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Research Article

INFLUENCE OF 'Mn' DOPING CONCENTRATION ON ZnO THIN FILMS BY SUCCESSIVE IONIC LAYER ADSORPTION AND REACTION (SILAR) METHOD

K. Rathi Devi [1]., Selvan G[2]., Karunakaran M[3]*., Rajesh Kanna G[4]., Kasirajan K[3] and Maheswari S[5]

[1]Department of Physics, Sethupathy Govt. Arts College, Ramanathapuram - 623 502, India
[2]Department of Physics, Thanthai Hans Roever College, Perambalur - 621 220, India
[3]Department of Physics, Alagappa Government Arts College, Karaikudi-630 003, India
[4]Department of Electronics, Government. Arts College for Women, Ramanathapuram- 623 502, India
[5]Department of Physics, Caussanel college of Arts and Science, Muthupettai- 623 523, India

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A B S T R A C T

In the present study, Mn doped ZnO TFs have been deposited on glass substrate by modified Successive Ionic Layer Absorption and Reaction (SILAR) method by varying Mn concentration (5%, 10% and 15%). The prepared films were annealed at 250° C and characterized by structural, morphological and optical properties by means of X-ray diffraction, HR-SEM and UV-visible NIR spectrometer respectively. The influence of doping concentration on structural, morphological and optical properties was studied in details. The powder XRD revealed that the prepared samples have polycrystalline nature with hexagonal structure. The surface morphology of the films shows an inconsistency with structure results. The optical band gap of the coated films was found in the range of 3.3 - 3.5 eV.

INTRODUCTION

The ZnO is the raw and abundant materials. The characterization of ZnO thin films have been an attractive research area for the past few years. It has the wurtzite structure is an n-type semiconductor with the direct band gap around 3.37 eV [1]. The Zinc Oxide is one of the technologically important transparent conducting materials compared to other II-VI group compounds. Zinc Oxide has a large exciton binding energy, which makes the exciton stable even at room temperature. It has the promising applications such as chemical sensors, piezoelectric transducer, transparent electrode, light emitting diodes, laser diodes, UV-photo detectors, gas sensors, etc [2-6]. The different synthesis methods to available to grow undoped and dope ZnO nano structured thin films using Successive Ionic Layer Absorption and Reaction [SILAR] [7], PECVD [8], Spray Pyrolysis [9-10], Sol-gel method [11], RF Magnetron Sputtering [12].

In this study the ZnO thin films synthesized by the successive ionic layer absorption and reaction method [SILAR]. It has the four beaker systems. In past few years the SILAR method is further developed the technique of modified SILAR method. In this method is very simple, low cost and easily prepared the films [13].

Corresponding author:* **Karunakaran M
Department of Physics, Alagappa Government Arts College, Karaikudi-630 003, India

In this method the prepared TFs is large area coated and the film is uniform. It has the well cleaned micro glass substrate only used.

Experimental procedure

Deposition of the films

Mn doped ZnO TFs were synthesized on glass substrate employing the modified SILAR method. Here Zinc sulphate and Sodium hydroxide and Manganese sulphate monohydrate were the precursor material and doping source material respectively. All the chemicals were AR grade and purchased from Merck India. Before undertaking the deposition, The cleaning process of the substrate is as follows: (i) glean the substrates well with distilled water; and then (ii) immersed the glass substrate in hot chromic acid in 2 hrs at the temperature maintained at 90° C followed by (iii) clean with soap solution, then (iv) clean with distilled water and finally treated with acetone.

Initially 0.2 M of Zinc Sulphate ($ZnSO_4.7H_2O$) and 4 g NaOH pellets were dissolved in 50 ml of distilled water and stirred using magnetic stirrer for 10 minutes. After that, different percentage of Mn (5 at %, 10 at % and 15 at %) were added to the precursor solution for doping. At the same time keep the pH at ~12.

