Growth Of ZnO Nanostructured Thin Films By Non-Conventional Sol-Gel Method And The Effect Of Annealing Temperature On Its Properties

M Alrefaee\(^1\), U P Singh\(^2\) and S K Das\(^3\)

\(^1\)Dept. of Physics, School of Applied Sciences, Kalinga Institute Of Industrial Technology Deemed to be University, Bhubaneswar, Odisha, 751024, India.
\(^2\)School of Electronics Engineering, Kalinga Institute of Industrial Technology, Deemed to be University, Bhubaneswar, Odisha, 751024, India.
\(^3\)School of Physics, Gangadhar Meher University, AmrutaVihar, Sambalpur, Odisha, Pin- 768004, India.

\(^*\)Corresponding Author: skdas@gmuniversity.ac.in, skdas.gmu@gmail.com

Abstract: The present work demonstrates the growth of Zinc oxide (ZnO) thin films from its powder precursor by using non-conventional sol-gel technique. The structural, morphological and optical properties of obtained thin films were studied under different annealing temperatures. X-ray diffraction (XRD) analysis confirmed hexagonal wurtzite structures for both annealed and pristine thin films. The crystallite size was found between 14 and 16 nm. Field Emission Scanning Electron Microscope (FESEM) images showed that the films have approximately uniform morphologies, consisting in several flower-like aggregates with nanosized multi petals. From the optical properties it was found that with the increase in the annealing temperature there is an increase in the absorption coefficient in the visible wavelength range. It was also noticed that the increase in annealing temperature caused a decrease in bandgap (E\(_g\)) and increase in Extinction coefficient. Urbach energy decreased with the increase annealing temperature up to 250°C, afterwards the Urbach energy increased with the increase in the annealing temperature. The causes for these observations are discussed.

Key words: ZnO, Sol gel, Thin films, Energy band gap, Absorption coefficient, Urbach energy

1. Introduction:
Zinc oxide is a group II-VI semiconductor. This material has been studied widely in the recent decade because of its special physical, chemical properties such as high optical transparency (band gap 3.2 eV), good electrical conductivity, piezoelectricity, chemical stability and thermal stability etc.[1,2]. These features make ZnO thin films very attractive for different applications like transparent conductors, gas sensors, semiconductor heterojunctions and solar cells [3]. Nowadays, various methods are used to synthesis ZnO thin films such as pulsed laser deposition, spray pyrolysis, sputtering, chemical bath deposition, chemical vapour deposition and sol–gel process [4]. Among them sol-gel is one of the best methods because of its simplicity and cost effectiveness of the required equipments. In all the reported conventional sol-gel works Zinc Acetate, Zinc Nitrate and Zinc Chloride have been taken as precursors. Recently it has been demonstrated that a non-conventional method can be adopted to grow metal oxide nanostructured thin films from its powder precursor. This has been demonstrated
for growth of TiO$_2$ nanostructured thin films [5]. This method has the advantages that the used precursor is extremely chemically and thermally stable. Well control of various characteristics of the grown thin films is another big advantage of this method. In the present work, a similar non-conventional method has been used to grow nanostructured ZnO thin films on glass substrates taking ZnO powder as precursor. Details investigation of effect of annealing temperature on structural, morphological, optical and electronic properties of the grown thin films have been carried out and the result discussed in detail.

2. Experimental details

2.1. Growth of thin films

The growth procedures of ZnO thin films are shown in the flow chart (Figure 1). It consists of three major steps-like preparation of sol-gel, preparation of thin films and annealing the thin films. The details of these steps are given below.

![Flow chart showing the procedure of ZnO thin films preparation](image)

2.1.1. Preparation of sol-gel

For preparation of sol-gel, firstly, 30 ml of sodium hydroxide (NaOH) solution was prepared with concentration 10 mol/L by using distilled water as a solvent, after that 4.883 g of ZnO powder was added to NaOH solution with continuously stirring for 12 hours. In this process, ZnO reacted with NaOH and produced dissolvable sodium zincate (Na$_2$ZnO$_2$). The chemical reaction equations in this process can be written as [6]

$$\text{ZnO(s)} + 2\text{NaOH(aq)} \rightarrow \text{Na}_2\text{ZnO}_2(aq) + \text{H}_2\text{O(l)}$$

(1)

2.1.2. Preparation of thin films:

Dip-coating technique was used to prepare ZnO thin films. For this, first the cleaned glass substrates were immersed in the sodium zincate gel for 1 min, after that dipped in a hot water bath maintained near boiling point for 10 s which leads to break down of the complex and forming a thin layer of ZnO [7].

$$\text{Na}_2\text{ZnO}_2(aq) + \text{H}_2\text{O(l)} \rightarrow \text{ZnO} + 2\text{NaOH(aq)}$$

(2)
A part of ZnO deposited onto the substrate and another part precipitated down in the hot water bath. After depositing, the substrates were dried in an oven at 100 °C for 15 min. To increase the thickness of the thin films the process was repeated up to 10 times.

