

Characterisation and Antibacterial Application of Co doped ZnO Thin Films Deposited by SILAR Technique

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Abstract: Zinc Oxide (ZnO) and Cobalt (Co) doped ZnO thin films were prepared using SILAR technique. The structural, optical properties and antibacterial activity were analyzed for different Co doping ratio (3%, 5%, 7%) annealed at 250°C. X-Ray Diffraction (XRD) pattern exhibits hexagonal structure along with c-axis orientation. Field Emission Scanning Electron Microscope (FESEM) confirms the occurrence of flower-like structure for ZnO and Spherical shaped structure for Co doped ZnO thin films. Optical properties were studied using UV-Visible spectroscopy and the band gap changes as the doping ratio of Co increases from 3% to 7%. The maximum zone of inhibition was studied against the bacteria *E.coli* (Gram-negative) and *S.aureus* (Gram-positive).

Keywords: Co doped ZnO, XRD, FESEM, UV-Vis, Band gap, Antibacterial activity

I. INTRODUCTION

ZnO thin films can be prepared by a variety of methods like chemical and physical deposition methods namely sputtering, pulse laser deposition etc [1]. Chemical deposition methods are relatively simpler and cost effective. However, for commercial application, it is necessary to develop a low temperature deposition technology for the growth of ZnO films [2]. ZnO thin films synthesized using SILAR technique has the advantages of being effective and simple. SILAR is a wet chemical route for the synthesis of thin films in which the basic building blocks are ions where the preparative parameters are easily controllable. Doping ZnO with transition metal (Co) exhibits wide direct bandgap (3.37 eV), high exciton binding energy (60 meV), low cost, non-toxicity, and stability over a wide temperature range [3-5]. Cobalt complexes show interesting antibacterial, antimicrobial, antitumor, and many other biological activities [6]. In the present study, ZnO and Co doped (3%, 5%, 7%) ZnO thin films were deposited on glass substrate by SILAR technique annealed at 250°C. The structural, morphology, optical properties and antibacterial applications of the ZnO and Co doped ZnO thin films have been studied.

II. MATERIALS AND METHODOLOGY

A. Deposition of thin film

ZnO thin films were deposited on glass substrate by the modified SILAR technique [7]. For Co doping, cobalt acetate $[(CH_3COO)_2Co \cdot 4H_2O]$ was used along with the solute. These were mixed together in different nominal volume ratios to obtain 3%, 5%, 7% Co doped ZnO thin films. The cationic bath is zinc complex solution kept at room temperature (RT) and the anionic bath is of distilled water maintained near boiling point (96°C–98°C). The cleaned substrate (glass) was alternatively dipped in the baths, containing the zinc complex solution and hot deionised water for different timings and cycles. The coated glass substrate was dried and annealed at a temperature of 250°C for 1 hour.

B. Antibacterial Assessment

The thin films were tested on the following organisms, *E.coli*, *S. aureus*. The selected microorganisms were obtained from PSG Institute of Medical Science and Research, Coimbatore. The antibacterial efficacies of the thin films were assessed using agar diffusion method. Sterile Muller Hinton (MHA) agar was dispensed in sterile Petri dishes. The culture specimen was adjusted to 10^8 cfu/ml. Using sterile cotton swab the test organisms were swabbed over the surface of the agar plate. The prepared films were placed in the centre of the plate and gently pressed. The plates were incubated at 37°C for 18-24 hours. The incubated plates were examined for the interruption of growth over the inoculums. The size of the clear zone was used to evaluate the inhibitory effect of the test films.