In normal SILAR, four beakers were used. Anionic and cationic precursor solutions are taken in separate beakers. But in a modified SILAR all the precursor solutions are taken in a single beaker. The well-cleaned substrates were immersed in the chemical bath for a 20 Seconds and followed by immersion in hot water for the same time at the temperature maintained at 95^{o} C. The process of solution dip (step 1) followed by hot water dipping (vary step 2) is repeated for 60 dipping cycle. The cleaned substrate was alternatively dipped for a predetermined period in Sodium Zincate bath and water bath kept at room temperature and near boiling point, respectively. The coated films were dried in air and annealed at a temperature of 250^{0}C for 1 hour, the films get uniformity.

The reaction mechanism for the formation of Mn doped ZnO TFs is given below

$Mn\ (SO_4.H_2O) \rightarrow Mn^{2+} + SO_4^{2-}$
$Zn\ (SO_4.7H_2O) \rightarrow Zn^{2+} + SO_4^{2-}$
$Na\ OH \rightarrow Na^{+} + OH^{-}$

The formation of Mn doped ZnO TFs process could be expressed as

$Mn\ (SO_4.H_2O) + Zn\ (SO_4.7H_2O) + NaOH \rightarrow Mn\ ZnO + 2NaSO_4 + H_2O$

Films Characterization

The various Mn concentration doped ZnO thin films were characterized using different techniques. The thicknesses of the films were measured by the weight gain method. The structural properties of the films were investigated by the X-ray diffraction (XRD) using CuKα (1.5406 A^{0}). The surface morphology of the samples was examined using (HR SEM). The optical properties of Mn doped ZnO thin films were characterized by using the ultraviolet-visible-near-infrared (UV-VIS-NIR) spectrophotometer (JASCO, V-630) in the range of 100 nm to 1100 nm.

RESULT AND DISCUSSION

Thickness Studies

Figure 1 shows film thickness variation as a function of Mn doping concentration values. The film thickness was estimated by the weight gain method using the formula [14]

$$t = m / A\rho \text{ ----------}\rightarrow \quad (1)$$

where 't' is the thickness of the film, '*m*' is the weight gain, '*A*' is the area of the coated film and 'ρ' is the density of the film (5.61 gm/cm^{3}). The film thickness increased with increase of solution doping Mn concentration value. The film thickness was estimated to be approximately 523 nm, 534 nm and 560 nm for Mn concentrations of 5%, 10% and 15% respectively. This is attributed to the increasing density of the solution with the addition of NaOH.

Structural Studies

The crystal structure of the prepared films has been analyzed by X-ray diffraction pattern. Figure 1 (a-c) shows the XRD pattern of various weight percentages of Mn doped ZnO TFs such as 5%, 10% and 15 %. All the TFs have the hexagonal structure. The observed d-spacing are matched with JCPDS file number (36-1451). Structural parameters such as Crystalline size (D), Dislocation density (δ), Micro strain (ε), Lattice distortion and Number of crystallites (N_c) values were calculated from XRD data.

The crystallite size D has been calculated from the Scherer formula [15, 16]

$$D = k\lambda / \beta \cos\theta \text{ ----------}\rightarrow \quad (2)$$

Where k is the shaping factor which takes value from 0.89 to 0.94, 'λ' is the wavelength of the Cu-k_α line, 'β' is the full width at half maxima (FWHM) in radians and 'θ' is the corresponding Bragg's angle. Dislocation density (δ) was evaluated using the relation [17]

$$\delta = 1/D^2 \text{ ----------}\rightarrow \quad (3)$$

The lesser value of (δ) obtained (2.8192X 10^{14}/ lines/m^{2}) for higher Mn concentration coated films. The strain (ε) is calculated from the following relation

$$\varepsilon = \beta \cos\theta / 4 \text{ ----------}\rightarrow \quad (4)$$

The lattice distortion was calculated from the formula

$$L.D = \beta / 4 \tan\theta \text{ ----------}\rightarrow \quad (5)$$

The calculated structural parameters are shown in Table 1.

