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Impact of Annealing on Structural and Optical Properties of ZnO Thin Films by SILAR Method and its Antimicrobial Applications

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***Abstract:** Preparation of Zinc Oxide (ZnO) thin films by modified Chemical Bath Deposition is known as Successive Ionic Layer Adsorption and Reaction (SILAR) method. The structural , optical properties, antibacterial and antifungal activities were studied for different post annealing temperature. X-Ray Diffraction (XRD) pattern confirms the crystalline nature and it exhibits hexagonal structure along with c-axis orientation. Field Emission Scanning Electron Microscope (FESEM) confirms the occurrence of a floral pattern and pinhole-free film. Energy Dispersive X-ray (EDAX) results confirms the existence of zinc and oxygen atoms. Optical properties were examined using UV-Visible spectroscopy. The band gap decreases as the annealing temperature increases from250°C to 450°C. Antibacterial activities against E. coli (Gram-negative) show the maximum zone of inhibition when compared to S.aureus (Gram-positive). Antifungal activities against Aspergillussp were also studied.*
***Keywords:** ZnO, XRD, FESEM, EDAX, Band gap, Antibacterial and antifungal activity*

I. INTRODUCTION

A variety of methods like chemical and physical deposition namely sputtering, pulse laser deposition and so on are used in the preparation of ZnO thin films[1]. Chemical techniques involving aqueous route are much cheaper. In order more commercially pure ZnO films must be prepared by a low temperature deposition technique. A low temperature deposition technology for the growth of ZnO films becomes mandatory because of this reason[2]. Instead of atoms, the basic building blocks are ions in the synthesis of thin films, where the preparative parameters are under control. ZnO thin films are deposited using a SILAR method, which is done by alternate dipping of substrate in the solution and hot deionised water. This method is mainly based on the adsorption and reaction of the ions from the solution and rinsing between every immersion with deionised water to avoid homogeneous precipitation in the solution[3]. The thin films can be grown on copper, silicon and glass substrates. The pros of SILAR technique are fruitfulness and unsophistication of the deposition equipment, controlled deposition rates, wide spectrum of deposition parameters for the control and the optimization of film properties, and film thickness. The process can be carried out on any base of substrate on which an organism does not require high quality target and vacuum at any stage. The thickness and deposition rate is balanced by changing the number of deposition cycles, and it is a low temperature chemical solution method and does not cause local over heating that can be adverse for materials to be deposited[4]. ZnO nanoparticles showcase attractive antibacterial properties due to increased specific surface area as the reduced particle size leading to enhanced particle surface reactivity. ZnO is a bio-safe material that consists of photo-oxidizing and photo catalysis influence on chemical and biological species. ZnO nanoparticles are said to be a non-toxic to human cells in lot of studies.[5]. That is why it is used as an antibacterial agent, noxious to microorganisms, and hold good biocompatibility to human cells[6]. The various antibacterial mechanisms of nanomaterials are mostly due to their high specific surface area-to-volume ratios[7], and their distinctive physico-chemical properties. However, the exert mechanisms are yet under debate, although several proposed ones are in choice and adopted. In the present analysis, ZnO thin films are deposited on glass substrate by SILAR technique and the films are post annealed at 250°C, 350°C and 450°C. Optical and Structural properties were analyzed using UV-Visible spectrometer, XRD, EDAX and FESEM. The Antibacterial and antifungal activities were assessed for all the three annealed thin films.

II. MATERIALS AND METHOD

A. Cleaning glass substrate

The glass substrate (75 mm x 25 mm x1.35 mm) is washed with soap water, deionized water and cleaned with acetone in ultrasonic bath. Finally, the substrate is kept in the hot air oven for 5 to 10 minutes.

B. Preparation of thin films

ZnO thin films are prepared on glass substrate by the SILAR technique. Zinc Acetate Dehydrates (ZAD), Ethanol and Monoethanolamine (MEA) were used as a precursor, solvent and stabilizing agent. The concentration of ZAD is 0.1M and Ethanol was 100ml. The concentration of ZAD and MEA was1:1 ratio[8]. The ZAD was dissolved in the mixture of ethanol and MEA and it is stirred for 45 minutes at room temperature and the pH value is neutral. The above complex was taken as a cationic precursor solution. The anionic precursor solution is hot deionised water whose temperature is maintained between 90°C to 100°C. The glass substrate was alternatively dipped in cationic and anionic bath solution for different timings and cycles. The prepared ZnO films were annealed at 250°C, 350°Cand 450°C for one hour.

