Effect of Temperature on Structural, Morphological and Optical Properties of ZnO Thin Films Deposited by Spray Pyrolysis Technique

Satish Kumar Verma*, B. Das# and C. K. Dixit*

*Department of Physics, DSMNRU, Lucknow, Uttar Pradesh, India
#Department of Physics, University of Lucknow, Lucknow, Uttar Pradesh, India

***Abstract-* The Pure zinc oxide (ZnO) thin films of different substrate temperature have been prepared on well cleaned glass substrate by improved spray pyrolysis technique. The gross structure of the annealed films have been examined by X- ray diffraction (XRD) technique using powder X- ray diffractometer which reveals the enhancement of crystallinity with increase in the deposition temperature. Surface morphology of the synthesized ZnO thin films have been analyzed by means of atomic force microscopy (AFM) which reveals average particle size of as synthesize ZnO thin films has been found to be 79 nm. The band gap as deposited ZnO have been examined by UV-Vis spectroscopy carried out in absorption mode by Double Beam UV- VIS Spectrophotometer with radiations in the range of λ= 190 nm to 1100 nm which is in the range of 3.03 eV to 3.16 eV.**

***Key Words:* ZnO nano particals, XRD, AFM, UV-VIS.**

I. INTRODUCTION

ZnO is a fascinating n-type metal oxide semiconductor material has hexagonal structure with a wide direct energy band gap of about 3.37eV at room temperature [1]. It has found number of applications such as surface acoustic wave devices [2], piezoelectric devices [3], gas sensors [4], solar photovoltaic cell [5], electrode material, light emitting diodes, laser diode [6,7]. Our aim towards fulfill the demand of energy through cheapest, best available and environment friendly sources such as Sun. To convert solar energy in to electrical energy solar cell is needed. A best cost effective solar cell fabricated through the cheapest semiconductor material, for the same we have chosen ZnO semiconductor material. In present work we have deposited thin films of ZnO with different substrate (deposition) temperature by spray pyrolysis technique for grow the nanoparticles. Spray pyrolysis technique is the best cost effective needs less consumables technique. The properties of thin films depend on their surface properties, particularly on thickness and surface roughness of that film. Due to the interest related to the specific properties of metal oxide thin films, present study is focused in the correlation of surface with deposition parameters and physical properties. The number of deposition techniques had been applied for deposition of ZnO thin films in order to found their best properties [8-17].

II. EXPERIMENTAL DETAILS

The number of thin films of pure ZnO was synthesized by spray pyrolysis method. Zinc acetate dihydrate $Zn(CH_3COO)_2.2H_2O$ (Merck, India) with double distilled water was used as precursor solution.

In order to get the 0.5M homogenous transparent solution of $Zn(CH_3COO)_2.2H_2O$,the 2.1949 gm of Zinc acetate dihydrate was dissolved in 20 ml double distilled water and stirred at 60℃ temperature for 2 h. The thin films were deposited on well cleaned microscopic glass (1.0 × 1.0 cm^2) substrates using a commercial nebulizer by spraying the above transparent precursor solution on preheated glass substrate at different substrate temperature (350 ℃, 400 ℃, 450 ℃, 500 ℃) using a resistive heating set-up.During deposition, the solution flow rate was maintained at 0.2 ml/min by the nebulizer. The distance between the spray nozzle and the substrate as well as the spray time was maintained at 3.0 cm and 30 second respectively. The as deposited films (1-10µm thickness) were annealed at 500 ℃ for 1 hour for crystallinity. The as deposited films of ZnO are transparent with faint white tint. The chemical reaction involved is as follows:

$$Zn(CH_3COO)_2.2H_2O + H_2O \xrightarrow{\Delta} ZnO \downarrow + 2CH_4 \uparrow + 2CO_2 \uparrow + 2H_2O$$