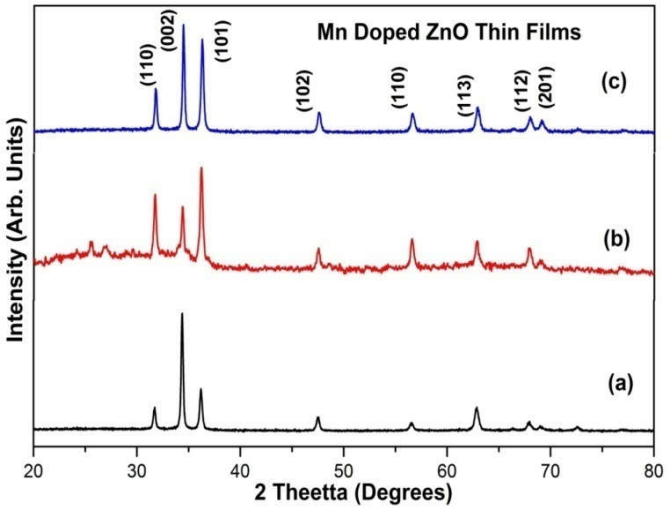

Figure 1 XRD pattern of Mn doped ZnO TFs with Mn percentage of (a) 5% (b) 10% and (c) 15%

Table 1 Microstructural parameters of Mn doped ZnO TFs

Mn (%)	Crystallite Size D(10^{-9}m)	Dislocation Density (δ) 10^{14} lines/m	Micro Strain (ε) ×10^{-3} Lines^{-2} m^{-4}	Lattice Distortion (LD)
5%	36.60	7.468	0.0805	0.1758
10%	39.71	6.3419	0.0690	0.1535
15%	59.56	2.8192	0.4447	0.1080

Morphological studies

The SEM images of Mn doped ZnO TFs for the different concentrations were displayed in figure 2. All the films are annealed at 250^{o}C shows the surface morphology to get uniformity. Figure 2 (a-c) represents the SEM images of Mn doped ZnO TFS deposited at 5%, 10, and 15% respectively. It can be observed that all the films are uniform and homogenous with closely packed spherical grains. The grain size is found to increase with increase in Mn doping level. The 5% Mn doped ZnO films looked porous while the higher doped films are compact respectively with the doping level. This can be due to the fact that the incorporation of Mn in the starting solution improves the nucleation process. Agglomeration of small grains in certain regions of the films is also evident from figure

2 (b & c). Such agglomeration makes difficult to evaluate the grain size from SEM images. Figure (a) shows the 5% of Mn it form the nano clusters shape. As the Mn percentage increases the morphology shows blossom-like structure. The surface morphology of Mn doped TFs are homogenous structure. Films are magnified view at 5µm scale its clearly shows that nano-clusters and blossom –like structure.

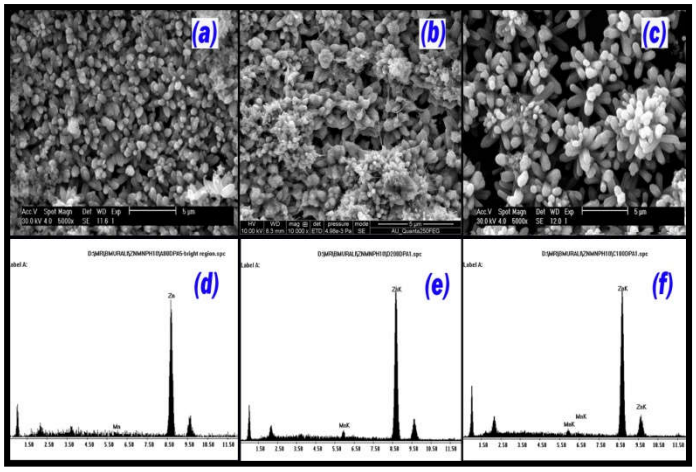

Figure 2 (a-c) SEM micrograph and (d-f) EDX spectrum of Mn doped ZnO TFs

EDAX studies

EDAX spectrum is used to investigate the elemental analysis of prepared films. Figure 2 (d-f) shows the EDAX spectrum of various Mn content doped ZnO thin films. The EDAX atomic percentage of various elements presents in Mn doped ZnO TFs are tabulated given below. In the EDAX spectrum the pure Zn compounds is majority places to occupied and doped Mn compounds is partially occupied in the films. When the doping concentration increases the Mn content also increases. The atomic percentage of Zn, O and Mn were presented table 2.