C. Antibacterial assay

The antibacterial assay was carried out by well diffusion method. Muller Hinton agar was prepared and sterilized. Sterile cotton swab is used on the agar surface during the log phase culture of the test specimens. The thin films were placed in the agar plates and the plates are incubated at 37°C for 24 hours. The incubated plates were tested for the interruption of growth sample. The zone of inhibition was calculated by measuring the diameter of the inhibited growth around the substrate.

D. Assessment of Antifungal Activity

The antifungal activity was carried out by agar diffusion method for ZnO thin films. Potato dextrose agar medium was used and the test organism was Aspergillus sp. Test specimens were taken, and they were cut into pieces according to convenient size (3.8 ± 0.5 cm). The prepared potato dextrose agar medium was dispensed in petridish and the spores of fungi were inoculate into sterile distilled water containing few glass beads and shaken energetically to bring the spores into suspension. 1.0±0.1 ml of inoculums was diffused equally over the surface of the agar. The test specimens were placed in agar medium and were incubated at 27°C. At the end of incubation period, the zone of mycosis underneath and alongside of the film was measured. The incubated plates were tested for interruption of growth of inoculums. The size of the clear zone was measured for evaluation of the inhibitory effect of the test thin films.

E. Thickness Measurement

The thickness of annealed ZnO thin films were calculated by the gravimetric weight difference method[9]in terms of deposited weight of a ZnO film on the glass substrate, per unit area (g/cm^2).It was calculated as

$$T = (w_2 - w_1)/A\rho \qquad (1)$$

where 'T' is film thickness, 'w_1' is weight of the glass substrate before coating of the film material in gm.'w_2' is weight of the glass substrate after coating of the film material in gm.'A' is area of the film in cm^2 and ρ is density of the film material ($\rho = 5.61\ g/cm^3$) . Table1 shows the measured thickness of all annealed ZnO thin films.

Table 1 Thickness of annealed ZnO thin films

Annealed temperature of ZnO thin films	Thickness of annealed of ZnO thin films (nm)
250°C	673
350°C	549
450°C	630

III. RESULTS AND DISCUSSION

A. XRD Analysis

ZnO thin films have been developed by SILAR technique at different annealing temperature. The XRD patterns of 250°C,350°C,and 450°C annealed ZnO thin films has peaks corresponding to (100),(002) and (101) planes of ZnO and are shown in figure 1.The peaks in the diffraction pattern indicate that ZnO with hexagonal wurtzite phase has been formed. The intensity of the peaks in the diffraction pattern is simultaneously increase with annealing temperature[10].This shows that grain growth also takes place simultaneously. The film at 450°C, exhibits a strong and intense (002) peak indicating the preferential orientation along the c-axis[11].

The crystalline size is determined using the Scherer's equation[12],

$$D = \frac{0.9\lambda}{\beta cos\theta} \qquad (2)$$

The strain (ε) is found using the relation

$$\varepsilon = \beta \cos\theta/4 \qquad (3)$$

The dislocation density (δ) is calculated using the equation

$$\delta = \frac{1}{D^2} \qquad (4)$$

The lattice constants 'a' and 'c' of the annealed ZnO thin films have been calculated and are given in Table 2. The values are closes to the standard JCPDS values (JCPDS card number 36-1451). The strain and dislocation density have been calculated for the annealed ZnO films and they are found to decrease with increase in annealing temperature[13].

