*International Multidisciplinary Innovative Research Journal*
*-An International refereed e-journal*

ISSN: 2456 – 4613
Volume – VII (1)
December - 2022

# PREPARATION AND CHARACTERIZATION OF ZnO THIN FILM WITH VARIOUS ANNEALING TEMPERATURE

[1]Reka Devi M and Yogalakshmi K [2]
[1,2] Assistant Professor(s) of Physics,
V.V.Vanniaperumal College for Women,
Virudhunagar,Tamilnadu.

**Corresponding author: rekadevim@vvvcollege.org**

## ABSTRACT

Transparent conductive zinc oxide films are of great importance due to their applications in various electronic and optoelectronic devices, such as solar cells, gas sensors, varistors and diodes. In this paper the preparation of ZnO thin films using dip coating method on glass substrate with various annealing temperature ranging from 100 ºC to 300 ºC in hot air oven, was discussed. Also, the characterization of prepared ZnO thin films was discussed. XRD and SEM analyses indicate that the 300°C annealing temperature of ZnO thin films illustrates the high crystalline size. From FTIR analysis, different transmittance peaks were observed and it clearly indicates the presence of ZnO.

**Keywords: Dip coating, FTIR, SEM, XRD, ZnO.**

## INTRODUCTION

Zinc Oxide (ZnO) is a group (II–VI) of *n*-type semiconducting material. ZnO has very good properties like high melting point, high thermal capacity, high conductivity and low coefficient of thermal expansion. At room temperature, the ZnO's direct band gap energy ($E_g$) value is 3.36 eV 9 (Kim and Leem 2021), exciton binding energy value is 60 meV and strong cohesive energy value is 1.89 eV. ZnO has low resistivity, expert transparency, high electron mobility of ~2000 $cm^2$/ (Vs) at 80 K and it is used for preparing variety of one–dimensional (1D) nanostructures like nanorods, nanoflakes and nanoneedles (Yu *et al.*, 2020 and Baviskar *et al.*, 2013).

ZnO is one of the most promising materials for the fabrication of next generation opto electronic devices in the UV region. ZnO has lot of probable applications like photo detectors, solar cells, light emitting diodes (LEDs), chemical and biological sensors (Lin *et al.*, 2022), the surface acoustic devices, transparent electrodes and heat mirrors, nanolasers, piezo electric nano–generators, photo–catalyst, Liquid crystal display and flat panel displays (Li Z *et al.* 2012; Otieno 2017 and Nouri *et al.*, 2017).

Different techniques have been used to deposit ZnO thin film in different substrate like spray pyrolysis (Nunes *et at.,* 2001), metal organic chemical vapor deposition (MOCVD), pulsed laser deposition (Lu *et al.*, 2000), magnetron sputtering (Jiang *et al.*, 2003), sol–gel process (dip coating or spin coating) (Lupan *et al.*, 2009 and Balakrishnan *et al.*, 2020), chemical and electro chemical deposition (Khallaf *et al.*, 2009), molecular beam epitaxy (Hacini *et al.,* 2021), electron beam evaporation (Goux *et al.*, 2005) etc.,. Among these techniques, sol–gel process has lot of advantages than other methods like homogeneous coating, low cost of apparatus, used to prepare high quality thin films in easy way and low crystallization temperature. Moreover, in sol–gel process the dip coating method was generally used because it has low cost, environment and eco friendly and easy to make solution and work in low deposition temperature.

The aim of this paper is preparation of ZnO thin films using dip coating method on glass substrate with various annealing temperature ranging from 100 ºC to 300 ºC in hot air oven. The structural and morphological analysis of prepared ZnO thin films was characterized and the results are discussed.

