



THICKNESS DEPENDENT MICROSTRUCTURE, OPTICAL AND PHOTO CONDUCTING PROPERTIES OF ZnO THIN FILMS PREPARED BY SPIN COATING PROCESS

S. Rajesh¹, T. Ganesh² and Francis P. Xavier³

¹-PG & Research Department of Physics, A.M Jain College, Chennai, India

²-PG & Research Department of Physics, Presidency College, Chennai, India

³-L.I.F.E Physics & Loyola ICAM-College of Engineering and Technology, Chennai, India

amjcraj@gmail.com

Received 03-01-2013, revised 21-01-2013, online 23-01-2013

ABSTRACT

ZnO thin films were prepared by sol gel process using spin coating technique. The precursor solution was prepared using Zinc acetate dehydrate, monoethanolamine and 2-methoxy ethanol. Films with thicknesses in the range 56 nm-170 nm were prepared on glass substrates. The thicknesses of the films were determined by Tolanski interferometric method. The XRD results indicate that the crystallite size is maximum and strain is minimum for the film with thickness of 112 nm, indicating better crystallization. The surface morphology studied by SEM shows an increase in the grain size up to a thickness of 112 nm and decreases for further increase in thickness. Optical transmittance showed least transmittance and maximum absorption for 112 nm film. Photo conductivity and photo response was best for the film with thickness of 112 nm.

Keywords: Thin film, sol-gel, thickness, ZnO, structure, optical, conduction

I. INTRODUCTION:

Zinc oxide (ZnO) is a direct and wide band gap (3.37 eV) semiconductor [1]. It has great potential for application due to its large excitonic binding energy of 60 meV at room temperature [2]. As-grown ZnO usually exhibits n-type conductivity ZnO thin films have wide applications in ultraviolet light emitters [3-5], transparent conductors [6-8], gas sensors [9] solar windows [10]. ZnO thin films can be prepared by various methods such as chemical vapour deposition CVD

[11-13], RF sputtering [14-15], spray pyrolysis, thermal vapour deposition [16] and sol-gel process. Sol-gel spin coating method for the preparation of zinc oxide is simple, cheaper and a more effective method to prepare ZnO films for optoelectronic devices. The structural, morphological and photoconducting properties of the ZnO film is influenced by the change in thickness of the film. In this paper, we report how the variation in the thickness of the ZnO thin films formed by spin coating, influences the structural, morphological, photoconducting and photo response properties which is

important for photodetectors and solar cell application.

II. Materials and Methods

In this study undoped ZnO thin films were prepared by sol gel and spin coating methods on glass substrates. The pre cursor solution of undoped ZnO was prepared by sol-gel method using Zinc acetate dihydrate, monoethanolamine (MEA) and 2-methoxy ethanol. All the chemicals were used as purchased without any purification. Zinc acetate dihydrate was first dissolved in a mixture of 2-methoxy ethanol and monoethanolamine at room temperature. The concentration of zinc acetate was 0.5 mol/litre and the molar ratio of monoethanolamine to zinc acetate was kept as 1:1 [17]. A homogenous and clear solution was obtained after stirring the solution for 1 h. Glass substrates were cleaned with acetone, methanol and isopropanol before the deposition of the films. The films were spin coated using spin coating unit SCU 2007 on the glass substrates at 2500 rpm for 20s. After spin coating, the substrates were pre-heated to 623 K for 15 minutes in a furnace to evaporate the excess solvent and to eliminate traces of organic components of the film from the solvent. This heat treatment was done at the rate of 4 K/min. The next coating was done over the film and the above process of heating was done. Films with thicknesses of 56 nm, 84 nm, 112 nm, 146 nm and 170 nm were prepared. The film thickness were determined by Tolanski interferometric method. The coated films were finally annealed to temperature of 773 K. The structural property was measured using.

X-ray diffraction patterns with Bruker AXS D8 model XRD. The surface morphology

was examined by SEM (FESEM FEI quanta) the optical transmittance for films of different thicknesses was measured using CARY5E UV-VIS-NIR spectrophotometer in the wavelength range 300nm-2500 nm. Photo conductivity and photo-response studies were carried for all the films under illumination of conductivity measurement apparatus is shown in fig.1 In this method thin copper wires were used as electrodes which were fixed using silver paint.