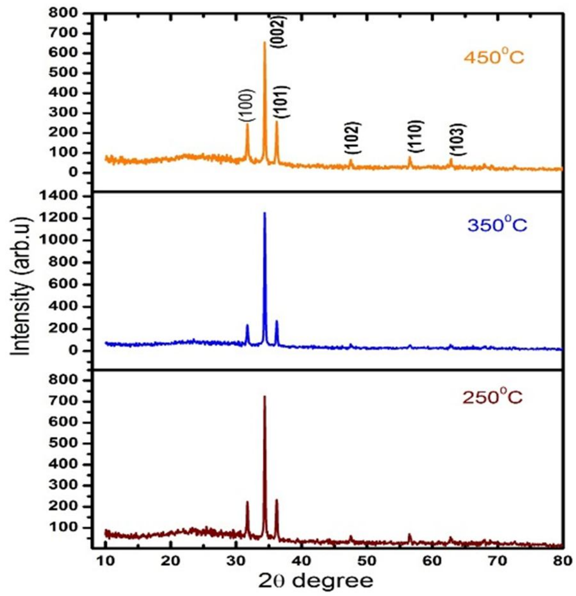


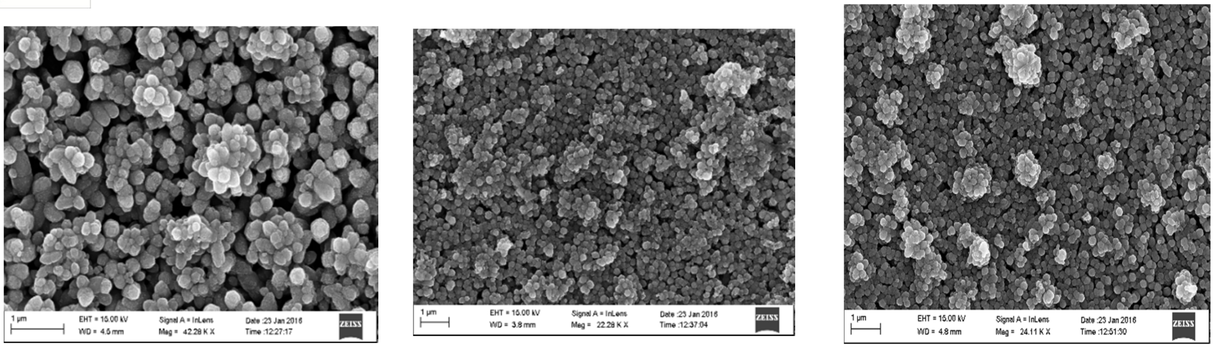
Fig.1 XRD pattern of ZnO thin films annealed at 250°C, 350°C & 450°C

B. *FESEM Analysis with EDAX*

Fig.2 shows the FESEM images of ZnO thin films annealed at250°C, 350°C and 450°C. A floral like structure was found for all the three annealed ZnO thin films. Tightly packed particles were found while increasing the annealing temperature from 250°C to 450°C[14]. FESEM image clearly shows that annealed films were homogeneous and pinhole free throughout the glass substrate.

Table.2 annealing temperature of the ZnO thin film

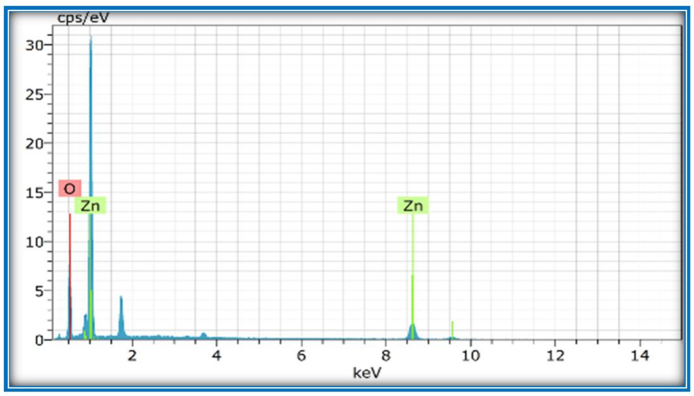
Annealed temperature of ZnO thin Film	2θ	FWHM	Crystalline size (D nm)	Strain(ε)	Dislocation Density (δ)	Lattice constants	
						a	c
250°C	34.5822	0.4483	16.92944749	0.001867	0.00348910	3.236	5.185
350°C	34.6096	0.448	16.93952404	0.001865	0.00348495	3.233	5.181
450°C	34.5903	0.4557	16.65416824	0.001898	0.00360540	3.235	5.183



(A) 250° C (B) 350° C (C) 450° C

Fig .2 FESEM images of ZnO thin films annealed at 250°C, 350°C& 450°C.

The EDAX spectra of the film annealed at 450°C is shown in Figure 3. The presence of Zn and O atoms are observed and the mass % of Zn and O atoms are also tabulated. This confirms that the prepared ZnO films have high quality.