III. RESULT and DISCUSSION

A. Structural characterization

The X-ray diffraction pattern was recorded by using powder X-ray diffractometer (Rigaku Ultima IV) at room temperature with monochromatic CuK_α radiation (λ=1.5406 Ǻ) in a wide range of Bragg angle 2θ from 20º to 80º with scanning rate and step of 0.5º min^{-1} and 0.02° respectively. XRD was employed to determine the phase analysis of each thin film deposited at different temperature, annealed at 500℃ as shown in figure 1. It can be seen that at 350℃the Zinc acetate are not completely decomposed. Three peaks (#) are observed due to Zinc acetate and four other peaks due to crystal growth of ZnO, which belong to (100), (002), (101), (110) hexagonal wurtzite phase of ZnO with space group $P6_3mc$ (JCPDS No. 89-1397). When the substrate temperature increases at 400℃only one peak (#) found due to Zinc acetatebut this peak completely disappear when substrate temperature increase to 450℃The crystallinity increases on increasing the substrate temperature up to 500℃The above XRD result shows that the crystallinity increases with increase the substrate temperature. The XRD patterns of all the samples indicated enhanced intensities for the peaks corresponding to (002) plane indicating preferential orientation along the c-axis. The Crystallite size of all deposited thin films ware calculated by Debye Scherer's formula [18]:

$$D = \frac{0.94\lambda}{\beta cos\theta} \quad \text{……….. (1)}$$

Where D, θ and $\boldsymbol{\lambda}$ are the mean crystallite size, Bragg angle and wavelength of incident x-ray (λ=1.5406 Å).

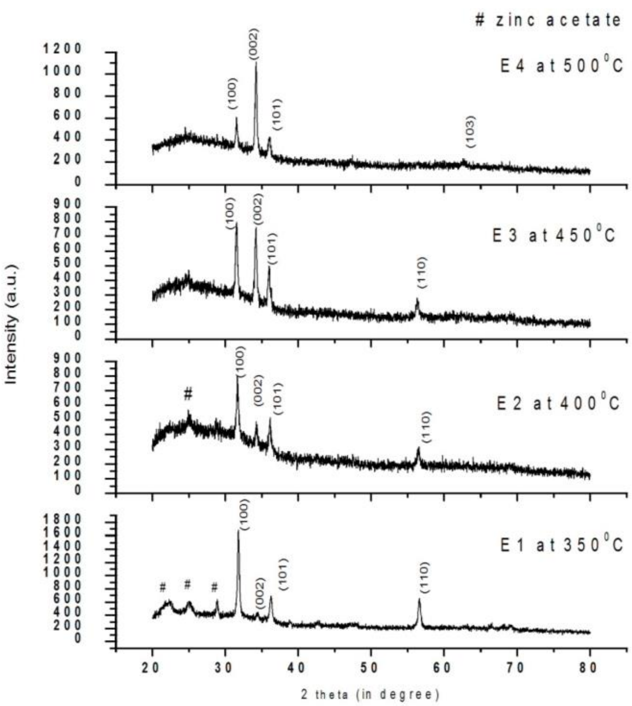


Figure 1. XRD spectra for pure ZnO thin films deposited at (E1) 350℃(E2) 400℃(E3) 450℃(E4) 500℃ substrate temperature.

The calculation shows that the average crystallites of as grown ZnO thin films at substrate temperature 350℃, 400℃, 450℃, 500℃ are 0.55nm, 0.56nm, 0.53nm, 0.60nm respectively. The lattice constant of unit cell is determined and given in table 1. by the formula for hexagonal structure:

$$\frac{1}{d^2} = \frac{4}{3}\left(\frac{h^2+k^2+l^2}{a^2}\right) + \frac{l^2}{c^2} \quad \text{……………. (2)}$$

Here a=b, d is the interplaner spacing, (h, k, l) are the miller indices and a, b, c are the lattice parameters.