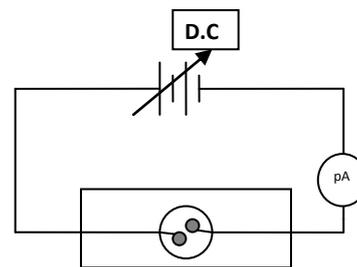


Fig.1: circuit diagram for photo-conductivity.

The distance between the electrodes was maintained at 1mm for all the films. The ends of the wire were connected in series with a DC power supply (0-500V) and a picoammeter (Keithley 6485).

III. RESULTS AND DISCUSSION

III.1 Structural property

Figure 2 Shows XRD pattern for films of different thickness. All the films have preferred orientation along [002] plane in addition to this [100], [101], [102], [110], [103] planes were also observed. The peak corresponding to reflections from powder XRD are in good agreement with the JCPDS data (card No.79002).Williamsons and Hall plot, shown in fig.3 was plotted to eliminate broadening of peaks due to instrumental error and the crystallite size and micro strain was obtained from the graph [18]. The crystallite size decreases as the thickness

increases and reaches a maximum value for 112 nm film, indicating better crystalline quality [19].

From above results the optimum thickness for the film with better crystallization is 112 nm.

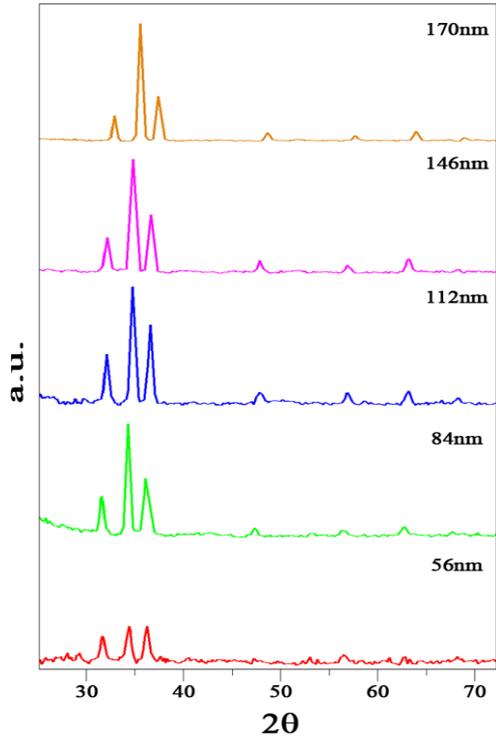


Fig.2: XRD pattern for films of different thicknesses.

The strain is minimum for the 112 nm film and it increases for further increase in thickness. The results are shown in Table 1.

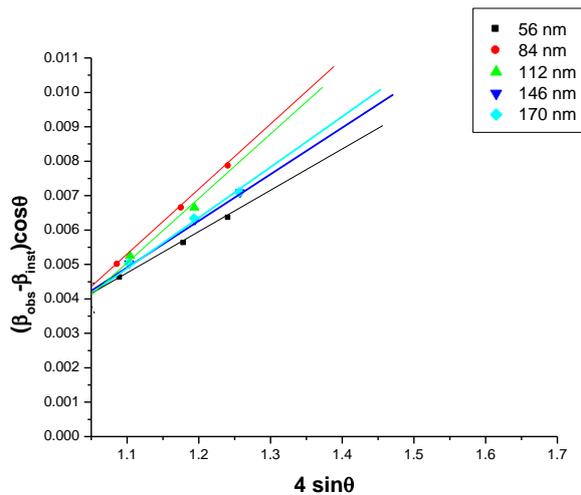


Fig.3: Williamsons-Hall plot for films of different thicknesses.

Table 1: Microstructural parameters for ZnO films of different thicknesses.