Element	**Mass %**
O	59.29
Zn	40.71

Fig.3EDAX spectra of ZnO thin film

C. Optical Studies

Transmittance spectra of ZnO thin films annealed at 250°C, 350°C and 450°C can be noted in Fig.4. ZnO films that exhibit transparency of about 30% in the areas visible. It was observed that the ZnO films annealed at 450°C has the highest transmittance and the ZnO film annealed at 350°C have lowest transmittance in the areas visible.

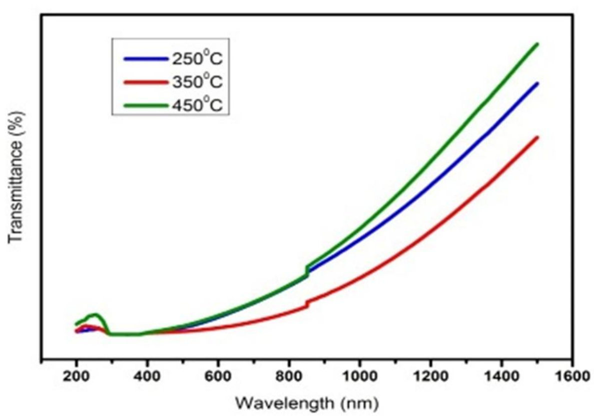


Fig.4 Transmittance spectra of ZnO thin films annealed at250°C, 350°C & 450°C.

The absorption coefficient (α) can be evaluated from the optical transmittance spectra with the use of the relation

$$\alpha = \frac{2.303 log10(\frac{1}{T})}{t} \qquad (5)$$

Where 'T' is the transmittance value at a particular wavelength (nm) and ' t' is the thickness of the thin film.

The probability of transition is identified by the relation

$$(\alpha h\upsilon)^p = A(h\upsilon - Eg) \qquad (6)$$

Where A is a constant, E_g is the energy gap, υ is the frequency of incident radiation and h is the Planck's constant. The exponent p is the number which gives an identity to the transition process, p = 2 for directly allowed transitions.

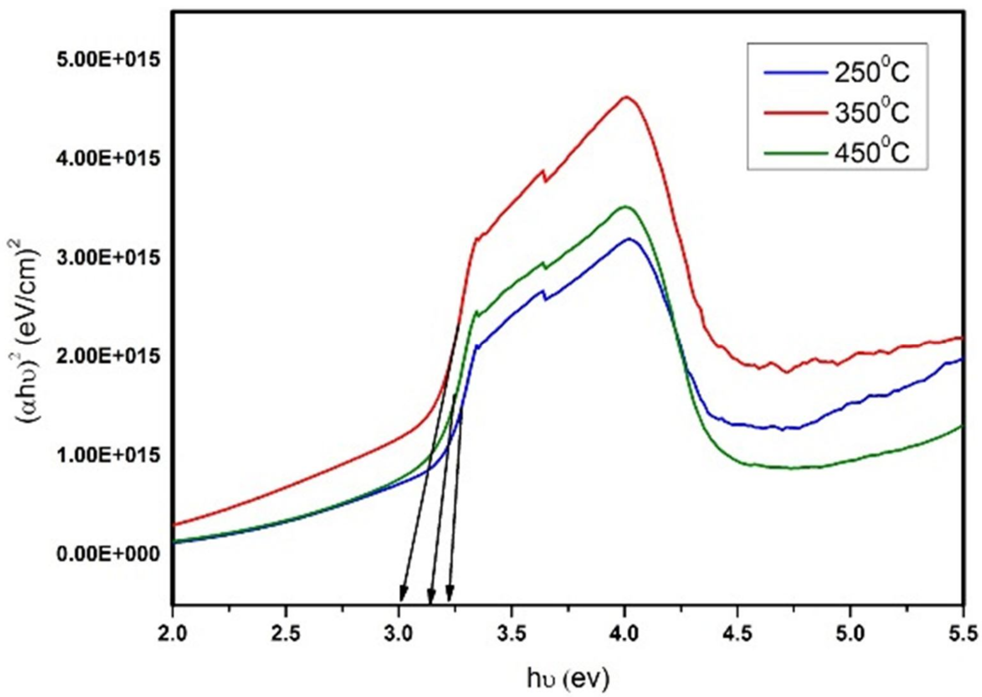


Fig.5plotsof $(\alpha h\nu)^2$vs hυ of ZnO thin film annealed at250°C, 350°C & 450°C.