III. RESULTS AND DISCUSSION

A. XRD analysis of ZnO and Co doped ZnO thin films

Figure 1 shows the typical XRD pattern of ZnO and Co doped ZnO thin films with different Co concentrations annealed at 250 °C. It can be seen that the entire diffraction peak could be indexed to hexagonal wurtzite type structure and the results are in good agreement with standard JCPDS data (card no. 36-1451). The reflection peaks at $2\theta = 32.32^\circ, 35.56^\circ, 37.37^\circ, 48.23^\circ, 56.16^\circ, 63.98^\circ$ and 68.45° correspond to (100), (002), (101), (102), (110), (103) and (112) reflection planes of ZnO respectively. There is no peak related to Co and cobalt based oxide based compounds at even 7% Co doped ZnO. The results suggested that the Co^{2+} was successfully incorporated to the Zn^{2+} sites in the ZnO crystal. As the Co dopant concentration increases, the peak intensity broadened and shifted towards the higher angle side, which indicated the decrease of the crystallinity of ZnO with the increase of Co concentrations. Various parameters of ZnO and Co doped ZnO thin films annealed at 250 °C were calculated and shown in Table 1. It was noted that the calculated average grain size of the ZnO films was decreased after doping of Co ions. This could be attributed to smaller ionic radius of Co^{2+} (0.125 nm) than that of Zn^{2+} (0.137 nm).

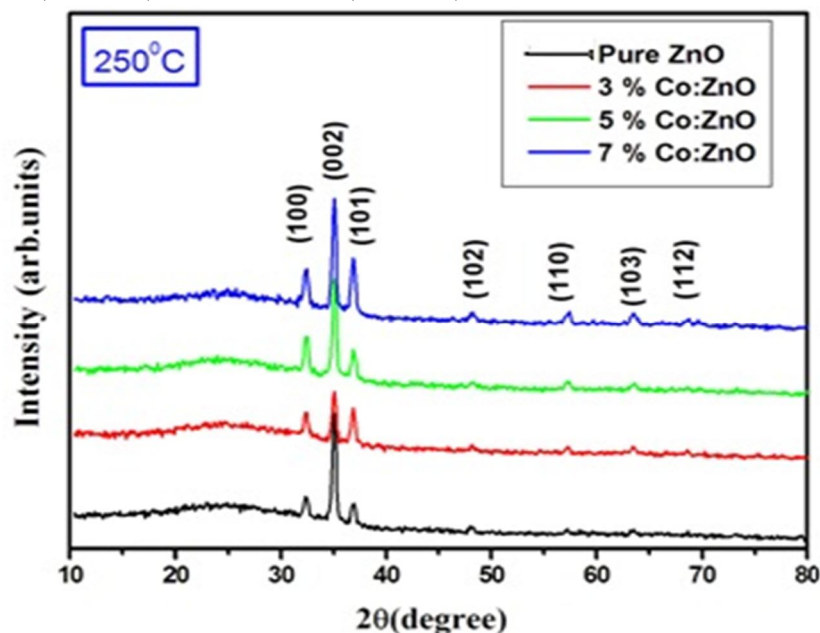


Figure 1: XRD pattern of ZnO and Co doped ZnO thin films annealed at 250 °C

Table 1: Various parameters of ZnO and Co doped ZnO thin films annealed at 250 °C

Annealing Temperature 250 °C						
Thin film	2 theta	FWHM	Hkl	D(nm)	Dislocation density	Strain
Pure ZnO	34.5821	0.4483	002	19.4	2.66E+15	0.001868
3% Co doped ZnO	34.6182	0.4636	002	18.7	2.85E+15	0.001931
5% Co doped ZnO	34.6182	0.4636	002	18.6	2.88E+15	0.001942
7% Co doped ZnO	34.5919	0.4497	002	19.3	2.68E+15	0.001873

B. FESEM analysis of ZnO and Co doped ZnO thin films

The FESEM images of ZnO and Co doped ZnO thin films with different doping ratio annealed at 250 °C were shown in Figure 2. It was clearly seen that a flower like structure was observed for ZnO thin film. For Co doped thin films, spherical shaped with small grains were observed. The decrease in grain size by Co doping was also confirmed with XRD results.

