

Effect of Co-Doping on Structural and Optical Properties of ZnO Thin Films

L. V. Thakre, L. H. Kathwate, V. D. Mote*

Thin Films and Materials Science Research Laboratory, Department of Physics, Dayanand Science College,
Latur- 413512, Maharashtra, India

ABSTRACT

Here, we report the effect of Co-doping on structural and optical properties of ZnO thin films prepared via simple and cost effective spray pyrolysis technique. The x-ray diffraction (XRD) confirmed the formation of the hexagonal wurtzite structure of undoped and Co-doped ZnO thin films with preferential growth along c-axis and had no phase impurity. The average crystallite size of prepared films calculated by Scherrer's formula and found to be 18.11 nm for ZnO and 14.12 nm for Co doped ZnO films. The calculated energy band gap exhibited a red shift upon doping with energy band gap reduced from 3.20 eV to 3.12 eV for the studied doping content. These studies show that the synthesized films have the potential to be used as a transparent electrode in optoelectronic devices such as solar cells.

Keywords : Thin Films, Zno, Spray Pyrolysis, X-Ray Diffraction, Uv-Vis Spectroscopy.

I. INTRODUCTION

Zinc oxide (ZnO) is perhaps the most prominent metal oxide semiconductors. It is an n-type semiconductor of hexagonal (wurtzite) structure with direct and wide band gap energy of about 3.37 eV at room temperature [1]. It is a flexible material with great electrical and optical properties, thermal and chemical stability, abundant in nature, low cost and non-harmful [2-3]. Due to this versatility ZnO is generally used in various commercial applications such as integrated optics, chemical sensors, solar cell, transition, photocatalysis, gas sensor etc. [4-6]. There are various techniques for the deposition of ZnO thin film such as pulsed laser deposition, spray pyrolysis, SILAR, chemical bath deposition, RF magnetron sputtering and electrochemical deposition method [7-11]. Considering the inexpensiveness and ease of

fabrication spray pyrolysis has been adopted as widely used deposition method.

Over the last few years transition metal doped ZnO has been studied briefly by researcher due its potential application in spintronic and photonic devices. Through the literature review ZnO based semiconductor can present ferromagnetic behaviour at room temperature when doped with transition metal such as Co, Ni and Mn [12-14]. Undoped ZnO material has much intrinsic defects so, when transition metal is doped with ZnO structure it can alter the intrinsic defects levels which helps to improve magnetic properties of spintronic as well as for gas sensing application. In this work undoped and Co-doped ZnO thin films were synthesized onconring borosilicate glass substrate by chemical spray pyrolysis method. The structural and optical properties of the obtained thin films were systematically investigated.

II. EXPERIMENTAL DETAILS

The undoped and Co-doped ZnO thin films were prepared by spray pyrolysis technique onto a glass substrate using zinc acetate dehydrate ($\text{Zn}(\text{CH}_3\text{CO})_2 \cdot 2\text{H}_2\text{O}$) (99.5%, Merck India) and cobalt acetate monohydrate ($\text{Co}(\text{CH}_3\text{CO})_2 \cdot \text{H}_2\text{O}$) (99.0%, Merck India). Before the deposition the substrate were cleaned with freshly prepared chromic acid, followed by labolene solution and double distilled water. Lastly the substrate was ultrasonically cleaned for 10 min. The precursor solution (0.1 M) was prepared by dissolving required amount of zinc acetate in double distilled water and stirred at room temperature for 30 min, to obtain a clear and homogeneous solution. Precursor solution was sprayed with the constant flow rate onto preheated corning borosilicate glass substrate held at optimized substrate temperature of 400°C by large area spray pyrolysis. Compressed air was used as carrier gas. Nozzles to substrate distance and carrier gas pressure were kept constant during the deposition. Similarly Co-doped ZnO thin film deposition was carried out by using the atomic ratio of C/Zn is 2 at %. The structural properties and crystallinity of the deposited thin films was studied by X-ray diffraction (Philips PW-3710) with $\text{Cu K}\alpha$ radiation. Optical absorption of the films were recorded by UV-visible spectrophotometer (Shimadzu 2450).

