International Journal of Modern Science and Technology, 2020;5(7):196-203.
ISSN: 2456-0235.
www.ijmst.co

Research Article

Effect of 'Mg' doping concentration on ZnO thin films by Successive Ionic Layer Adsorption and Reaction (SILAR) Method

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Abstract

Mg doped zinc oxide (ZnO) thin films have been successfully coated onto glass substrates at various Mg doping level such as 0, 5, 10, and 15 wt. % by low cost Successive Ionic Layer Adsorption and Reaction (SILAR) coating technique. The film thickness was estimated using weight gain method and it revealed that the film thickness increased with Mg doping concentration values. The prepared film structural, morphological, optical and electrical properties were studied using X-ray diffraction (XRD), scanning electron microscope (SEM) and UV-Vis-NIR spectrophotometer respectively. The structure of the films were found to be hexagonal structure with polycrystalline in nature with preferential orientation along (002) plane. X-ray line profile analysis was used to evaluate the micro structural parameters such as crystallite size, micro strain, dislocation density and stacking fault probability. The crystallite size values are decreased with increase of Mg doping concentration values and maximum value of crystallite size was estimated at 47 nm at doping concentration of 0%. Morphological results showed that the concentration of the Mg has a marked effect on morphology of the ZnO thin films. The optical studies revealed that the band gap can be tailored between 3.93 eV to 3.955 eV by altering doping concentration. EDX studies showed that the presence of Zinc, oxygen and magnesium content.

Keywords: Zinc oxide; Thin films; Structural studies; Morphological studies; Optical properties.

Introduction

Transparent conductive oxide (TCO) thin films occupy an important place in the domain of the microelectronics and the optoelectronics. Among the family of TCO, Zinc oxide (ZnO) thin films are attractive in the semiconductor field due to their good optical characteristics, high stability and excellent electrical properties, among others [1–5]. They have been frequently used in several electronic applications such as transparent conducting materials, piezoelectric transducers, solar cells, surface acoustic wave filters, heat mirrors, and liquid crystal displays [6-11]. In addition to their potential in optoelectronic devices, now a day they are being used as gas chemical sensors due to their high surface sensitivity [12].

Several techniques have been proposed and developed for the preparation of ZnO thin films such as magnetron sputtering [13], spray pyrolysis [14], metal-organic chemical vapor deposition (MOCVD) [15], pulsed laser deposition (PLD) [16], arc plasma evaporation [17], dip-coating [18] and ion plating [19]. Among these deposition techniques, Successive Ionic Layer Adsorption and Reaction (SILAR) has many advantages such as simplicity, low cost and reproducibility [20]. Moreover anion and cation precursor in different baths offers good control over the deposition parameters such as pH, deposition temperature and time, etc. The only disadvantage of this technique is the formation of hydroxide phase while oxide growth and slow growth rate. The ZnO and MgO are the wide energy bandgap material; both the ionic radii of Mg^{2+} and Zn^{2+} are almost similar. So Mg doping with ZnO is seen as an efficient way to improve the properties of ZnO nanostructures. The Mg doping to ZnO adjusts the grain size and bandgap. Doping of Mg into ZnO is expected to modify the absorption,

Received: 24.06.2020; Received after Revision: 22.07.2020; Accepted: 22.07.2020; Published: 28.07.2020

physical, and chemical properties of ZnO, it is widely used in sensors, light emitting diodes or solar cells.

The objective of the present work is Mg doped ZnO thin films were deposited by SILAR technique on amorphous glass substrates and the influence of Mg doping concentration (0, 5, 10 and 15 at wt. % on the micro-structural, morphological and optoelectronic properties of ZnO thin films is investigated.

Material and methods

Materials used

Zinc Sulphate, sodium hydroxide (NaOH) and magnesium sulphate ($MgSO_4$) were purchased from e-Merck (99%) and used without further purification. Double distilled water was used throughout the synthesis process.

