deposition, Chemical Vapor Deposition, Pulsed Laser Deposition, Vacuum Evaporation, and Chemical Deposition etc.[10-17]. Among them, chemical deposition has attracted our interest for the preparation of nanostructured thin films due to the following advantages: (a) its simplicity and low cost, (b) its capability to achieve large area coatings, (c) its low deposition temperature. These advantages result in a low cost processes that has a reduced environmental impact and a minimum undesirable inter-diffusion of components in multilayer structures. The chemical deposition technique is an aqueous-chemical method which involves the hydrolysis of metal ions in solutions, followed by controlled heterogeneous precipitation on a substrate. It is an emerging field of research in the nanostructured thin films area. The desirable properties of the thin film can be reached by the optimization of the process

parameters and post-deposition processing technique. It allows monitoring the size of nano and microparticles, their surface morphology and arrangement on substrate. This technique allows us to generate advanced functional metal oxides nano- and micro-particulate thin films at relatively low temperature from aqueous solution.

Post-deposition annealing process is being guided largely by the requirements of defects removal and electrical conductivity in metal oxide thin films. Recently, microwave-based rapid annealing systems have been introduced as an alternative thermal annealing equipment solution. The properties of the metal oxide films, especially the structural electrical and Optical ones, can be improved by proper post-deposition rapid microwave processing. Rapid microwave processing is based on rapid radiative heating and cooling of substrates in vacuum or in the presence of inert atmosphere [18-20].

Therefore in present work we deposited ZnO metal oxide thin films on different substrates by Chemical Bath Deposition Technique and the influence of Microwave annealing on its Structural, Surface Morphology and Optical properties of as deposited films by XRD, SEM, FTIR and UV-VIS Spectrophotometer has been studied. We also studied the influence of the change in preparative parameters on the deposition rate of thin films.

2. Material and Methods:

To prepare Metal Oxide films, aqueous solutions of Zinc Source and Thiourea with calculated proportion was added in 130 ml of de-ionized water. Complexing agent ammonia was added slowly to adjust the pH of the solution. The solution was stirred and transferred to another container containing substrate. The resulting solution was kept at $70 \pm 2^\circ\text{C}$ for 1 hour. The substrate used is commercial glass slide. Cleaning of substrate is important in fabrication of thin films, cleaning steps and growth procedure is reported elsewhere [29]. After 20-30 minutes the bath solution in beaker turned whitish, thus indicating the onset ZnS deposition on the glass slide. After a reaction time of 1 hour the glass slides were taken out and dried in air for 15 minutes. Then for the post annealing treatment the as deposited films were kept in Microwave Oven for one hour at 300 watts and then reduced down to room temperature. The ZnS films get oxidized in the oven to form thin films of ZnO.

The crystallographic structure of films were analyzed with x-ray diffractometer (EXPERT-PRO) by using Cu-K α lines ($\lambda = 1.542\text{\AA}$). The average grain size in the fabricated films was obtained from a Debye-Scherrer's formula. Surface morphology was examined by JEOL model JSM-6400 scanning electron microscope (SEM) and it was used to capture the SEM images at different magnifications. The optical transmission spectra for a range of samples were obtained in UV-VIS-NIR region using Perkin-Elmer UV-VIS lambda-35 spectrometer. [21]

3. Results and Discussion:

3.1. XRD Studies:

Figure 1. shows the X-ray diffraction pattern of ZnO thin films obtained from post annealing Microwave treatment over ZnS films at various temperatures. The XRD pattern confirms that the ZnS films get oxidized in the oven to form ZnO thin films. It was found that cubic structured ZnS is completely oxidized at Microwave annealing temperature to form a hexagonal ZnO. The film shows reflections from (100), (002) and (101) planes, indicating the formation of ZnO nano particles having pure hexagonal structure (matches with JCPDF data).

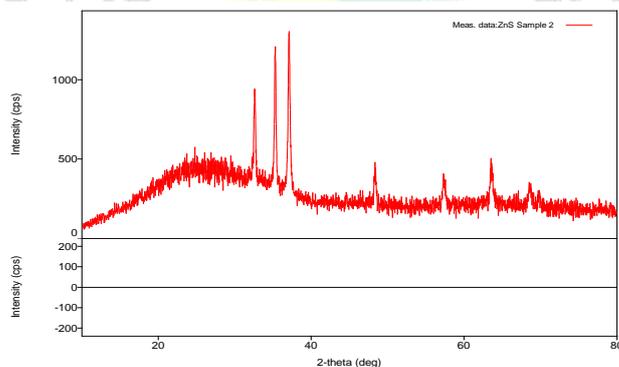


Figure 1: XRD patterns of ZnO thin films fabricated at different Temperatures.