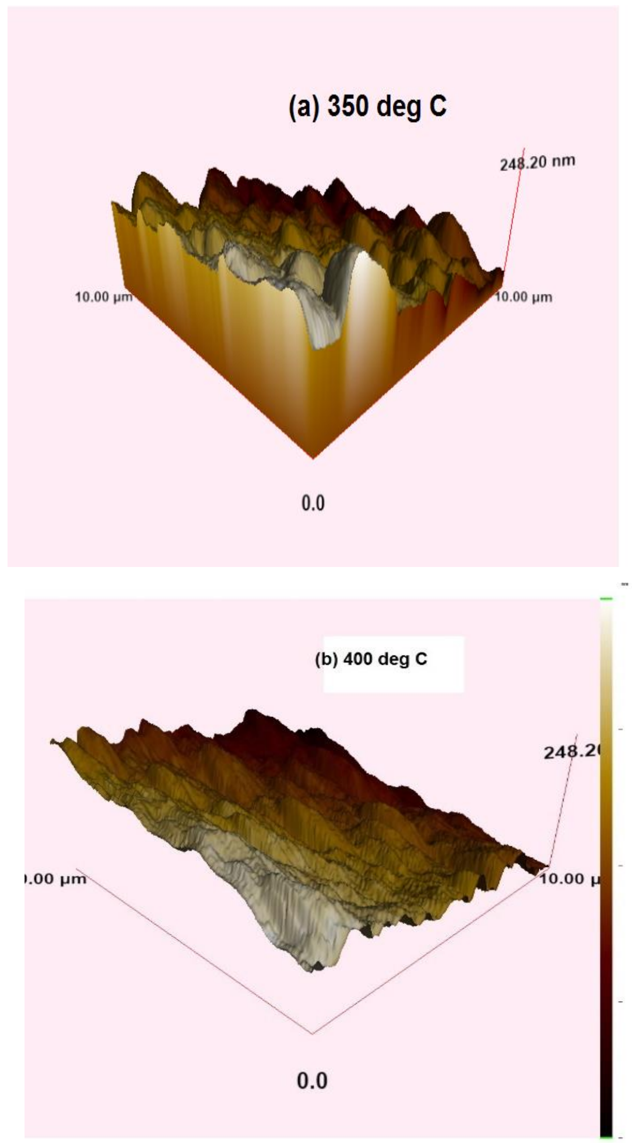
TABLE 1.

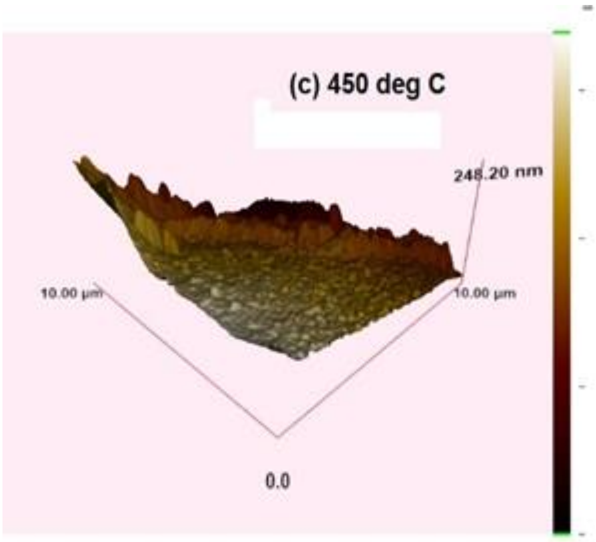
LATTICE PARAMETER FOR UNIT CELL OF ZNO DEPOSITED IN DIFFERENT SUBSTRATE TEMPERATURE.

Substrate temp. (℃)	Interplaner spacing d (A°)	a= b (nm)	c (nm)
350	1.62371	0.32474	0.52033
400	1.62476	0.32495	0.52663
450	1.63217	0.32643	0.52715
500	2.48333	0.32586	0.52277

B. Surface morphology

The surface morphology and roughness of pure ZnO thin films were explored with the help of Atomic Force Microscope (AFM) (Nano magnetics).Since the atomic force microscopic technique is powerful methods for providing the information about the surface morphology (e.g. porosity, cracks, roughness, size, and orientation of grains etc.) of as synthesized pure ZnO thin films deposited at different substrate temperatures.





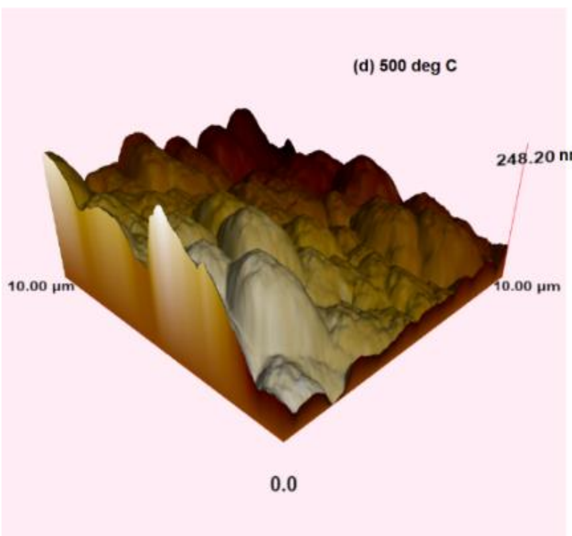


Figure 2. AFM image of pure ZnO Thin films deposited at different substrate temperatures (a) 350℃, (b) 400℃, (c) 450℃ and (d) 500℃.