Synthesis

ZnO thin films were prepared using Modified SILAR technique involving double dip. Before deposition, the glass substrates were cleaned by chromic acid followed by cleaning with an alkali and acetone. The well-cleaned substrates were immersed in the chemical bath for a known standardized time followed by immersion in hot water for the same time for hydrogenation. The process of solution dip (step 1) followed by hot water dipping (step 2) is repeated for 80 times. 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. According to the following equation, the complex layer deposited on the substrate during the dipping in sodium zincate bath will be decomposed to ZnO due to dipping in hot water. The proposed reaction mechanism is according to the eqs. (1) and (2) [21].

$$ZnSO_4 + 2\,NaOH \rightarrow Na_2ZnO_2 + H_2SO_4 \uparrow \quad (1)$$

$$Na_2ZnO_2 + H_2O \rightarrow ZnO + 2\,NaOH \quad (2)$$

Part of the ZnO so formed was deposited onto the substrate as a strongly adherent film and the remainder formed as a precipitate. For Mg doping required amount of magnesium sulphate was used as a doping material. In the presesnt work Mg doping level is varied from 0 % to 15 wt. % in the steps of 5 wt. %.

Characterization studies

The structural properties of various molar solution concentration prepared Zinc oxide films was investigated by X-ray diffraction using X' pert PRO (PANalytical) diffractometer with CuKα radiation (λ = 0.15405 nm) and employing a scanning rate of 5^0 min^{-1} over a range of 20–80^0 at the room temperature. The morphological characteristics of the thin film after calcinations were examined by scanning electron microscope (Philips Model XL 30). In order to determine the band gap energy of the films, optical transmission study was carried using Perkin Elmer Lambda 35 spectrophotometer.

Result and discussion

Thickness studies

Figure 1 shows film thickness variation as a function of solution concentration values. The film thickness was estimated by the weight gain method using the eq. (3) [22]

$$t = m / A\rho \quad (3)$$

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 concentration value. It may be due to the replacement of Zn^{2+} by Mg^{2+} in the prepared Mg doped ZnO thin films. The film thickness was estimated to be approximately 1.36 µm, 1.49 µm, 1.53 µm and 1.67 µm for Mg doping concentration of ZnO thin films 0, 5, 10, and 15 wt. % respectively. This is attributed to the increasing density of the solution with the addition of Mg ions.

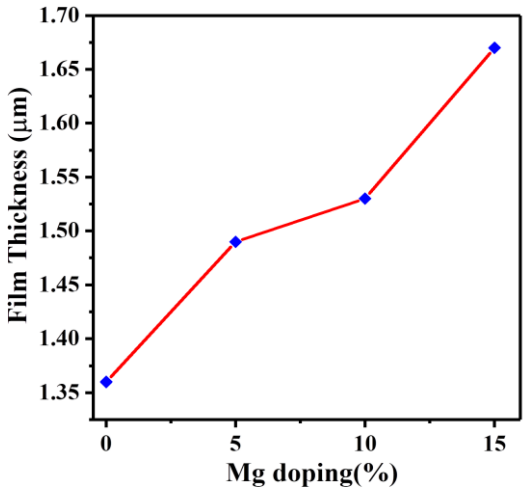

Figure 1. Film thickness of undoped and Mg doped ZnO thin films

Structural studies

X-ray diffraction patterns recorded for the SILAR coated Mg doped ZnO thin films on to glass substrates at various Mg doping level are shown in Figure 2. The XRD studies revealed that the SILAR coated ZnO films exhibited hexagonal structure with polycrystalline in nature. The observed 'd' spacing values were indexed with JCPDS standards (No. 36-1451). The XRD results revealed that the (002) lattice orientation is preferentially oriented for zinc oxide thin films prepared at various Mg doping concentration value. Also other peaks corresponding to planes (100), (101), (102), (110), (103), (112) and (201) lattice orientations were present. The sharpness and intensity of the predominant peak decreased with increase of Mg doping level.