2.1.3. Annealing of the thin films
The prepared films have been annealed in a furnace at three different temperature 250°, 500° and 750°C for 2 hours in air atmosphere.

2.2. Characterization of the thin films
X-Ray diffraction analysis (XRD) was used to characterize the structure of obtained thin films. The diffraction angle was scanned in the range 20°–80°. A Shimadzu XRD-6100 system was used for this study. Field emission scanning electron microscopy (FESEM) was used to study the surface morphology of the films. A Shimadzu UV-VIS-2450 system was used to study the optical properties of the obtained thin films.

3. Results and discussions

3.1. Structural characterization
XRD analysis results of obtained thin films are presented in Figure 2. This shows 11 diffraction peaks at different 2θ values. The XRD pattern of the sample reveals a number of peaks corresponding to ZnO for (100), (002), (101), (102), (110), (103) (200), (112), (201), (004) and (202) planes. All the peaks had a well match with wurtzite structure of ZnO and have a hexagonal phase. The clear diffraction peaks indicates the crystalline structure of the films.

The XRD further shows that the intensity of the (101) peak for the sample annealed at 750°C is highest. This indicates the highest degree of crystalline orientation for this temperature. This result is found almost same as the case of ZnO thin films grown by conventional method [8-19]. With annealing, the position of the peaks shifts towards higher values of 2θ, this result is same of as what has been observed in conventional solgel process of thin film growth [14, 15, 20].

![Figure 2. The XRD spectra of ZnO thin films](image-url)
3.2. Crystallite size estimation

The crystallite sizes were calculated using Debye-Scherrer formula

\[ D = \frac{0.94 \lambda}{\beta \cos \theta} \]  

(3)

Where, \( D \) is the crystallite size, \( \lambda \) is the wavelength of used X-ray, \( \beta \) is the full width at half maximum (FWHM) of a respective line and \( \theta \) is the Bragg diffraction angle. There are three dominant diffraction peaks (100), (002), and (101); so they were considered for the calculation. The average crystallite sizes of the nanoparticles observed was 14-16 nm for the obtained thin films (Table 1) whereas the average crystallite sizes of ZnO row powder was 153-198 nm(Table 2). It means the crystallite size has been reduced drastically by our process.

Table 1. Average sizes of crystallites corresponding to ZnO thin films.

| Plane | Annealing temperature (°C) | 2θ (deg) | FWHM (deg) | D (nm) |
|-------|-----------------------------|----------|------------|-------|
| (100) | null                        | 31.55    | 0.62       | 14    |
|       | 250                         | 31.56    | 0.54       | 16    |
|       | 500                         | 31.56    | 0.58       | 15    |
|       | 750                         | 31.58    | 0.55       | 16    |
|       | null                        | 34.22    | 0.54       | 16    |
| (002) | 250                         | 34.24    | 0.52       | 17    |
|       | 500                         | 34.25    | 0.54       | 16    |
|       | 750                         | 34.28    | 0.54       | 16    |
|       | null                        | 36.04    | 0.63       | 14    |
| (101) | 250                         | 36.06    | 0.55       | 16    |
|       | 500                         | 36.06    | 0.59       | 15    |
|       | 750                         | 36.08    | 0.57       | 15    |

Table 2. Average sizes of crystallites corresponding to ZnO row powder.

| Plane | 2θ (deg) | FWHM (deg) | D (nm) |
|-------|----------|------------|-------|
| (100) | 31.83    | 0.072      | 153   |
| (002) | 34.49    | 0.060      | 198   |
| (101) | 36.32    | 0.070      | 160   |

3.3 Morphology analysis

The FESEM images of the samples at different magnifications are shown in Figure 3. This shows that films have approximately uniform morphologies, consisting of several flower-like aggregates with nanosized multi petals.
3.4. Optical properties