Thickness of films (nm)	Crystallite size from XRD (nm)	Micro strain X 10 ⁻³	Dislocation Density X 10 ⁻¹⁵ Lines/m ²	Bond Length
56	35.1	11.29	0.8	1.9440
84	32.3	17.44	0.9	1.9684
112	37	9.66	0.7	1.9804
146	31.6	13.28	1.01	1.9791
170	31	12.73	1.04	1.9837

III.2 Surface morphology

Figure 4 shows the SEM images for films of different thicknesses. All the films are crack free and film of thickness 112 nm shows uniform distribution of grains, which is an indication for good quality film and thereby for conduction of charge carriers.

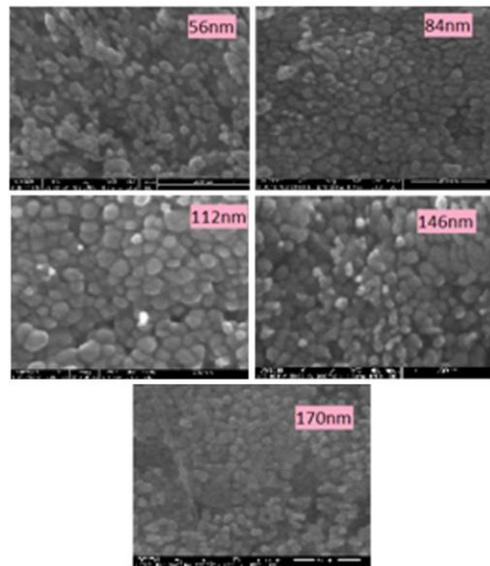


Fig.4: SEM images for films of thicknesses a) 56 nm, b) 84 nm, c) 112 nm, d)146 nm, e)170 nm.

The grain size increases up to 112 nm and decreases for further increase in thickness.

III.3 Optical properties

The optical transmittance for films of various thicknesses in the UV region is shown in fig.5 absorption in the UV region. The transmittance decreases as thickness increases from 56 nm to 112 nm but increases for 142 nm and 170 nm films.

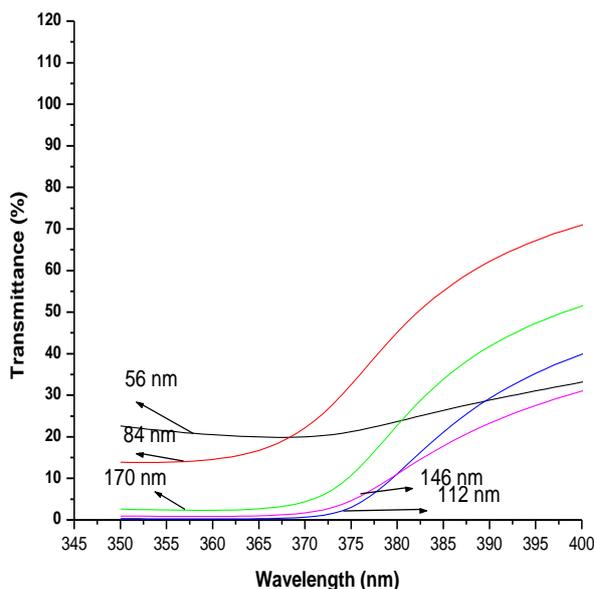


Fig.5: Transmittance for films of different thicknesses.

The increased transmittance for 142 nm and 170 nm thickness films is because of the decrease in the grain size of the films. The decreased transmittance for the 112 nm thickness film is an indication of maximum absorbance which is attributed to the better crystalline quality of the film.

III.4 Photoconductivity

The variation of photoconductivity for films of various thicknesses is shown in fig.6 It is found that the photo current increases as the thickness of the film increases and reaches maximum for film of thickness 112 nm and decreases for further increase in the thickness

of the film. This is due to better surface morphology and crystallization of the films confirmed by XRD and SEM