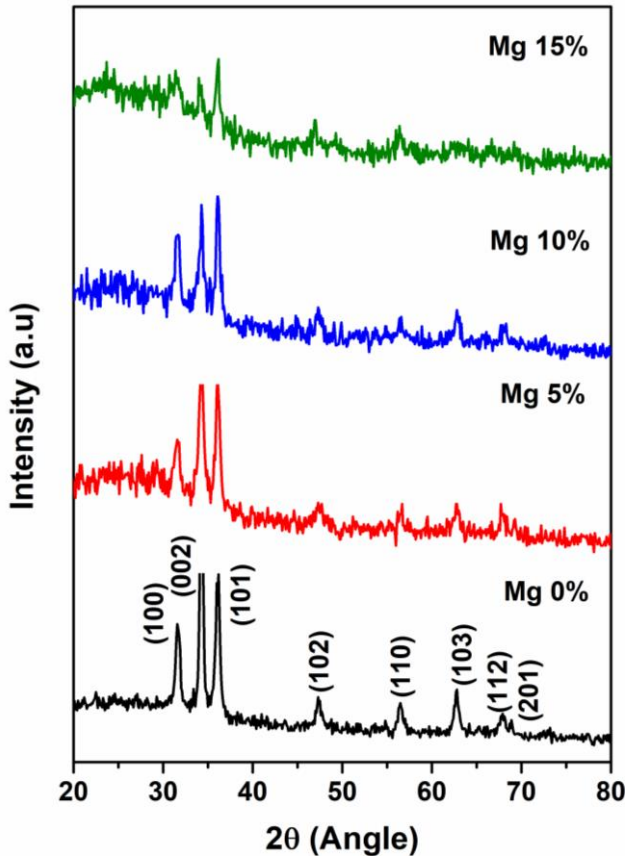

Figure 2. XRD pattern of Mg doped ZnO thin films

The XRD pattern of the undoped ZnO thin film shows a highly intense (002) reflection peak. However, this pattern for Mg doped ZnO thin films shows peak only along (002) plane (but with diminishing intensity with the increasing wt. % of Mg), which finally almost disappears for higher doped ZnO thin film. It suggests that formation of hexagonal phase in ZnO is hindered by incorporation of more amount of Mg into ZnO lattice, thus suppressing the crystalline behavior of the grown films. This indicates that an increase in doping concentration deteriorates the crystallinity of films, which may be the consequence of the stress developed due to the difference in size between Zn^{2+} and Mg^{2+} ions. The micro-structural parameters of Mg doped ZnO thin films are given in Table 1. The crystallite size of the prepared sample is calculated from the Debye-Scherer's formula. Let 'k' is the shape factor = 0.94, λ be the wavelength of X-rays used and β and θ are full width at half maximum and Bragg's angles corresponding to the maximum intensity peak. The Debye-Scherer's (DS) formula [23] is given as eq. (4).

$$D = \frac{k\lambda}{\beta Cos\theta} \qquad (4)$$

According to uniform deformation model, we consider the prepared material is isotopic in nature and the strain is assumed to be uniform in all crystallographic direction. The Williamson-Hall equation according to UDM is given by eq. (5) [24].

$$\beta_{hkl} \cos\theta_{hkl} = \frac{K\lambda}{D} + 4\varepsilon \sin\theta_{hkl} \qquad (5)$$

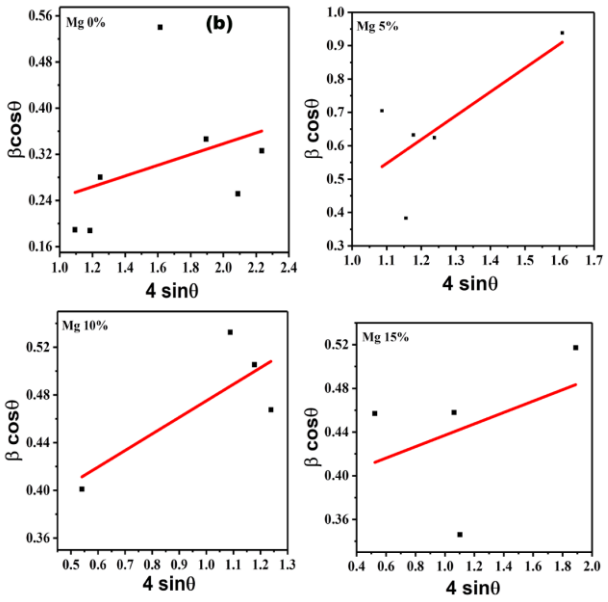

Figure 3. The Williamson–Hall analysis of Mg doped ZnO thin films with different Mg doping concentrations assuming UDM

Dislocations an imperfection in crystal associated with the misregistry of lattice existing in different parts of the crystal. Dislocation density (δ) was evaluated using the eq. (6) [25-28].

$$\delta = \frac{1}{D^2} \quad (6)$$

The strain (ε) is calculated from eq. (7).

$$\varepsilon = \frac{\beta \cos\theta}{4} \quad (7)$$

The X-ray diffraction peak of films corresponding texture coefficient (TC) is estimated using eq. (8) [29].

$$T_C(h_i k_i l_i) = \frac{I(h_i k_i l_i)}{I_0(h_i k_i l_i)} \left[\frac{1}{n} \Sigma \frac{I(h_i k_i l_i)}{I_0(h_i k_i l_i)} \right]^{-1} \quad (8)$$

where I_0 represents the standard intensity, I is the observed intensity of ($h_i k_i l_i$) plane and n is the reflection number.