3.4.1. Absorption coefficient

The absorption coefficient spectra of ZnO thin films (average thickness about 4600 nm) are shown in Figure 4. From this figure it can be noticed that with the increase of the annealing temperature there is increase of absorption coefficient in the visible wavelength rang. This result is similar to the reported result with ZnO thin film grown by conventional method [13].
3.4.2 The band gap
The band gaps of the thin films are obtained from the Tauc plot (Figure 5). The values of the obtained bandgaps are given in Table 3. It can be observed from this Table that for the pristine sample the bandgap is 3.27 eV. This is close to the value of the bandgap reported by others for ZnO [8]. It was also found that the bandgap values decreased with increase in annealing temperature. The lowest value of the bandgap was found to 3.07 eV for the annealing temperature 750°C. Generally with the increase of the annealing temperature the gain size increases. This increase in grain size may have resulted in decrease of the bandgap as it has been found in the ZnO thin films grown by conventional methods [13,16,17].

Table 3. Band gap values of obtained for ZnO thin films annealed at different temperatures

| Annealing temperature (°C) | Band gap (eV) |
|---------------------------|---------------|
| Null (No annealing)       | 3.27          |
| 250                       | 3.20          |
| 500                       | 3.15          |
| 750                       | 3.07          |
3.4.3. Extinction coefficient (K)

Figure 6 shows the extinction coefficient spectra of the grown thin films. It can be noticed from this Figure that the increase in the annealing temperature cause an increase in extinction coefficient in the visible wavelength range. This observation is similar to the reported result with ZnO thin film grown by conventional method[13].

![Figure 6. Extinction coefficient spectra of the ZnO thin films.](image)

3.4.4 Urbach energy

The Urbach energy refers to disorders and presence of defects which occurs during the process of film growth. The Urbach energy describes the transition between the valence band tail to the conduction band edge which can be expressed by

\[
\alpha = \alpha_0 \cdot e^{\left(\frac{h\nu}{E_U}\right)} \tag{4}
\]

Where \( \alpha_0 \) is a constant, \( E_U \) is the Urbach energy.

By taking the logarithm of both sides of equation (4) we get

\[
\ln(\alpha) = \ln(\alpha_0) + \frac{1}{E_U} \cdot h\nu \tag{5}
\]

The plot for the above equation for the obtained ZnO thin films is shown in Figure7.

![Figure 7. Ln(α) against the incident photon energy (hv)](image)

The Urbach energies values obtained from this plot are given in Table 4.
It can be found from this Table that Urbach energy is 0.134 eV for ZnO thin films without annealing. This is almost same as the value obtained by Jannane et. al[23], with the undoped ZnO thin films prepared from Zinc acetate precursor. It is to note that the Urbach energy decreased to 0.109 eV for the films annealed at 250°C. After that, it increased to 0.150 eV and 0.273 eV for films annealed at 500°C and 750°C respectively. These values indicate that there is decrease of the disorder with the increase of the annealing temperature up to 250 °C, after that with increasing the annealing temperature the disorder increased. Formation of oxygen vacancy could one of such disorder. Our observation of higher absorption and extinction coefficient in the visible wavelength range may be arising because of this fact.

3.5. Comparison/significance of the current work over the reported work

From the above discussion it is found that the properties of ZnO thin film prepared from ZnO powder precursor is almost same as what is observed with the conventionally reported work where mostly Zinc acetate and Zinc Nitrate etc. were taken as precursors[8-19]. However unlike the conventional methods, the precursor (ZnO powder) used for our work is extremely chemically and thermally stable. It is to note also that the XRD study indicates that ZnO thin film can also be formed without going for any heat treatment by our reported sol-gel process with ZnO powder as precursor. This is a unique finding of this work as in the convention sol-gel method the ZnO thin film cannot be formed without going for heat treatment. Recently it has been demonstrated that fabrics coated with ZnO can be found to be very useful for the special photocatalysis application [24-26] and Flame-Retardant Coatings [27]. As the thin film reported by us can be grown without giving any heat treatment, so it gives a unique advantage for coating of fabrics for such applications.

Further it is to note that various authors [8-17].have done studies on influence of temperature on the structural, electrical and optical properties of ZnO thin films. However no one has done any systematic study on effect of temperature on the Urbach Energy. Here we did this study systematically and demonstrated that there is an optimize temperature where it is minimum. For our case this temperature is 250°C.