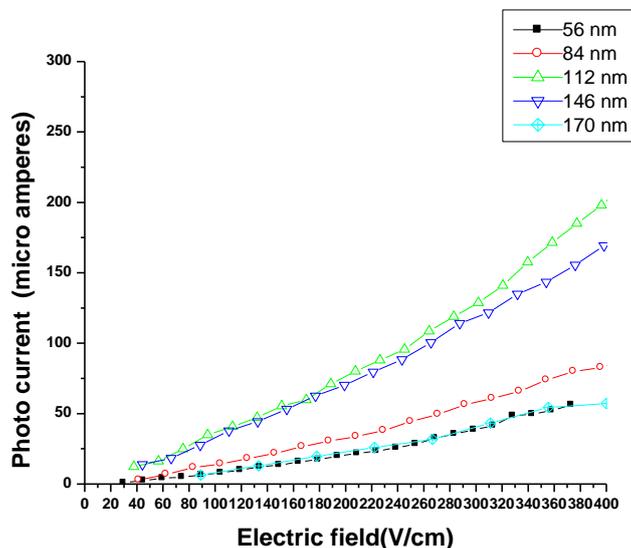


Fig.6: Photo conductivity for films of different thicknesses.

III.5 Photo response

The photo-response for films of different is shown in fig.7 The graph exhibits the exponential time dependence of the current in two different regions following $I=I_0(1-e^{-t/\tau_1})$ and $I=I_0(e^{-t/\tau_2})$, for rise and decay, respectively The rise and decay time are tabulated for different films in Table 2. The slow photo response for all the films is due to absorption and desorption of oxygen on the surface of the films [20-21]. It is found that the film of thickness 112 nm show a quick rise time and significantly larger decay time this is due to optimum grain size and lesser strain of the film [22] This shows the film with 112 nm thickness is more Photo-sensitive compared to other films prepared. From the photo response graph

there is not much change in the response for the film 84nm and 146nm.

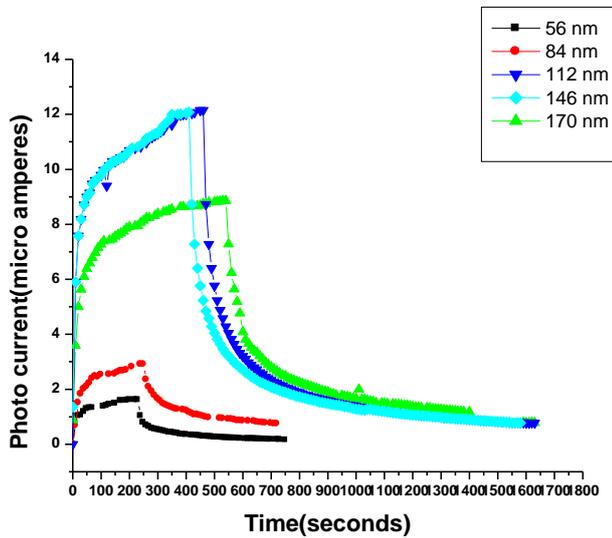


Fig.7: Photo response for ZnO films of different thicknesses.

Table 2: Rise and decay time for films of different thicknesses.

Thickness (nm)	Rise time(s)	Decay time(s)
56	68	113
84	27	270
112	9	101
146	16	105
170	28	169

IV. CONCLUSION

ZnO thin films of thicknesses 56nm, 84nm, 112 nm, 146 nm, 170 nm were coated. Film

of thickness 112 nm shows better crystallization and surface morphology. The photoconductivity was found to be maximum for film of thickness 112 nm. Photo response study of the films indicates a lower rise time value for 112 nm film making it suitable for photo diode devices.

References

[1] M.H.Yuang, Y.Wu, H.Feick, N.Tran, E.Weber and P.Yang, "Catalytic growth of zinc oxide nano wires by vapor transport", *Adv. Mater.*, **13**, 113 (2001).

[2] C.Klingshim. "The Luminescence of ZnO under one and two quantum excitation", *Phys. Status Solidi B* **71**, 547 (1975).

[3] D.m.Bagnall, Y.F.Chen, Z.Zhu, T.Yao, S.Koyama, M.Y.Shen, T.Goto, "Optically pumped lasing of ZnO at room temperature", *Appl. Phys. .Lett.*, **70**, 2230 (1997).

[4] Z.K.Tang, G.K.Wong, P.Yu, M.Kawasaki, A.Ohtomo, H.Koinuma, Y.Segawa, "Room temperature ultraviolet laser emission from self assembled ZnO microcrystallite thin films", *Appl. Phys. Lett.*, **72**, 3270 (1998).