Table 1. Micro-structural parameters of Mg doped ZnO thin films

Mg doping level (wt. at %)	Lattice Constants (A^o)		Crystallite size (D) nm		Micro strain (ε) × 10^{-3}	Dislocation density (δ) × 10^{15} lines m^{-2} (δ)	T.C
	a	c	D.S	W.H			
0	3.24	6.01	47	54	2.434	5.596	1.684
5	3.02	5.60	12	15	8.521	6.787	1.293
10	3.94	6.08	16	21	6.004	3.739	1.316
15	3.98	5.77	17	22	0.014	3.354	2.290

Morphological studies

Figures 4(a-d) shows the typical SEM micrographs of ZnO thin films prepared by SILAR coating technique. SEM image Figure 3(a) of solution contain 0% Mg concentration prepared ZnO thin film has exhibited with flowery shaped bigger and smaller grains are obtained, and some voids. The spherical shaped smaller grains are obtained from Mg doping concentration of 5% (Figure 3(b)). The smaller grains tend to form larger grains due to agglomeration. When the doping concentration is increased from 5% to 10% the morphology of the film is found to be constituted by continuous spherical grains and some voids are shown in Figure 3(c). Grain size are decreased when increase the Mg doping level from 10% to 15%.

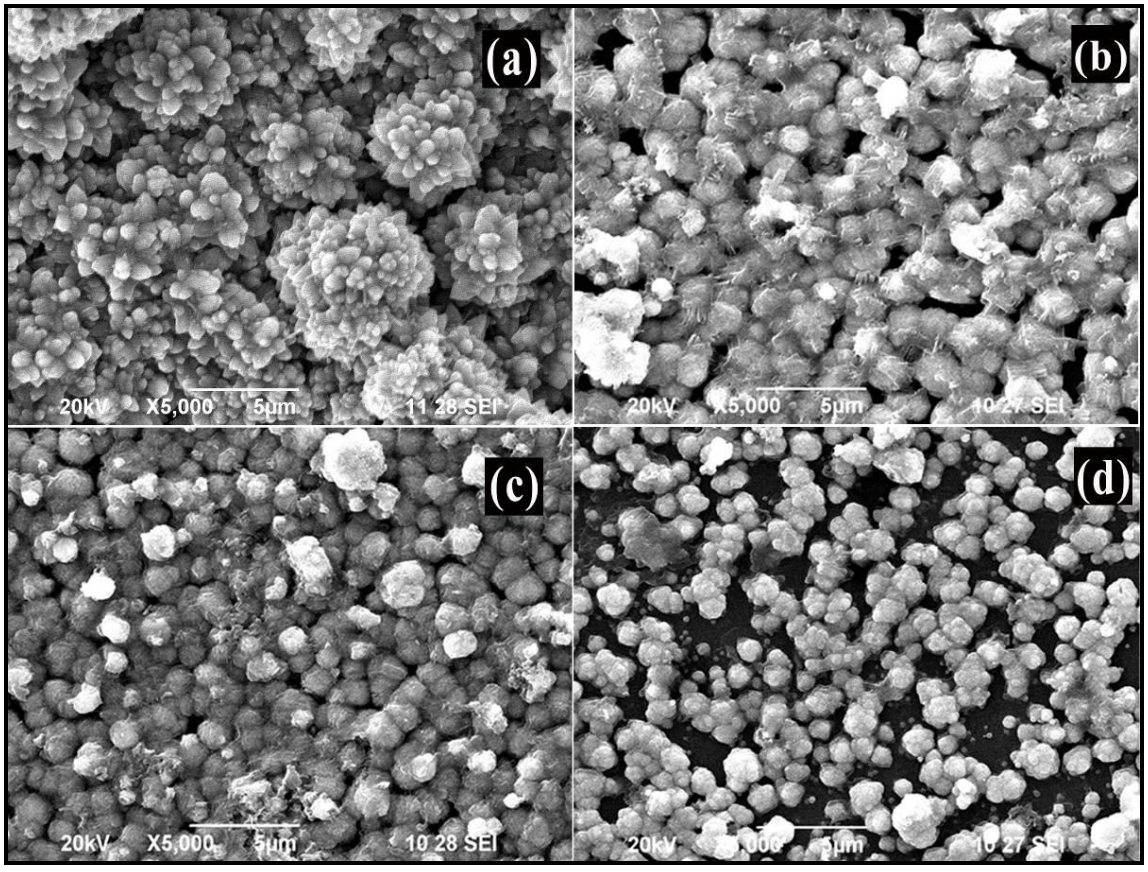

Figure 4. SEM Image of ZnO thin films at various level of Mg doping (a) 0% Mg (b) 5% Mg (c) 10% and (d) 15% Mg