The average size of grain (g) have been obtained from the XRD patterns using Debye-Scherrer's formula, [22-24]

$$g = K\lambda / \beta \cos\theta \quad (1)$$

Where,

K = constant taken to be 0.94, λ = wavelength of X-ray used (1.542 \AA), β = FWHM of the peak and θ = Bragg's angle. The grain sizes were found to be within the range from 16 to 157nm. This confirms the good crystallinity of the samples.

3.2. Surface Morphology Studies:

The surface morphology of deposited ZnO thin films were investigated by SEM at different magnifications as shown in Figure 2. The deposits are compact, pinhole free with spherical grains from few nanometers up to clusters of 157 nm and the films are well covered on the substrate. From the figure, it is observed that the small nanosized grains engaged in a fibrous- like structure and nanoribbons which clearly indicates the nanocrystalline nature along with some amorphous phase of ZnO thin films. The average grain size of the nanoparticles is about 130 nm. [25-27].

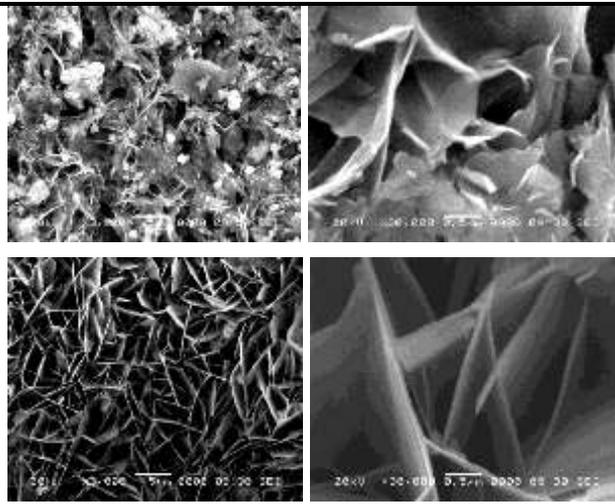


Figure 2. Scanning Electron Micrograph of as deposited ZnO thin film at different magnification.

3.3 Optical Studies:

The optical energy band gap (E_g) was determined by plotting $(\alpha h\nu)^2$ versus ' $h\nu$ ' at different annealing temperature and thickness and then extrapolating the straight line portion to the energy axis at $\alpha = 0$ (Figure 3.1). It was observed that the band gap of the film obtained at higher annealing temperature is 3.3eV [28, 29].

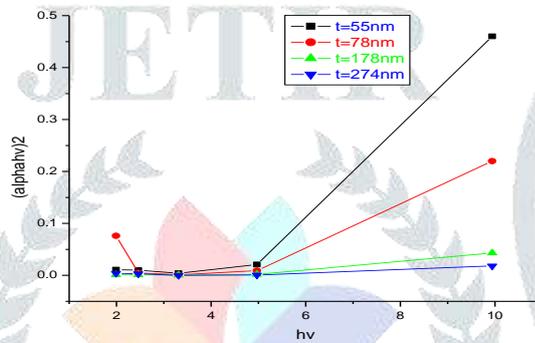


Figure 12 Graph between $(\alpha h\nu)^2$ versus $h\nu$

.Figure 3.1 Plot of $(\alpha h\nu)^2$ vs $h\nu$ for ZnO thin films fabricated at different temperature.

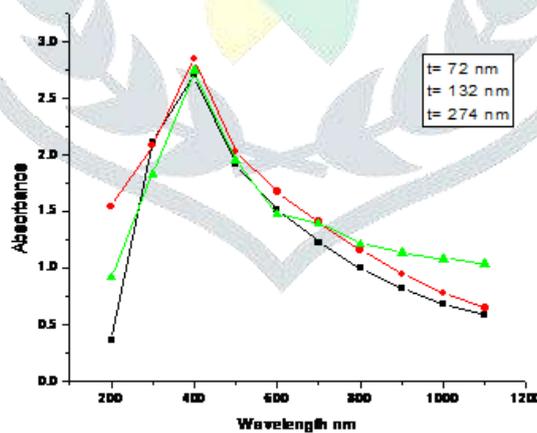


Figure 3.2 Absorption spectrum of ZnO thin films at different annealing temperature and thickness.