4. Conclusions

This work demonstrates the growth of ZnO thin films from its powder precursor by using non-conventional solgel technique. The structural, morphology and optical parameters were studied for the thin films grown with different annealing temperature 250°C, 500°C and 750°C. The XRD analysis confirmed hexagonal wurtzite structure. The crystalline size was found to be within the range of 14 nm-16 nm. FESEM images showed that the films have approximately uniform morphologies, consisting in several flower-like aggregates with nanosized multi petals. Optical properties showed that increase in annealing temperature cause an increase in the absorption coefficient. It was also found that the increase in annealing temperature caused a decrease in band gap from 3.27 eV to 3.07 eV and increase in Extinction coefficient. Urbach energy decreased from 0.134 eV to 0.109 eV with increase the annealing temperature up to 250°C, afterwards it increased to 0.273 eV with the increase of annealing temperature to 750°C. This non-conventional method has also the advantages that its precursor (ZnO powder) is extremely chemically and thermally stable. It has also the unique advantage that the nanostructured ZnO thin film can be grown without calcinations and hence found to be very useful for applications like second harmonic generation, ultrafast laser pulse diagnostics, chemical sensor, dye sensitized solar cell, photocatalysis etc.
Acknowledgment
SKD acknowledge Department of Science and Technology, Nanomission, Govt. of India (Project File Number: SR/NM/NT-1046/2016 (G)) for the financial support.