Fig. 5 showed that the plot of $(\alpha h\nu)^2$ versus (hν), indicates the direct band gap nature of the films. The optical band gap energy was found as 3.22 eV for 250°C, 3.05eV for 350°C and 3.14eV for 450°C[15].

D. Antibacterial studies

Fig.6 shows the antibacterial activity of ZnO thin films annealed at 250°C, 350°C and 450°C. The maximum zone of inhibition against E.coli was observed in ZnO film annealed at 350°C of about 13mm and S.aureus of about 9mm annealed at 250°C. Then, suspensions with different concentrations were prepared to test antibacterial activity in liquid nutrient broth. The films exhibit the best antibacterial activity for both organisms studied which is accepting the fact that antibacterial activity depends on the particle size and particle shape[16] with increase in antibacterial activity observed for decreasing size[17]. The different cell wall is responsible for the variation in activity against these two types of bacteria. Gram-positive bacteria typically have one cytoplasmic membrane and thick wall composed of multilayers of peptidoglycan[18]. Whereas gram-negative bacteria have more complex cell wall structure, with a layer of peptidoglycan between outer membrane and cytoplasmic membrane[19]. That is why the cell membrane of gram-positive bacteria gets easily damaged. In both cases, antibacterial activity of ZnO can be dedicated to the damage of cell membranes, which leads to leakage of cell contents and cell death.

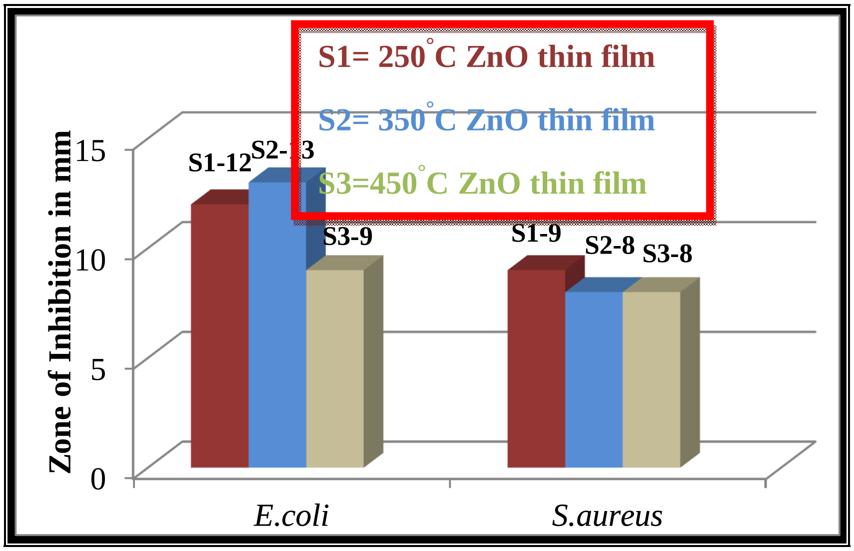


Fig.6 Antibacterial activity of ZnO thin film annealed at 250°C, 350°C & 450°C.

E. Antifungal studies

Antifungal activity against Aspergillussp on ZnO thin films were shown in fig 7. Zone of inhibition for four days incubation was found to be 18 mm, 22 mm and 18 mm for 250º C, 350º C and 450º C annealed ZnO thin films respectively. Antifungal activity of 350º C annealed ZnO thin film was found to be high when comparing to other films.

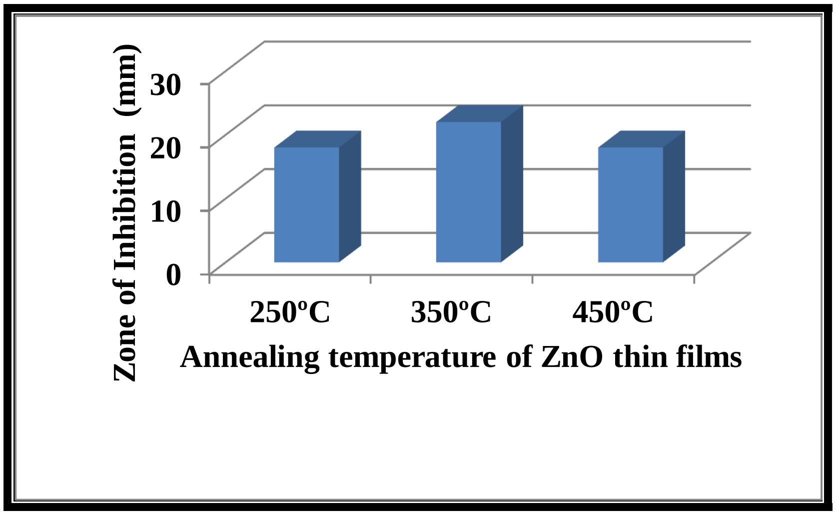


Fig.7 Antifungal activity of ZnO thin film annealed at 250°C, 350°C & 450°C.