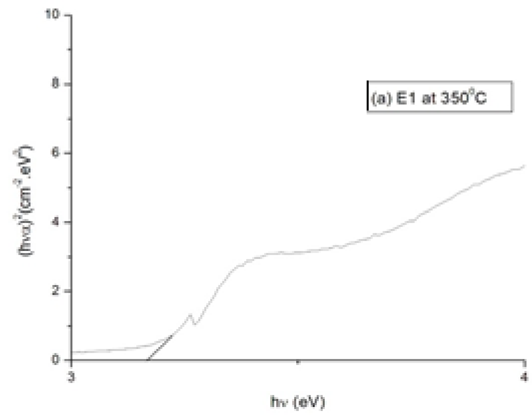
The studies of thin film surface morphologies were carried out by using atomic force microscopy measurement. All thin films were scanned at several different locations on the film surface.

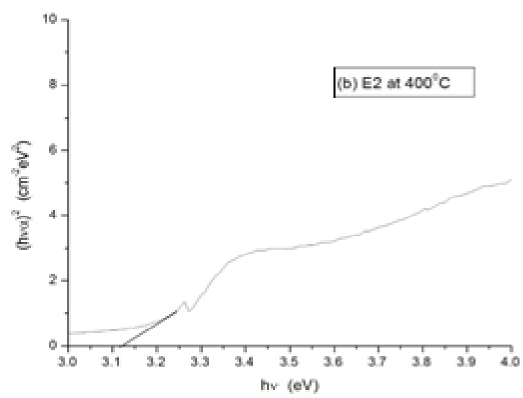
TABLE 2

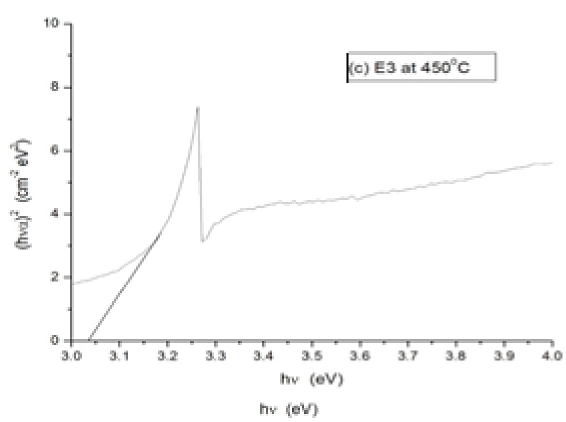
CRYSTALLITE SIZE, PARTICLE SIZE AND ROUGHNESS OF THE PURE ZNO THIN FILMS

Substrate Temperature ℃	Crystallite Size (nm)	Particle Size (nm)	Roughness (nm)
350	0.55	57.01	11.23
400	0.56	70.00	18.25
450	0.53	78.71	19.72
500	0.60	109.00	17.26

Surface morphologies vary significantly among pure ZnO thin films deposited at different substrate temperatures. Figure 2 shows AFM image from those films deposited at different temperatures but at the same initial conditions. They show the effect of substrate temperature on thin film morphology. As the substrate temperature increases particle size also increases. This increase in size of particle is due to the agglomeration of the crystallite. As the temperature increases more and more crystallite agglomeration takes place which result the increased of the size of the particle as clear in table 1 and figure 2. The shape of the particle size is nearly spherical as revealed from the AFM images. The variation of particle size, crystallite size and roughness with annealing temperature are shown in table 2.







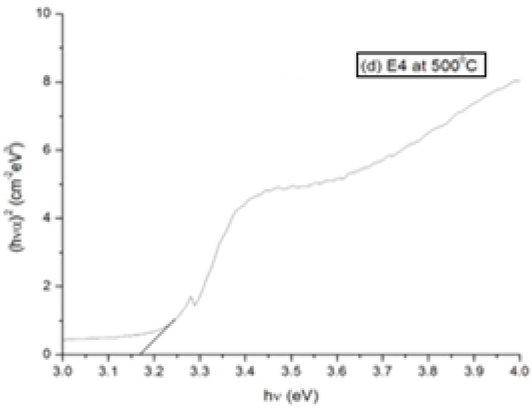


Figure 3. Tauc's plots of ZnO thin films deposited at different substrate temperature (a) 350℃, (b) 400℃, (c) 450℃ and (d) 500℃.