References
[1] Marouf S, Beniaiche A, Guessas H and Azizi A 2017 Morphological, Structural, Optical Properties of ZnO Thin Films Deposited by Dip Coating Method Materials Research 20 88 doi: 10.1590/1980-5373-MR-2015-0751
[2] Ilican S, Gorgun K, Aksoy S, Caglar Y and Caglar M 2017 Fabrication of p-Si/n-ZnO:Alheterojunction diode, determination of electrical parameters Journal of Molecular Structure 1156 675 doi: 10.1016/j.molstruc.2017.11.121
[3] Wu GM, Chen YF and Lu HC 2011 Aluminum-Doped Zinc Oxide Thin Films Prepared by Sol-Gel, RF Magnetron Sputtering Acta Physica Polonica in Proc of the 8th Int Conf ION 120 149 doi: 10.12693/PhysPolA.120.149
[4] Zhou H, Yi D, Yu Z, Xiao L and Li J 2007 Preparation Of Aluminum Doped Zinc Oxide Films, The Study Of Their Microstructure, Electrical, Optical Properties Thin Solid Films 515 6909 doi: 10.1016/j.tsf.2007.01.041
[5] Devi M, Panigrahi MR and Singh U P 2015 Microstructures, Optical, Electrical Properties Of TiO2 Thin Films Prepared By Unconventional Sol–Gel Route J Mater Sci: Mater Electron 26 1186 doi: 10.1007/s10854-014-2523-9
[6] Ai-liang C, Dong X, Xing-yu C, X heng L and Xiong ZW 2016 Effect of Calcium On The Solubility Of Zinc Oxide In The Sodium Hydroxide Solution In: Zhang L, Allanore A, Wang C, Yurko J, Crapps J. Materials Processing Fundamentals :Springe Cham 257 doi: 10.1007/978-3-319-48197-5
[7] Mondal S, Kanta K and Mitra P 2013 Preparation Of ZnO Film On P-Si, I-V Characteristics Of P-Si/n ZnO Materials Research,16 94
[8] KUO S,Lai F, Chen W, Cheng C, Kuo H and Wang S 2006 Ultraviolet Lasing of Sol–Gel-Derived Zinc Oxide Polycrystalline Films Jpn. J. Appl. Phys 45 3662 doi: 10.1143/JJAP.45.3662
[9] Sengupta J, Sahoo R, Bardhan K and Mukherjee C 2011 Influence Of Annealing Temperature On The Structural, Topographical And Optical Properties Of Sol–Gel Derived ZnO Thin Films Materials Letters 65 2572 doi: 10.1016/j.matlet.2011.06.021
[10] Sakthivel R, Ganesh A, Geetha A, Anandh B and Kannusamy R 2017 Effect Of Post Annealing On Antibacterial Activity Of ZnO thin Films Prepared by Modified Silar Technique Orient. J. of chem 33 355 doi: 10.13005/ojc/330142
[11] Ping X, Shao-Bo S, Lan L, Xiao-Song Z and Ya-Xin W 2010 Effects of Annealing Temperature on Structural and Optical Properties of ZnO Thin Films Chine. Phys. Lett 27(4) p 1 doi: 10.1088/0256-307X/27/4/047803
[12] Zaier A, Meftah A, Jaber A, Abdelaziz A and Aida M 2015 Annealing Effects On The Structural, Electrical And Optical Properties Of ZnO Thin Films Prepared By Thermal Evaporation Technique Journal of King Saud University – Science 27 356 doi: 10.1016/j.jksus.2015.04.007
[13] Sanjeev S and Kekuda D 2015 Effect Of Annealing Temperature On The Structural , Optical Properties Of Zinc Oxide (ZnO) Thin Films Prepared By Spin Coating Process, in IOP Conf. Series : Materials Science; Engineering 73 012149 doi:10.1088/1757-899X/73/1/012149
[14] Sabeeh S and Jassam R 2010 The Effect Of Annealing Temperature And Al Dopant On Characterization Of ZnO Thin Films Prepared By Sol-Gel Method Results in Physics 18 212 doi: 10.1016/j.rinp.2018.05.033
[15] Farooqi M and Srivastava R 2020 Effect Of Annealing Temperature On Structural, Photoluminescence And Photoconductivity Properties of ZnO Thin Film Deposited on Glass Substrate by Sol–Gel Spin Coating Method Proc. Natl. Acad. Sci., India, Sect. A Phys. Sci 90 845 doi: 10.1007/s40010-019-00648-x
[16] Raji R and Gopchandran K 2017 ZnO Nanostructures With Tunable Visible Luminescence: Effects Of Chemical Reduction And Annealing Journal of Science: Advanced Materials and Devices 2 p 51 doi: 10.1016/j.jsamd.2017.02.002
[17] Zhao M, Sun Z, Zhang Z, Geng X, Wu W, Lien S and Zhu W 2020 Suppression Of Oxygen Vacancy Defects In sALD-ZnO Films Annealed in Different Conditions Materials 13 1 doi: 10.1016/j.jsamd.2017.02.002
[18] Speaks D W 2020 Effect Of Concentration, Aging, And Annealing On Sol Gel ZnO And Al-doped ZnO Thin Films Int Journal of Mechanical and Materials Engineering 15 1 doi: 10.1186/s40712-019-0113-6
[19] Nevárez G, García J, Hernández J, Becerra O, Chen F, Shen Q and Zhang L 2016 Optical And Electrical Properties Of (002) Oriented ZnO Films Prepared On Amorphous Substrates By Sol-Gel Spin-Coating Materials Research 13 113 doi: 10.1590/1980-5373-MR-2016-0808
[20] Kumar V and Kanjilal D 2018 Influence Of Post-Deposition Annealing On Structural, Optical And Transport Properties Of Nanocomposite ZnO-Ag Thin Films Materials Science in Semiconductor Processing 81 22 doi: 10.1016/j.mssp.2018.03.002
[21] Chin H and Chao L 2013 The Effect Of Thermal Annealing Processes On Structural And Photoluminescence Of Zinc Oxide Thin Film Journal of Nanomaterials 1 doi: 10.3390/ma13183910
[22] Enigochitr AS, Ponmani S and Perumal P 2014 Effect of Aluminium Doping On Structural, Optical And Electrical Properties Of Silar Prepared ZnO Thin Films National Conf on Material for Energy Storage and Conversion : Int Journal of Chem Tech Research; 6 5241 doi: 10.1155/2013/424953
[23] Jannane T, Manoua M, Liba A, Fazouan N, El Hichou A, Almaggoussi A, Outzourhit A and Chaik M 2017 Sol-gel Aluminum-doped ZnO Thin Films: Synthesis And Characterization J. Materials, Environ. Sci 8 160
[24] Sudrajat H 2018 Superior Photocatalytic Activity Of Polyester Fabrics Coated With Zinc Oxide From Waste Hot Dipping Zinc Journal of Cleaner Production 172 1722 doi: 10.1016/j.jclepro.2017.12.024
[25] Nourbakhsh S, Montazer, M and khandaghabadi Z 2016 Zinc Oxide Nano Particles Coating On Polyester Fabric Functionalized Through Alkali Treatment Journal of Industrial Textiles 47 1006 doi:10.1177/1528083716657819
[26] Karthik S, Siva P, Balu K, Suriyaprabha R, Rajendran V Rajendran V and Maaza M 2017 Acalypha indica–mediated Green Synthesis Of ZnO Nanostructures Under Differential Thermal Treatment: Effect On Textile Coating, Hydrophobicity, UV Resistance, And Antibacterial Activity Advanced Powder Technology 28 3184 doi: 10.1016/j.apt.2017.09.033
[27] Wang Y, Shen R, Wang Q and Vasquez Y 2018 ZnO Microstructures As Flame-Retardant Coatings On Cotton Fabrics ACS Omega 3 6330 doi:10.1021/acsomega.8b00371