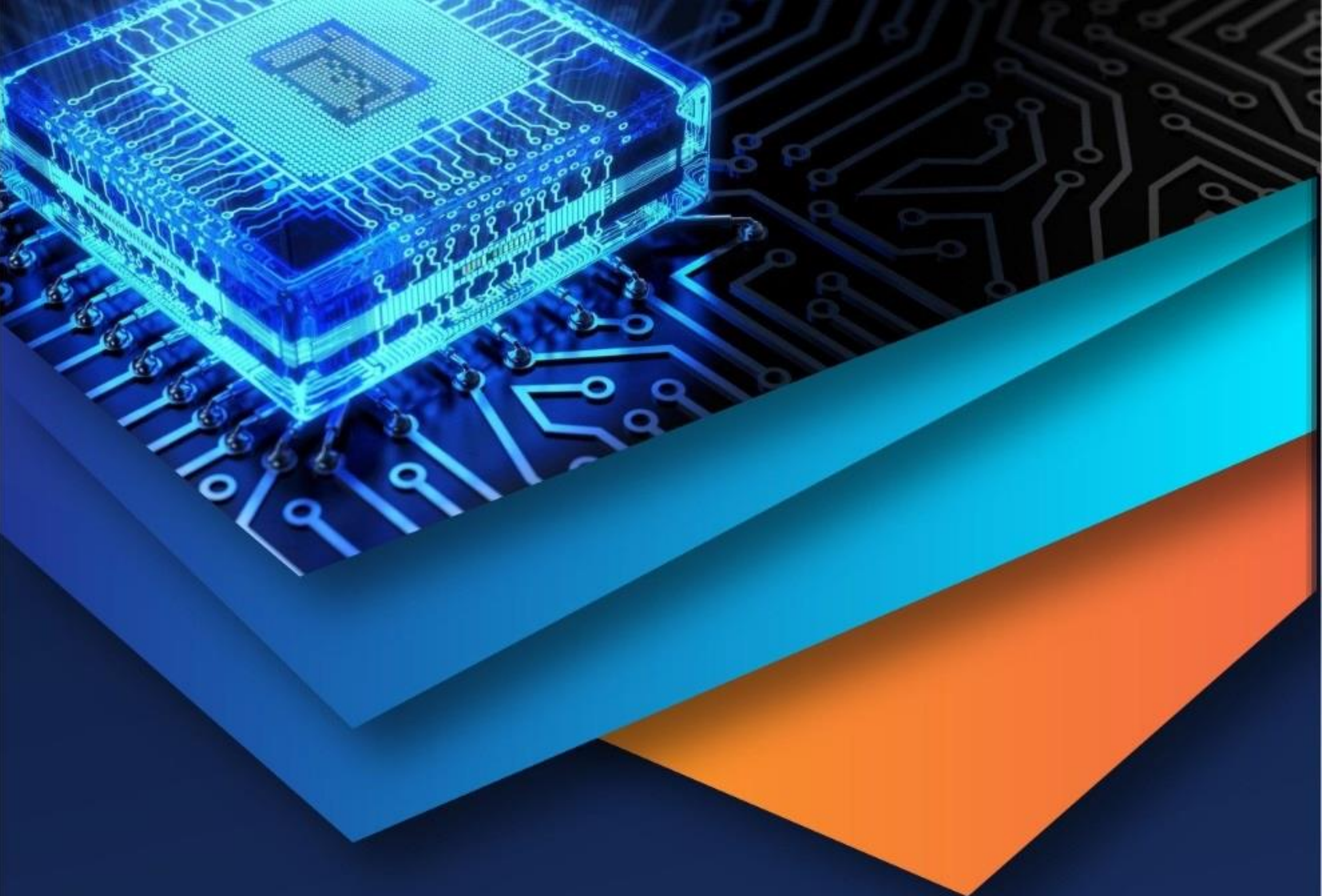
In the present study 0.1 mg/ml concentration showed maximum antifungal activity against Aspergillussp. Moreover the concentration dependency as well as particle size is the factors determining the maximum antifungal activity against Penicillium expansum[20].It is concluded that ZnO has the maximum antifungal activity when compared to other nanoparticles with minimum concentration[21].