## METHODOLOGY

### Synthesis of ZnO thin film

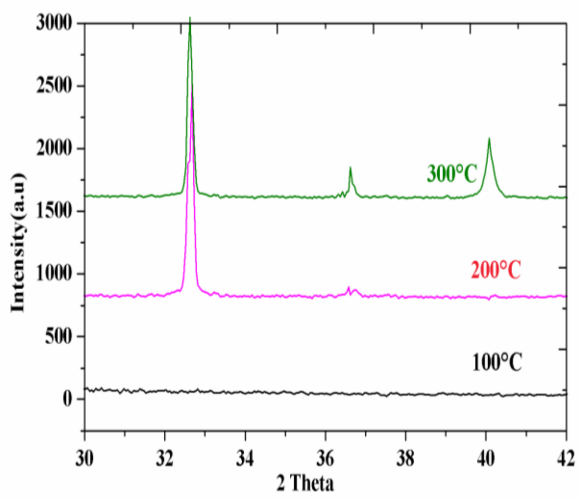
The quantity of 0.1mole of zinc acetate dihydrate solution was dissolved in 100 ml of distilled water and stirred continuously for 1 hr at room temperature. The resulting solution was maintained at a pH value 7.0 by adding 0.1 mole of HCl solution drop by drop. The cleaned glass substrate was first dipped in zinc acetate solution with a with-drawl speed of 1cm/ min and then dipped in hot water solution for the same with-drawl speed. This dipping process was repeated for 50 times. The same procedure was followed for preparing three ZnO thin film samples. Finally, the prepared samples were annealed in hot air oven at three different temperatures like 100, 200 and 300 °C for 1 hr (Kalpana Rajan *et al.*, 2012).

## RESULT AND DISCUSSION

### XRD analysis

The XRD spectra of ZnO thin film annealed at 100°C, 200°C and 300 °C is given in the figure 1. X- ray diffraction (XRD) analysis of ZnO thin film annealed at 100°C exhibits the amorphous nature and no crystalline peaks were observed. At 200 °C annealing temperature of ZnO thin film observed the peaks at 32.5° and small hump peak at 36.5° which indicates the lattice plane at (100) and (101) (Saleh *et al.*, 2012; Khan *et at.*, 2011 and Zaier *et al.*, 2015).

**Fig.1 XRD pattern of ZnO thin film at different annealing temperatures**




The XRD pattern of ZnO thin film annealed at 300 °C produces the diffraction peaks (*2θ*) at 32.7°, 36.6° and 39.8° corresponding to the hkl lattice planes (100), (101) and (102) respectively (JCPDS card No. 00–036–1451).The observed sharp intensity peaks clearly indicate the synthesized ZnO thin film at 300°C has hexagonal wurtzite structure.

The peak intensities are increased with increasing annealing temperature. The maximum intensity peak was observed at 300°C. (Purwaningsih *et al.*, 2020 and Toe *et al.*, 2020). The intensity of the increased peak indicates the highest grain size at 300°C. The values were illustrated in table1.

**Table 1: X–ray diffraction data for ZnO thin film with various annealing**

| Temperature (°C) | 2 *θ* (degree) | hkl | Average grain Size (in nm) | Strain | Dislocation density ($\times 10^{14}$ lines / $m^2$) |
|---|---|---|---|---|---|
| 100 | Amorphous nature | | | | |
| 200 | 32.0<br>36.2 | (100)<br>(101) | 21 | 0.0018 | 22.67 |
| 300 | 32.7<br>36.6<br>39.8 | (100)<br>(101)<br>(102) | 28 | 0.0012 | 12.75 |

### Temperature

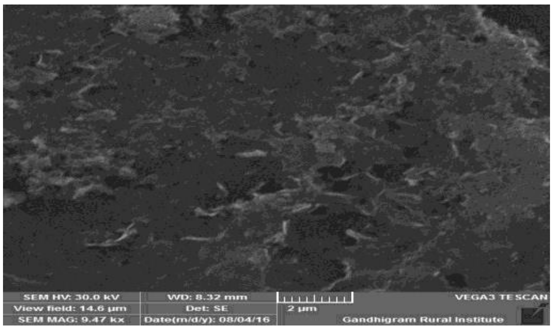
The average grain size (*D*) of the samples was calculated by Debye–Scherer's formula. At high temperature, more energy should be available for the atoms; so that they may diffuse and occupy the correct site in the crystal lattice with lower surface energy, in turn, grow larger in size. This behavior may be attributed due to high annealing temperature that enhances the more energy and mobility. It will cause an improvement in the crystalline quality of ZnO thin film.