III. RESULTS AND DISCUSSION

3.1 Structural properties

Figure 1 shows the XRD patterns of undoped and Co-doped ZnO thin films. The diffraction peaks are quite sharp and intense which shows the polycrystalline nature of the films with wurtzite crystal structure. XRD patterns are in agreement with the JCPDS card No. 36-1451. There are no other peaks in the Co doped ZnO thin film confirms the formation of single phase films and reveals that substitution of Zn ions

with Co without altering the crystal structure of ZnO. In the observed (100), (002), (102), (110) and (103) crystallographic planes, it is found that the intensity of (002) plane was predominant. In addition, the position of (002) plane shifted slightly ($\approx 0.05^\circ$) from $2\theta = 34.44^\circ$ in undoped ZnO film to higher angle as Co-doping ($2\theta = 34.44^\circ$) indicating that Co ions substitute Zn ions in the ZnO lattice.

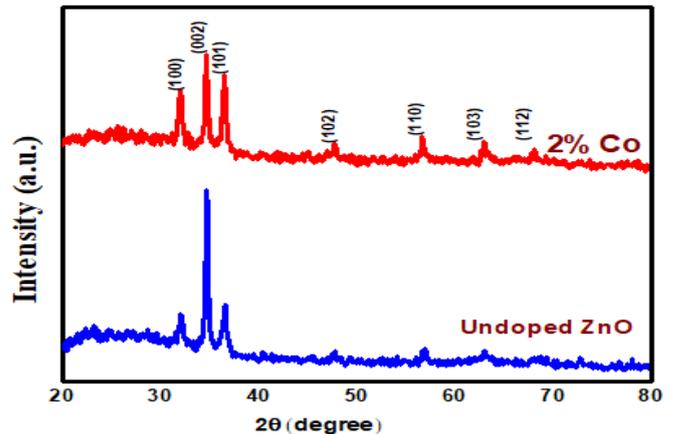


Figure 1. The XRD pattern of undoped and Co-doped ZnO thin films

The lattice parameters of 'a' and 'c' of the prepared film was calculated by using relation [15];

$$\frac{1}{d_{hkl}^2} = \frac{4(h^2 + hk + k^2)}{3a^2} + \frac{l^2}{c^2} \quad (1)$$

Where d_{hkl} is the lattice planes distance and h, k, and l are Miller indices. This was done by calculating d_{hkl} using Bragg's law, where θ is Bragg's angle; λ is the X-ray wavelength which is 1.5406 \AA for the $\text{CuK}\alpha$ line, and n is an integer representing the order. The calculated value of lattice parameter listed in table 1. The lattice parameters of undoped ZnO is found to be $a = 0.324 \text{ nm}$ and $c = 0.520 \text{ nm}$, which is consistence with JCPDC Card No. 36-1451. In addition, the lattice parameters for Co - doped ZnO thin films are $a = 0.3230 \text{ nm}$ and $c = 0.519 \text{ nm}$. It is observed that value of lattice parameters decrease for Co-doped ZnO film. The decrease in crystallite size and slight shift in (002) peak position of Co-doped film may be due to the lower radii of Co^{+2} ($\sim 0.65 \text{ \AA}$) [16] ions than that of

Zn²⁺ (~0.74 Å) ions [17]. The average crystallite size of the undoped and Co doped ZnO thin films were calculated from the broadening of diffracting peaks of the plane using Scherrer formula [18];

$$D = \frac{0.94\lambda}{\beta \cos\theta} \quad (2)$$

Where $\lambda = 1.5406\text{\AA}$, β is the full width at half maxima and θ is Bragg's angle. The calculated value depicted in table 1. The estimated crystallite size was found to be 18.11nm and 14.12nm for undoped and Co-doped ZnO thin films. It is may be due the presence of scattered Co ions which might have create thermodynamical barriers in turn slowed down the growth process [19]. The microstrain of films was calculated using the following formula [20];

$$\varepsilon p = \frac{\beta}{4 \tan\theta} \quad (3)$$

The value microstrain for Co-doped ZnO thin film has increased compared to the undoped ZnO thin film. The increasing value of microstrain may be due to the decrease in crystallite size.