IV. CONCLUSION

ZnO thin films were prepared by SILAR technique for three annealing temperature. The Nanocrystalline hexagonal structure was revealed by XRD with a preferred orientation along c-axis (002) and the lattice constants 'a' and 'c' values are also calculated and also matches with the standard value. The elemental composition determined by EDAX confirmed the presence of elements Zinc and Oxygen. The band gap decreases from 3.22eV to 3.05eV as the annealing temperature increases from 250°C to 450°C. The 250°C and 350°C ZnO thin film gives the maximum antibacterial activity against S.aureus and E.coli Antifungal activity of 350º C annealed ZnO thin film shows the maximum zone of inhibition when compared to other ZnO thin films.

REFERENCE

[1] Yongning, H.E.; Zhang , J.W.; Yang, X.D.; QingAn,X.U.; ChangChun, Z. Sci China Ser E-Tech Sci, 2007, 50,290-301
[2] ShampaMondal.;Shatabda Bhattacharya. Advances in Materials Science and Engineering, 2013,2013 Article ID 38238
[3] Raidou, A.; Benmalek, F.; Sall, T.; Aggour, M.; Qachaou, A.; Laanab, L.; Fahoume, M. Open Access Library Journal, 2014 1: e588
[4] Hiten, S.; Dhruba, C.; Sarma, K.C. Inter Journal of Innovative Rese in Science, Engineering and Technology, 2014, 3(10), 16957-1696
[5] Colon, G.; Ward, B.C.; Webster, T.J. Jour Biomed Mater Res, 2006, 78(3),595-60
[6] Padmavathy,N.; Vijayaraghavan, R. Sci. Technol. Adv. Mat. 2008,9,1-7
[7] Seil, J.T.; Taylor, E.N.; Webster, T.J. IEEE, 2009; 1–2
[8] ZiaulRaza, K.;MohdShoeb, K.; Mohammad Z,; MohdShahid, K. Materi science and Appli, 2011, 2, 340-34
[9] Harun, G. Eastern Anatolian Journal of Science,2015,1(2), 77-8
[10] Malevu, T.D.; Ocaya, R.O. Int. J. Electrochem. Sci, 2015,10 ,1752 – 1761
[11] Shan, F.K.; Liu, G. X. Journal of the Korean Physical Society, 2009, 54(2), 916-920
[12] Cullity, B.D.; Stock, S.R. Elements of X- ray diffraction, third edition, Prentice Hall, New Jersey , 2001
[13] FaLiao,Y.;Huanga,T.W. journal of magnetism and materials,2007, 310, 818-820
[14] Jen-Cheng Wang,; Fang-Ching,; Yu-Ting Liang,; Hung-Ing Chen,; Chung-Yuan Tsai,; Chia-Hui Fang,; Tzer-En Nee, Nanoscale Res Lett. 2012, 7(1), 270.
[15] ShuxiaGuo, S.; Zuliang, D. J.Magnetism and magnetic materials, 2012, 324, 782-785
[16] Xu.T.; Xie, C.S. Progress of Org. Coat, 2003, 46,297-301
[17] Yamamoto, O. Int. J. Inorg. Mater. 2001, 3(7), 643-646
[18] Fu. G, P.S.; Vary, C.T.; Lin, J. Phys. Chem., B, 2005, 109,8889-889
[19] Brayner, R.R.; Ferrari-Iliou, N.; Brivois, S.; Djediat,M.F.; Benedetti, F. Fiévet, Nano Lett., 2006, 6 ,866-870
[20] Ekthammathat, N.; Thongtem, S.; Thongtem, T.; Phuruangrat A. PowderTechnology, 2014, 254, 199-205
[21] Eskandari, M.; Haghighi, N.; Ahmadi, V.; Haghighi, F.;Mohammadi, S.H.R.. Physica B , 2011,406, 112–114.
[22]



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