Similarly, when increasing the temperature, the strain and dislocation density values were found decreasing. The observed results were illustrated in table 1.The dislocation density value was found at 22.67 for 200°C and 12.75 for 300°C and the strain values were observed at 0.0018 for 200°C and 0.0012 for 300°C. This may be caused due to the decrease in concentration of lattice imperfection. It may be arisen due to lattice misfit in the ZnO thin film and improved the crystalline nature of ZnO thin film (Salim and Amroun 2022)

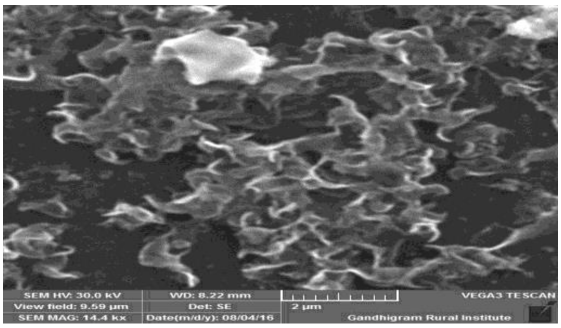
## SEM analysis

**Fig. 2 SEM photographs of ZnO thin film annealed at (a) 100, (b) 200 and (c) 300 ºC**

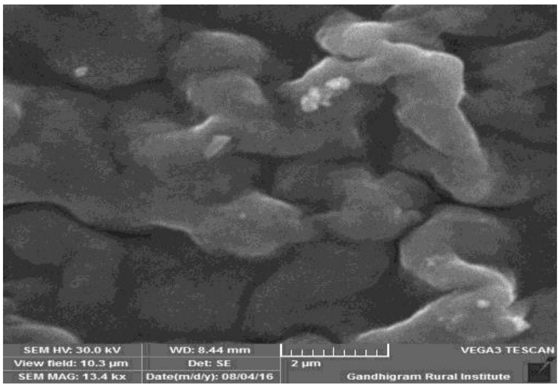
**(a) 100 ºC**




**(b) 200 ºC**



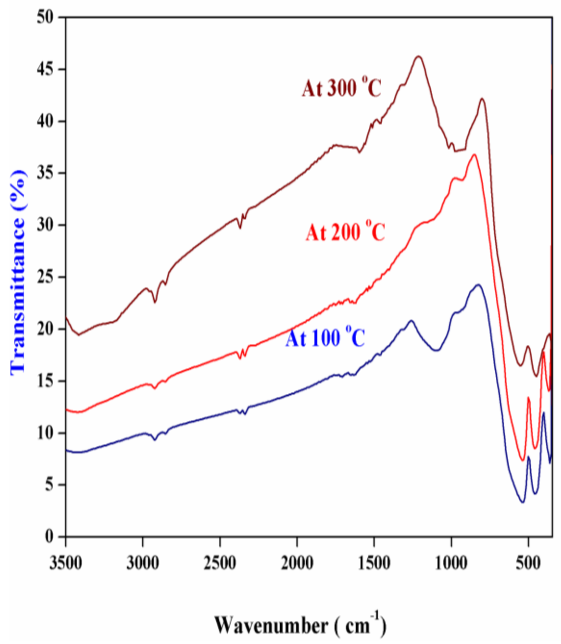

**(c) 300 ºC**




The surface morphology of ZnO thin film annealed at 100, 200 and 300 ºC and their respective SEM photographs have been depicted in figure.2. The surface morphology of ZnO thin film annealed at 100 ºC illustrates that the irregular form of ganglia like hills surface morphology with some cracks was observed. At 200 ºC of ZnO thin film the same ganglia like hills surface morphology was observed with crystalline size of about 23 nm. Similar morphology was observed in 300ºC annealing temperature of ZnO thin film but the cracks were decreased with increasing annealing temperature.

As the crystalline size increases the volume and size of the ganglia like hills also increased. This is caused, when the annealing temperature is increased from 200 ºC to 300 ºC. (Saravanakumar *et al.*, 2014 and Sakthivel *et al.*, 2017). This variations were observed due to increase in diffusion of charges which causes increase crystalline size of the sample at 300 ºC which confirmed from XRD data.