C. Optical Study

The UV-Vis spectroscopy carried out in absorption mode by Double Beam UV- VIS Spectrophotometer with radiations in the range of **λ**= 190 nm to 1100 nm. The energy band gap of deposited thin films, deposited at different substrate temperature 350℃, 400℃, 450℃, 500℃ are 3.16 eV, 3.12 eV, 3.03 eV, 3.16 eV respectively were achievedand shown in Tauc's plots (figure 3). ZnO have wide band gap about 3.3 eV at room temperature. Advantage associated with a large band gap include higher breakdown voltage ability to sustain large electric current lower electronic noise, high temperature and high power operation while those with lower band gap (below 3.3 eV) can be use as absorber layers in solar cells.

IV. Conclusions

Pure ZnO thin films were deposited by spray pyrolysis method at different substrate temperature. At low substrate temperature (350℃) thin film shows the partially decomposition of Zinc acetate into ZnO nanoparticles. The completely decomposition of Zinc acetateand crystallinity achieved at substrate temperature ≥ 450℃. The results of XRD analysis have confirmed the formation of pure ZnO with hexagonal wurtzite structure. The lattice constant of unit cell is determined as a=b=0.32586 nmand c= 0.52277 nm. The crystallite size is calculated to be about 0.56nm. The average particle size of as synthesize ZnO thin films has been found to be 79 nm by AFM. The grains of the pure ZnO thin films are nearly spherical in shape. The deposited thin films of pure ZnO shows a very high crystallite orientation along c-axis. The band gap obtained through absorption mode UV-Visible spectrum is in the range of 3.03 eV to 3.16 eV.

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References

[1]. Mang, et al., *solid state commun*. 94, 251, (1995).
[2]. T. Lamara et al., *Diamond and related materials*, 3, 581, (2004).
[3]. T. M Barnes et al., *Journal of crystal Growth*, 274, 412, (2005).
[4]. J. Q. Xu, etal., *sensors &actualtorsB:chemical*,66, 277,(2000).
[5]. R. Tena-Zaera, A. Katty, S. Bastide, C. Lévy-Clément, B. O'Regan, and V. Muñoz-Sanjosé, *Thin Solid Films* 483, 372 2005.
[6]. S.Y. Lee, E.S. Shim, H.S. Kang, S.S. Pang, *Thin Solid Films*, 473, 31 (2005).
[7]. M.H. Huang, S. Mao, H. Feick, H. Yan, Y. Wu, H. Kind, E. Weber, P. Yang, *Science*, 292, 1897 (2001).
[8]. M. Joseph, H. Tabata, H. Saeki, K. Ueda and T. Kawai, *Physica B: CondensedMatter*, Vol.302-303, 2001, pp. 140-148.
[9]. J. M. Bian, X. M. Li, X. D. Gao, W. D. Yu and L. D. Chen, *Applied Physics Letters*, Vol. 84, No. 4, 2004, p. 541.
[10]. J. M. Bian, X. M. Li, C.Y. Zhang, W. D. Yu and X. D. Gao, *Applied Physics Letters*, Vol. 84, No. 19, 2004, pp. 3783-3785.
[11]. Y. Zhang, X. M. Li, J. M. Bian, W. D. Yu and X. D. Gao, *Solid State Communications*, Vol. 132, No. 2, 2004, pp. 75-78.
[12]. J. F. Rommeluere, L. Svob, F. Jomard, J. Mimila-Arroyo, A. Lusson, V. Salletand Y. Marfaing, *Applied Physics Letters*, Vol. 83, No. 2, 2003, pp. 287-289.
[13]. C. Lin and S. Y. Chen, *Applied Physics Letters*, Vol. 84, No. 24, 2004, pp. 5040-5042.
[14]. K. Minegishi, Y. Koiwai, Y. Kikuchi, K. Yano, M. Kasugaand A. Shimizu. *Japanese Journal of Applied Physics*, Vol. 36(2), No. 11A, 1997, pp. L1453-L1455.
[15]. T. M. Barnes, K. Olson and C. A. Wolden, *Applied Physics Letters*, Vol. 86, No. 11, 2005, Article ID 112112.
[16]. G. K. Paul and S. K. Sen, *Materials Letters*, Vol. 57, No. 3, 2002, pp. 742-746.
[17]. J. M. Bian, X. M. Li, C. Y. Zhang, W. D. Yu and X. D. Gao, *Applied PhysicsLetters*, Vol. 85, No. 18, 2004, pp. 4070-4072.
[18]. Z. R. Khan , et al., Materials science & engineering : B, 174, 145, 2010.