3.2 Optical Study

In order to study optical properties of prepared films, the optical absorption of the samples has been recorded in the range 200 - 800 nm using UV-visible spectroscopy as shown in figure 2(a). The spectrum shows the decrease in absorption with an increase in wavelength near band edge for Co-doped ZnO thin film. In addition, the redshift for Co-doped ZnO thin film. This implies that increase in effective band gap of the film. The band gap of the prepared film was calculated using the equation [21];

$$\alpha h\nu = A(h\nu - E_g)^2 \quad (4)$$

Where, α -absorption coefficient, $h\nu$ -incident photon energy, E_g -optical band gap energy. From the linear fit of the plot $(\alpha h\nu)^2$ versus photon energy (E) as shown in figure 2(b), we estimate the value of 3.20 eV and 3.12eV for undoped and Co-doped ZnO films respectively. The decrease in the optical band gap of ZnO films with Co-doping is related to the sp-d exchange interaction between the band electrons and

localized d electrons of Co²⁺ ions. The value of bandgap obtained agrees with the previously results [22-23].

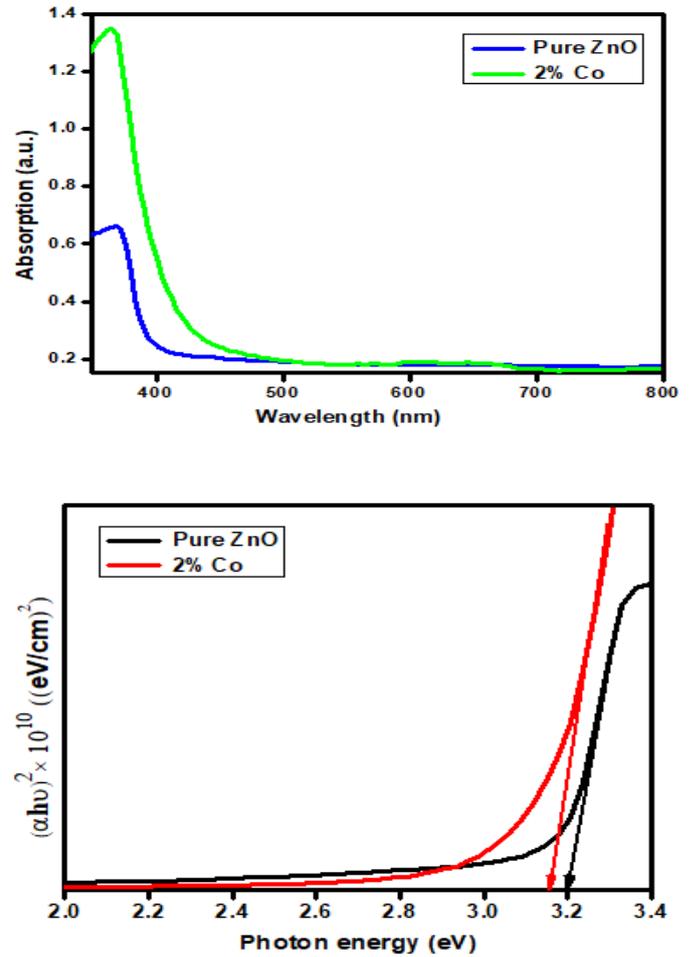


Figure 2. (a) Optical absorption spectra of undoped and Co-doped ZnO thin films. (b) The plot of $(\alpha h\nu)^2$ vs. $(h\nu)$ for undoped and Co-doped ZnO thin films.