**Fig.3 Fourier Transform Infrared spectra of ZnO thin film at different annealing temperature**




FTIR spectra of ZnO thin film with different annealing temperature as shown in fig.3. At 100,200 and 300°C annealing temperature of ZnO thin film, the peaks were observed at 490 $cm^{-1}$ and 505$cm^{-1}$ which are due to Zn–O zinc oxide bond or oxygen deficiency and stretching vibration mode respectively. In all the films studied, raising the temperature above 200°C, a broad peak observed at 1550$cm^{-1}$(300°C) corresponds to C=O symmetric group. All the samples show a low intense peak at 2450$cm^{-1}$ which attributes to the bending vibrations of O=C=O mode. C-H stretching vibrations of alkane groups was observed at 2950 $cm^{-1}$ in all three annealing temperature of ZnO samples. (Wang *et al.*, 2018 and. Al-Baradi *et al.*, 2020)

**Table 2: Characteristic FTIR peak spectra of ZnO thin film**

| Wave number ($cm^{-1}$) | | | Assignment |
|---|---|---|---|
| 100 °C | 200 °C | 300 °C | |
| 490 | 490 | 490 | Zn–O zinc oxide bond |
| 505 | 505 | 505 | |
| - | - | 1550 | Symmetric C=O group vibration |
| 2450 | 2450 | 2450 | bending vibrations of O=C=O |
| 2950 | 2950 | 2950 | C-H stretching vibrations of alkane groups |

## CONCLUSION

In this paper, the preparation of ZnO thin films at different annealing temperatures like 100, 200 and 300°C using dip coating method was discussed. The prepared thin films were structurally characterized by XRD, SEM and FTIR analysis. XRD and SEM analyses indicate that the 300°C annealing temperature of ZnO thin films illustrate the high crystalline nature with high crystallite size of ganglia like hills surface morphology structure were observed. FTIR study clearly indicates the presence of ZnO samples due to the presence of spectral bonding. It is suggested that this prepared ZnO thin film is the preferable one for a candidate who will opt for optoelectronic applications such as photovoltaic solar cells and diode fabrication.

## REFERENCES

1. Al-Baradi AM, Altowairqi FA, Atta AA, Badawi A, Algarni SA, Almalki ASA, Hassanien AM , Alodhayb A, Kamal AM and El-Nahass MM (2020). Structural and optical characteristic features of RF sputtered CdS/ZnO thin films, *Chin. Phys. B*, 29:080702-1-080702-7.
2. Baviskar PK, Nikam PR, Gargote SS, Ennaoui A and Sankapal BR (2013). Controlled synthesis of ZnO nanostructures with assorted morphologies via simple solution chemistry, *J. Alloys Compd*, 551:233-242.
3. Balakrishnan G, Sinha V, Peethala YP, Kumar M, Golden, Nimal RJ, Hameed J, Batoo KM and Raslan EH (2020). Structural and optical properties of ZnO thin film prepared by sol-gel spin coating, *Materials Science-Poland*, 38:17-22.
4. Goux A, Pauporte T, Chivot J and Lincot D (2005) Temperature effects on ZnO electrode position, *Electrochim. Acta*, 50:2239-2248.
5. Hacini N, Ghamnia M, Dahamni MA, Boukhachem A, Pireaux JJ and Houssiau L (2021) Compositional, Structural, Morphological and Optical Properties of ZnO Thin Films Prepared by PECVD Technique, *Coatings*, 11:202-1-202-11.
6. Jiang X, Wong FL, Fung MK and Lee ST (2003). Aluminum-doped zinc oxide films as transparent conductive electrode for organic light-emitting devices, *Appl.Phys. Lett*, 83:1875-1877.
7. Kalita A and Kalita MPC (2018). Effects of size reduction on microstructural, optical, vibrational, magnetic and photocatalytic properties of ZnO nanocrystals, *Materials Characterization*, 137:109-118
8. Kalpana S, Marimuthu KN and Priya M (2012). Synthesis of Zno Nano Rods by Dip Coating Method, *Arch. Appl. Sci. Res*, 4:1996-2001.
9. Khallaf H, Chai G, Lupan O, Chow L, Park S and Schulte A (2009). Investigation of chemical bath deposition of ZnO thin films using six different complexing agents, *J. Phys. D: Appl. Phys,* 42:135304-135308.
10. Khan ZR, Khan MS, Zulfequar M and Khan MS (2011). Optical and Structural Properties of ZnO Thin Films Fabricated by Sol-Gel