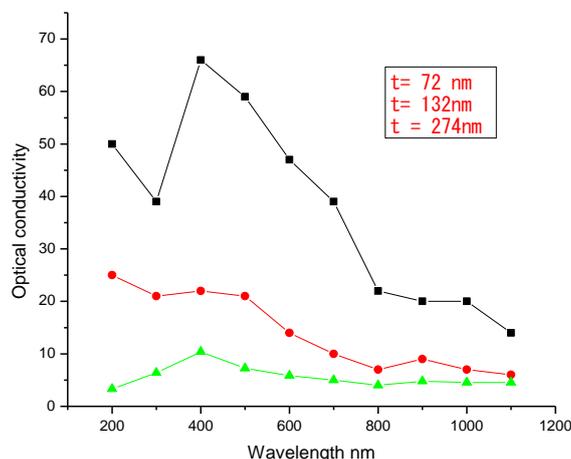


Figure 3.3 Optical Conductivity of ZnO thin films at different Wavelength and thickness.

Fig. 3.2 shows the absorption spectrum of ZnO nanoparticles at different microwave annealing temperatures and thickness. A typical exciton absorption at 362 nm is observed in the absorption spectrum at different microwave temperature, which is blue shifted with respect to the bulk absorption edge appearing at 380nm at room temperature. It is clear that the absorption edge systematically shifts to the lower wavelength or higher energy with decreasing size of the nanoparticle. This pronounced and systematic shift in the absorption edge is due to the quantum size effect by microwave annealing. Thus the average particle size can be determined from the inflection point in the absorption vs. wavelength spectrum

Fig. 3.3 shows the variation of Optical conductivity for ZnO thin films as a function of Wavelength which using following equation.

$$\sigma = \alpha \eta c / 4 \pi \quad (2)$$

It is clear that, the optical conductivity decreases with increasing wavelength and this can be increase in absorption. so the absorption studies revealed that the fabricated films are very low absorptive at the visible region and is more suitable for the fabrication of solar cells [30-33].

4. Conclusion:

In present work we deposited ZnO metal oxide thin films on different substrates by Chemical Bath Deposition Technique and the influence of Microwave Annealing on its Structural, Surface Morphology and Optical properties of as deposited films by XRD, SEM, FTIR and UV-VIS Spectrophotometer has been studied. The X-ray diffraction analysis showed that film is polycrystalline with pure hexagonal structure. The grain size estimated is in the range of 16 to 157nm. The band gap is also calculated from the equation relating absorption co-efficient to wavelength. The band gap indicates the film is transmitting within the visible range and the band gaps changes because of the grain size of the films. The film has a direct band gap with an optical value of 3.31eV which is in good agreement with the standard value. A typical exciton absorption at 362 nm is observed in the absorption spectrum at different microwave temperature, which is blue shifted with respect to the bulk absorption edge appearing at 380nm at room temperature. It is clear that the absorption edge systematically shifts to the lower wavelength or higher energy with decreasing size of the nanoparticle. This pronounced and systematic shift in the absorption edge is due to the quantum size effect by microwave annealing. It is also clear that, the optical conductivity decreases with increasing wavelength and this can be increase in absorption. So the absorption studies revealed that the fabricated films are very low absorptive at the visible region and is more suitable for the fabrication of solar cells

We also observed that, the change in preparative parameters affects the deposition rate of thin films. From the observation, it is clear that the growth rate increases as the deposition temperature, deposition time, molarities of the solution increases. It is also clear that the growth rate increases as the film thickness and grain sizes increases while band gap decreases. This makes the films suitable for various optoelectronic and sensor applications.

References:

- [1] Kraus T, Malaquin L, Schmid H, Riess W, Spencer ND, Wolf H, *Nanoparticle printing with single-particle resolution. Nature Nanotechnol.* 2:570, 2007.
- [2] J. Y. Lao, J. Y. Huang, D. Z. Wang, Z. F. Ren, D. Steeves, B. Kimball, and W. Poter, *Appl. Phys. A Materials Science & Processing*, 78, 539 (2004); P. X. Gao and Z. L. Wang, *Journal of Applied Physics*, 97, 044304, 2005.
- [3] O. K. Varghese and C. A. Grimes, *Journal of Nanoscience and Nanotechnology*, 3, 277, 2003.
- [4] H. J. Fan, W. Lee, R. Scholz, A. Dadgar, A. Krost, K.Nielsch, and M. Zacharias, *Nanotechnology*, 16, 913, 2005.
- [5] Y. Xia, P. Yang, Y. Sun, Y. Wu, B. Mayers, B. Gates, Y. Yin, F. Kim, and H. Yan, *Adv. Mater.* 15, 353, 2003.
- [6] K. Hara, T. Horiguchi, T. Kinoshita, K. Sayama, H. Sugihara, and H. Arakawa, *Sol. Energy Mater. Sol. Cells*, 64, 115, 2000.
- [7] R. Singh, M. Fakhruddin, and K. F. Poole, *Applied Surf. Sci.*, 168, 198, 2000.
- [8] I.Kaur, D.K.Pandya, and K.L.Chopra, *J.Solid - State Science and Technology*, Vol.128 No.4, PP.943-948, 1980.
- [9] R. S. Rusu, G.I.Rusu, *Journal of Optoelectronics and Advanced Materials*, Vol. 7, PP. 823- 828, 2005.
- [10] S. Kuriakose, B. Satpati, S. Mohapatra, *Adv. Mater. Lett.* Vol. 6 No. 3, PP. 217, 2015.