IV. CONCLUSION

Nanostructured undoped and Co-doped ZnO thin films were successfully prepared by simple and cost effective spray pyrolysis technique at substrate temperature 400°C. The XRD analysis reveals that all prepared thin films have hexagonal wurtzite crystal structure with a (002) preferential growth. The decrease in the lattice parameter of Co-doped ZnO thin films implying Co²⁺ ions were homogenously incorporation into ZnO lattices. The average crystallite size increases with Co-doping, while the

value of microstrain decreases with Co-doping. The UV-visible spectroscopy analysis indicates the band gap energy decreased from 3.20 eV to 3.22 eV due to Co-doping. The structural and optical properties of prepared films show that films might be useful for the optoelectronic application devices.

V. REFERENCES

- [1]. S. Inamdar, V. Ganbavle, K.Rajpure, SuperlatticesMicrostruct. 76 (2014), 253–263.
- [2]. O. Lupan, T. Pauporte, L. Chow, B. Viana, F. Pelle', L.K. Ono, B. RoldanCuenya, H. Heinrich, Appl. Surf. Sci. 256 (2010), 1895–1907.
- [3]. M.Alex, M. Gupta, F. R. Chowdhury, M. Shen, K. Bothe, K. Shankar, Y.Tsui, D. W. Barlage, Solid-State Electron. 76 (2012), 104–108 .
- [4]. D. Look, Mater. Sci. Eng. B 80 (2001), 383.
- [5]. A.Djurisic, X. Chen, Y.H. Leung, A. Man Ching Ng, J. Mater. Chem. 22 (2012), 6526.
- [6]. D.C. Look, J. Electron. Mater. 35 (2006), 1299.
- [7]. S. Balamurali, R. Chandramohan, N. Suriyamurthy, T. Mahalingam, Journal of Materials Science: Materials in Electronics 24 (2013), 1782–7.
- [8]. Deva Arun Kumar K et al. Solid State Sciences 78 (2018), 58–68.
- [9]. L. Mustafaa, S. Anjuma, S. Waseema, S. Bashirb, K. Mahmoodb, M. Saleemcand E. Ahmad, Optik 161 (2018), 54–63.
- [10]. S. Benramachea, A. Rahalb, B.Benhaoua, Optik 125 (2014), 663–666.
- [11]. S. Kahraman, H.M. Cakmak, S. Cetinkaya, F. Bayansal, H.A. Cetinkara, H.S. Guder, J. Cryst. Growth 363 (2013), 86–92.
- [12]. H. Ohno, D. Chiba, F. Matsukura, T. Omly, Abe E, Dietl T, Ohno Y and Ohtani K, Nature 408, (2000), 944–6
- [13]. Z. Wang¹, R. Samaraweera, C. Reichl , W. Wegscheider andR. Mani, Scientific Reports 6 (2016), 38516.
- [14]. J. Lenz and A. Edelstein, IEEE Sensors Journal 6 (2016), 631–49.
- [15]. R. Wahab, G. Ansari, Y. Kim, H. Seo, G. Kim, G. Khang, et al., Mater Res Bull 42 (2007), 1640-8.
- [16]. M. Nair, M. Nirmala, K. Rekha, A. Anukaliani, Mater. Lett, 65 (2011), 1797-1800.
- [17]. M. Vagadia, A. Ravalia, U. Khachar, P. Solanki, R. Doshi, S. Rayaprol, Mater. Res. Bull. 46, (2011), 1933-1937.
- [18]. S.Maniv, A.Zangvil, J. Appl. Phys.47 (1978), 2787–2792.
- [19]. S. Wang, P. Li, H. Liu, J. Li, Y. Wei, J. Alloys Compd. 505, (2010), 362-366.
- [20]. P. Suat, M. Reza, S.Ozen, V. Senay, H.Yudar, S.Korkmaz, Vacuum 141 (2017), 210-215.
- [21]. J.Tauc, R.Grigorovici, A.Vancu,Phys.Stat.Sol.15 (1966), 627–637
- [22]. Z.Kayani, I. Shah,B.Zulfiqar, S.Riaz, S.Naseemand A. Sabah,Zeitschrift fur Naturforschung A 73 (2017),13–21.
- [23]. L. Mustafaa, S. Anjuma, S. Waseema, S. Bashirb, K. Mahmoodb, A. Saleemc, Optik 161(2018), 54–63.