Method, *Materials Sciences and Applications*, 2:340-345

11. Kim D and Leem JM, (2021). Crystallization of ZnO thin films without polymer substrate deformation via thermal dissipation annealing method for next generation wearable devices, *RSC Adv*, 11: 876-882
12. Li Z (2012). Fabrication and morphology dependent magnetic properties of cobalt nanoarrays via template-assisted electrode position, *RSC Advances*, 2:3447–3450.
13. Lin Q, Zhang F, Zhao N and Yang P (2022). Influence of Annealing Temperature on Optical Properties of Sandwiched ZnO/Metal/ZnO Transparent Conductive Thin Films, *Micromachines,* 13:296-1-296-11.
14. Lu F, Ni H Q, Mai ZH and Ren Z N (2000). The effects of thermal annealing on ZnO thin films grown by pulsed laser deposition, *J. Appl. Phys*, 88:498-502.
15. Lupan O, Shishiyanu S, Ursaki V, Khallaf H, Chow L, Shishiyanu T, Sontea V, Monaico E and Railean S (2009). Synthesis of nanostructured Al-doped zinc oxide films on Si for solarcells applications, *Solar Energy Mater. Solar Cell*, 93:1417- 1422.
16. Nouri A, Beniaiche A, Soucase B M, Guessas H and Azizi A (2017). Photoluminescence study of Eu+3 doped ZnO nanocolumns prepared by electrode position method, *Optik-International Journal for Light and Electron Optics*, 139:104–110.
17. Nunes P, Fortunadeo E and Martins R (2001). Influence of the post-treatment on the properties of ZnO thin films, *Thin Solid Films*, 383:277-280.
18. Otieno F (2017). Structural and spectroscopic analysis of ex-situ annealed RF sputtered aluminium doped zinc oxide thin films, *Journal of applied physics*, 122, 075303
19. Purwaningsih SY, Zainuri M, Triwikantoro T, Pratapa S and Darminto D (2020). Structural, Optical and Defect State Analyses of ZnO Nanoparticle Films, *Ije Transactions B: Applications,* 33: 852-860.
20. Salim K and Amroun MN (2022). Study of the effects of annealing Temperature on the properties of ZnO thin films grown by spray pyrolysis Technique for

Photovoltaic applications, *Int. J. Thin. Film. Sci. Tec,* 11:19-28.

21. Sakthivel R, Shankar ganesh A, Geetha A, Anandh BA, Kannusamy R and Tamilselvan K (2017). Effect of Post Annealing on antibacterial activity of ZnO thin Films Prepared by modified Silar Technique, *Orient. J. Chem.*, 33:355-362.
22. Saleh WR, Saeed NM, Twej WA and Alwan M (2012). Synthesis Sol-Gel Derived Highly Transparent ZnO Thin Films for Optoelectronic Applications, *Advances in Materials Physics and Chemistry*, 2:11-16.
23. Saravanakumar M, Agilan S and Muthukumarasamy N (2014). Effect of Annealing Temperature on characterization of ZnO thin films by sol-gel method, *International Journal of Chem Tech Research*, 6:2941-2945.
24. Toe MZ, Matsuda A, Han SS, Yaacob KA and Pung SY (2020). Effect of annealing Temperature on the performance of ZnO Thin Film-based dye Sensitized Solar Cell, *3 rd International Postgraduate Conference on Materials, Minerals & Polymer (MAMIP)*, 020010-1-020010-8.
25. Yu M, Wang G, Zhao R, Liu E and Chen T (2020). Improved interfacial wetability in Cu/ZnO and its role in ZnO/Cu/ZnO sandwiched transparent electrode, *J. Mater. Sci. Techno*l, 37:123–127.
26. Wang J, Yu S and Zhang H (2019). Effect of surfactants on photoluminescence properties of ZnO synthesized by hydrothermal method, *Optik*, 180:20-26.
27. Zaier A, Meftah A, Jaber AY, Abdelaziz AA and Aida MS, (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*, 27:356-360.