Table 2 Atomic percentage of elements present in the TFs

Mn Concentration	Atomic percentage of		
	Zn	O	Mn
5%	71.89	28.11	0.43
10%	65.98	33.07	0.95
15%	64.78	34.14	1.08

Optical Studies

The absorption coefficient (α) can be calculated from the transmittance (T) values from the Lambert law.

$$\alpha = \frac{In(1/T)}{t} \qquad \text{----------}\rightarrow \qquad (7)$$

The variation of absorption coefficient with photon energy (hv) takes the form, where Eg is the band gap, 'A' is a constant related to the effective masses associated with the bands and n is a constant which is equal to one for a direct- gap material and four for an indirect-gap material. To decide whether the ZnO films have direct or indirect bang gap, $(\alpha hv)^2$ *vs.* (hv) *and* $(\alpha hv)^{1/2}$ *vs.* (hv) plots are drawn. Since better linearity is obtained in the $(\alpha hv)^2$ *vs.* (hv) plot, the direct band gap values are determined by extrapolating the linear portion of this plot to the energy axis (Figure 3).

$$\alpha = A(h\nu - Eg)^{n/2} \qquad \text{----------}\rightarrow \qquad (8)$$

The obtained energy band gap values of various concentrations of Mn doped ZnO TFs were given in table 3. The maximum band gab value 3.5 eV obtained for 5% Mn and lowest band gap value 3.3 eV for 10% Mn doped ZnO TFs.

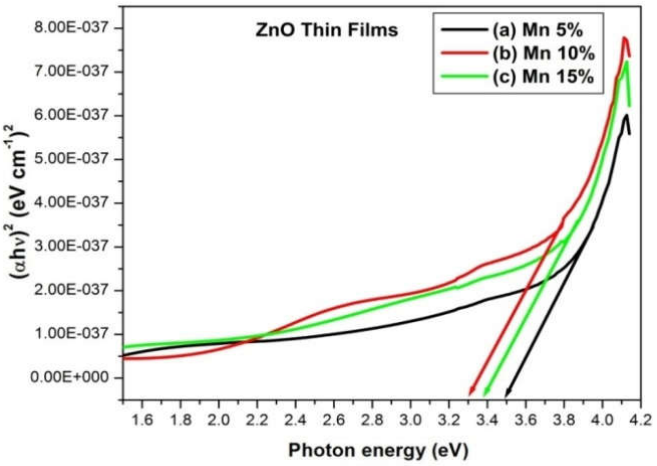

Figure 3 Optical band gap with various percentage of Mn doped ZnO TFs

Table 3 Energy band gap

Mn (%)	Energy band gap value in eV
5%	3.5
10%	3.3
15%	3.4

CONCLUSION

In wrinkle, Mn doped ZnO TFs were synthesis by modified SILAR method. The various Mn concentrations of the films are annealed at 250^o C. The annealed films were polycrystalline in nature with hexagonal structure. The surface morphology of the films shows an inconsistency with structure results. Surface morphology of the films has blossom-like structure for 15% Mn doped films. The minimum band gap was achieved for 10% Mn and maximum of 3.5 eV obtained for 5% Mn doped ZnO TFs. The estimated optical band gap in the range of 3.3 to 3.5 eV. In the wide band gap of 3.5 eV is perfectly matched the applications of optoelectronics and electronic device fabrications.

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