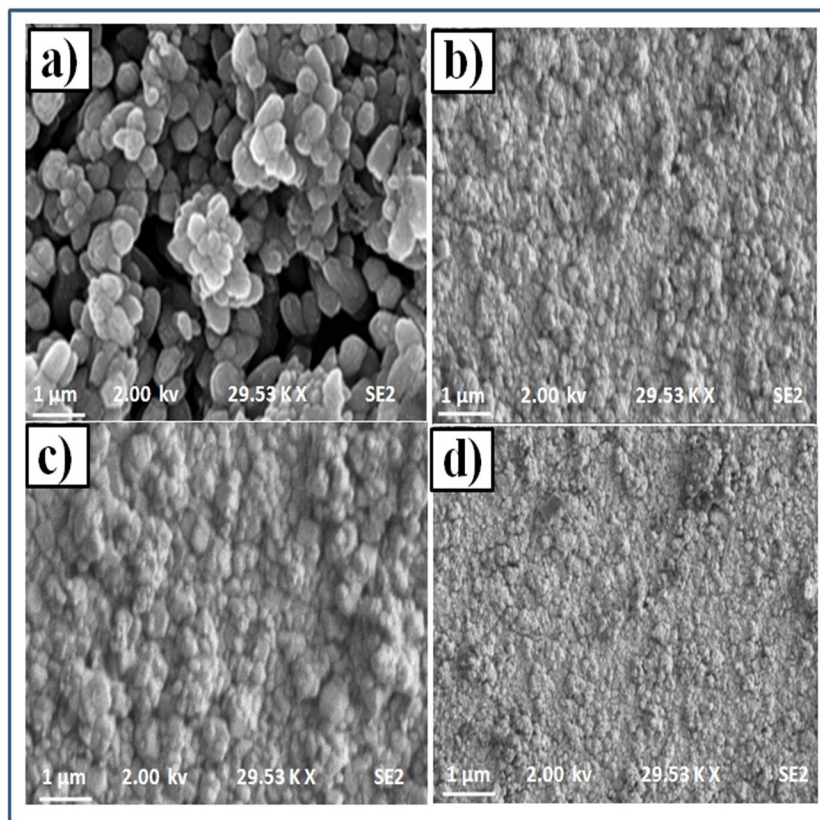


Figure 2: FESEM images of ZnO and Co doped ZnO at 250 °C annealed thin films

(a). ZnO (b). 3% Co doped ZnO, (c). 5% Co doped ZnO,
(d). 7% Co doped ZnO

C. UV-Vis spectra analysis of ZnO and Co doped ZnO thin films

Figure 3 show the UV-Vis transmission and absorption spectra of ZnO and Co doped ZnO thin films. ZnO thin films at 250° C shows a broad absorption in the ultraviolet region from 309-367nm. A red shift in absorption band was observed by Wang et al with increase in Co doping in ZnO thin films[8]. In Co doped ZnO films, the percentage transmittance is significantly improved by Co doping. The direct band gap of the ZnO and Co doped ZnO thin film decreases as doping ratio increases from 3% (3.83eV) to 7% (3.42eV)

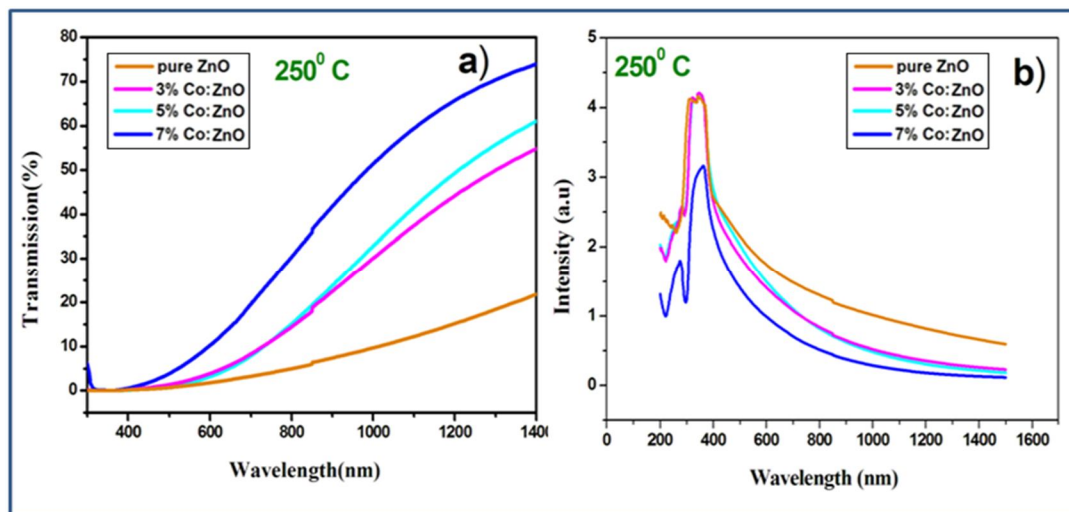


Figure 3: (a) UV-Vis transmittance spectra and (b) absorption spectra for ZnO and Co doped ZnO thin films annealed at 250 °C