- [11] F. Ahmed, S. Kumar, N. Arshi, M.S. Anwar, R. Prakash, *Adv. Mat. Lett.* Vol. 2 No. 3, PP. 183, 2011.
- [12] R.R. Thankalekshmi, S. Dixit, A.C. Rastogi, *Adv. Mat. Lett.* Vol. 4No.1, PP. 9, 2013.
- [13] Y.K. Mishra, G. Modi, V. Cretu, V. Postica, O. Lupan, T. Reimer, I. Paulowicz, V. Hrkac, W. Benecke, L. Kienle, R. Adelung, *ACS Appl. Mater. Interfaces* Vol. 7, PP.14303, 2015.
- [14] J. Huang, Z. Yin, Q. Zheng, *Energy Environ. Sci.* Vol. 4, PP. 3861, 2011.
- [15] J.W. Rasmussen, E. Martinez, P. Louka, D.G. Wingett, *Expert Opin. Drug Deliv.* Vol. 7 PP. 1063, 2010.
- [16] S. Dwivedi, R. Wahab, F. Khan, Y.K. Mishra, J. Musarrat, A.A. Al-Khedhairi, *PLoS One* Vol. 9 PP.111289, 2014
- [17] V. Hrkac, L. Kienle, S. Kaps, A. Lotnyk, Y.K. Mishra, U. Schürmann, V. Duppel, B. V. Lotsch, R. Adelung, *J. Appl. Cryst.* Vol. 46, PP. 396, 2013.
- [18] T. Reimer, I. Paulowicz, R. Rooder, S. Kaps, O. Lupan, S. Chemnitz, W. Benecke, C. Ronning, R. Adelung, Y.K. Mishra, *ACS Appl. Mater. Interfaces* Vol. 6,PP. 7806, 2014.
- [19] S. Baskoutas, P. Gabournis, S.N. Yannopoulos, V. Dracopoulos, L. Toth, A. Chrissanthopoulos, N. Bouropoulos, *Mater. Lett.* Vol. 62,PP. 1890, 2008.
- [20] M. Ahmad, C. Pan, Z. Luo, J. Zhu, *J. Phys. Chem. C* Vol. 114, PP. 9308, 2010.
- [21] J. Zhao, L. Wu, J. Zhi, *J. Mater. Chem.* Vol. 18, PP. 2459, 2008.
- [22] K.L. Foo, U. Hashim, K. Muhammad, C.H. Voon, *Nanoscale Res. Lett.* Vol. 9, PP. 429, 2014.
- [23] F.I.Ezema, and P.E.Ugwuoke, *the Pacific J. of science and Technology*, PP. 33-38, 2003.
- [24] M.Ortega, G.Santana, and A.M.Acevedo, *Superficies y Vaico*, Vol. 9,PP. 294- 295, 1999.
- [25] P.A.Radi, A.G.Brito, J.M.Madurro, and N.O.Dantas *Brazilian J. of Physics*, Vol.36, PP.412-414, 2006.
- [26] J.P. Borah and K.C. Sarma, *Acta Physica Polonica A* Vol. 114, No.4, 2008.
- [27] M.Y. Nadeem, Waqas Ahme, *Turk J Phy* Vol. 24, PP. 651,2000.
- [28] Jie Cheng, DongBo Fan, et al, *Semicond. Sci. Technol.* Vol.18, PP. 676, 2003.
- [29] S. S. Kawar, B. H. Pawar, *J. Material science : Mat. Electronics* , Vol. 6, 21, p. 906 – 909, 2010
- [30] B. S. Remadevi, R. Raveendran, A. V. Vaidyan, *Prammana J. Phy.*, Vol. 68, PP. 679,2007.
- [31] G.K. Williamson, W.H. Hall, *Acta Metall.* Vol. 1, PP. 22–31, 1953.
- [32] J.J. Kelly, D. Vanmaekelbergh, in: G. Hodes (Ed.), *Electrochemistry of Nanomaterials*, Wiley- VCH, Weinheim, pp. 103–136, 2001.
- [33] G. Cao, *Nanostructure and Nanomaterials*, first ed., Imperial College Press, London, 2004.