[5] D.M.Bagnall, Y.F.Chen, Z.Zhu, T Yao, M.Y.Shen, T.Goto, "High temperature excitonic stimulated emission from ZnO", *Appl. Phys. Lett.*, **73**, 1038 (1998).

[6] M.K.Jayaraj, A.Antony, M.Ramchandran "Transparent conducting Zinc oxide thin films prepared by off-axis rf magnetron sputtering", *Bull. Mater. .Sci.* **25**, 227 (2002).

[7] E.Fortunato, P.Barquinha, A.Pimentel, A.Goncalves, A.Marques, L.Periera, R.Martins, "Influence of post annealing temperature on the properties exhibited by ITO, IZO and GZO", *Thin Solid Films*", **515**, 8652 (2007).

[8] T.Minami, H.Nanto, S.Takata, "Optical properties of Aluminium doped ZnO thin films", *Thin Solid Films* **124**, 43 (1985)

[9] S.Devi, V.B.Subrahmanyam, S.C.Gadkari, S.K.Gupta, "NH₃ sensing properties of nanocrystalline ZnO based thick films", *An. Chem. Acta* **568**, 41 (2006).

[10] W.J.Jeong, S.K.Kim, G.C.Park, "Preparation and characteristics of ZnO thin films with high and low resistivity for an application of solar cell", *Thin Solid Films* **164**, 381 (1998).

- [11] M.Kasuga, M.Mochizuki," Orientation relationships of zinc oxide on sapphire in heteroepitaxial chemical vapor deposition" J. Cryst. Growth **54**,185 (1981).
- [12] S.K.Ghandhi, R.J.Field, J.R.Shealy, "Highly oriented zinc oxide films grown by the oxidation of diethyl zinc", Appl. Phys. Lett **37**, 449 (1980).
- [13] T.M.Barnes, J.Leaf, C.Fry, C.A.Wolden, "Room temperature chemical vapor deposition of c-axis ZnO", J. Cryst. Growth **274**, 412 (2005) .
- [14] Y.Zhou, P.J.Kelly, A.Poshill, O.A.Zeid,A. A.Alamjjar," The characteristics of aluminium doped zinc oxide films prepared by pulsed magnetron sputtering from powder targets", Thin Solid Films **447**, 33 (2004).
- [15] E.G.Fu,D.M.Zhuang,G.Zhang, Z.Ming, W.F.Yang, J.J.Liu, "Properties of transparent conductive ZnO:Al thin films prepared by magnetron sputtering", Micro. Electr. J. **35**, 383 (2004).
- [16] Farzana Chowdhury," Influence of thickness variation on the optical properties of ZnO thin films prepared by thermal evaporation method", J. Elect. Dev., **10**, 448 (2011).
- [17] G.Srinivasan, J.Kumar," Optical and structural characterization of zinc oxide thin films prepared by sol gel process", Cryst. Res. Technol, **41**, 893 (2006)
- [18] G. K. Williamson and W. H. Hall, "X-ray line broadening from filed Aluminium and Wolfram", Acta. Metal. **1**, 22 (1953).
- [19] M.F.A.Alias,H.Kh.Alamy, R.M.Alijarrah,'The role on the structural and electrical properties of DC magnetron sputtered Nano ZnO thin films', J. Elect. Dev., **14**, 1178 (2012).
- [20] S.Mridha, D.Basak, "Effect of thickness on the structural electrical and optical properties of ZnO films", Mat. Res. Bullt., **42**, 875 (2007).
- [21] S. E. Ahn, H. J. Ji, K. Kim, G. T. Kim, C. H. Bae, S. M. Park, Y. K. Kim,and J. S. Ha, "Origin of the slow photo response in an individual sol-gel synthesized ZnO nanowire", Appl. Phys. Lett. **90**, 153106 (2007).
- [22] S.Mridha, D.Basak," Thickness dependent photo conducting properties of ZnO films" Chem. Phy. Letters, **427**, 62 (2006).