D. Antibacterial activity of ZnO Co doped ZnO thin film

The Co doped ZnO thin film showed significant results when compared to ZnO thin films shown in Figure 4. The maximum zone of about 16mm against *E.coli* and 18mm against *S.aureus* was observed in 7 % and the annealing temperature of 250°C shown in Table 2 .This is because of the firm attachment of ZnO particles to the outer cell wall membrane of the bacteria. After that, ZnO particles begin to release oxygen species into the medium (bacteria), which inhibit the growth of cell leading to the distortion and leakage of the cell and finally the death of the cell [9]. The zone of inhibition which clearly indicates the mechanism of the biocidal action of the cobalt doped ZnO destroys the outer of the bacteria and leads to the death [10].

Table 2: Antibacterial activity of ZnO and Co doped ZnO thin film

Thin film	<i>E.coli</i>	<i>S.aureus</i>
ZnO	7	5
3%	11	11
5%	15	17
7%	16	18

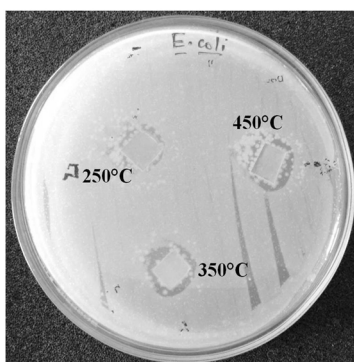


Figure 4(a)

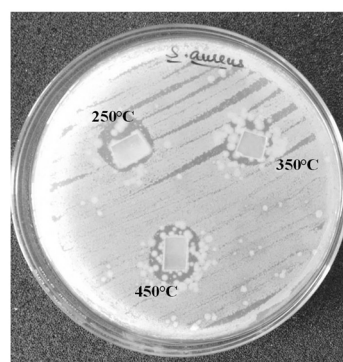


Figure 4(b)

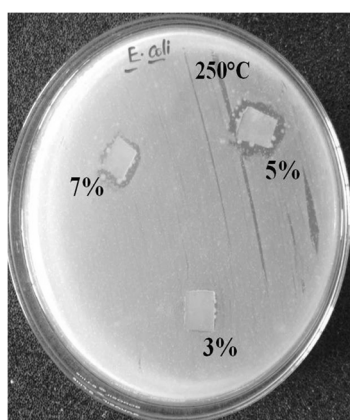


Figure 4(c)

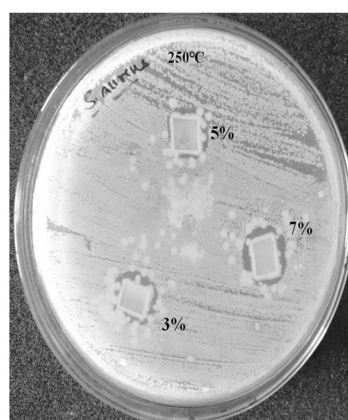


Figure 4(d)

Figure 4: Antibacterial activity of ZnO and Co doped ZnO thin film

IV. CONCLUSION

ZnO and Co doped ZnO thin films were prepared by SILAR technique annealed at 250 °C . XRD results reveals that ZnO with hexagonal wurtzite type structure and the results is in good agreement with standard JCPDS data (card no. 36-1451). FESEM pictures shows different morphologies for ZnO and Co doped ZnO thin films. Band gap decreases with increase in doping concentration. The antimicrobial effect of Co doped ZnO thin films increases with increase in cobalt concentration, because of the antimicrobial effect of cobalt along with zinc oxide.



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