EDX Studies:

Elemental analysis of ZnO thin films was carried out by EDX. Figure 5 represents the EDX spectrum of prepared ZnO thin film. Analysis shows the presence of only Zn and O elements in 0% Mg doped ZnO film. For 10% Mg doped ZnO thin film Mg ions also presence. EDX analysis confirms the presence of Zn and O elements in 0% Mg and Mg element also present in 10% Mg doped film without any other impurity, showing the high pure nature of the film. The EDX pattern for undoped and Mg doped ZnO (10 wt. %) films values was tabulated in table 2.

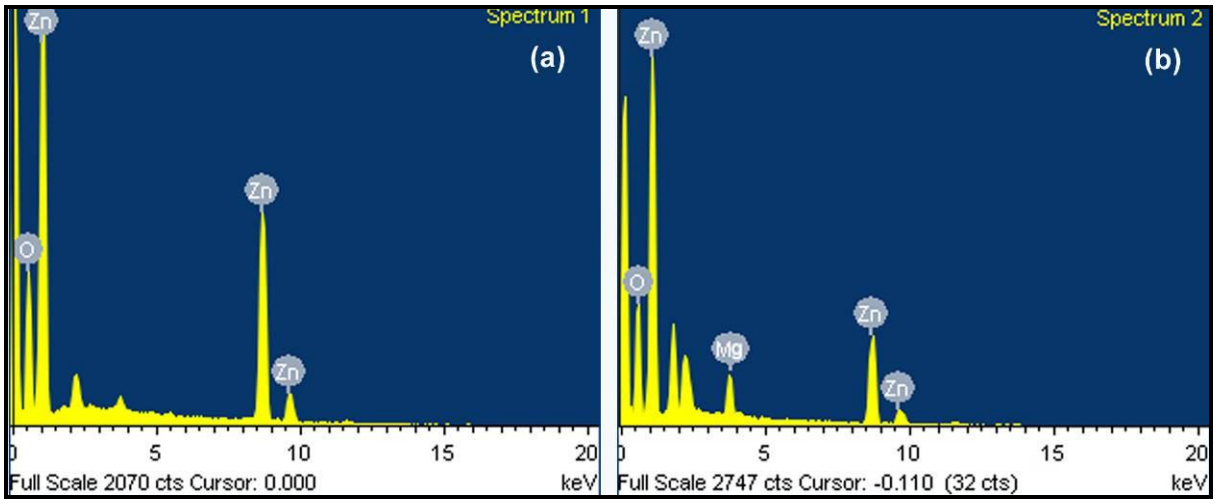

Figure 5. EDX Image of Mg doped ZnO Thin Films (a) 0% and (b) 10%

Table 2. Elemental composition of pure ZnO and Mg doped ZnO (10 wt. %) thin films

ZnO thin film			Mg doped ZnO thin film		
Element	Weight %	Atomic %	Element	Weight %	Atomic %
Zn K	75.57	42.38	Zn K	62.13	34.26
O K	24.43	57.62	Mg K	11.36	12.31
-	-	-	O K	26.51	53.43

Optical studies

Figure 6 shows the transmittance spectra of the ZnO film in the wavelength range from 300 to 1100 nm, deposited on glass substrate at different molar concentration of precursor solution. The optical properties of the films were studied with help of the absorbance in the UV-Vis region of spectra. The films have low absorbance in the visible range of the electromagnetic spectrum could be high transmittance. ZnO film has a sharp ultraviolet cut-off at approximately 380 nm.

The solution molar concentration of ZnO in the films could have markedly affected the optical properties of the grown films. The film coated with of 0% Mg doped film has shown a high transmittance of greater than 55% and it has been gradually decreased with the increase of Mg doping concentration in the SILAR. This reduction of the transmittance might be due to the increase in thickness of the films with the concentration of $ZnSO_4$ and $MgSO_4$. It is also been noticed that, there is slight shift of optical absorption edge towards red region as the solution molar concentration increases, it suggest that there is a increase in the optical band gap (*Eg*). The sharp absorption edge obtained for all the films has clearly shown the crystalline quality of the films. The absorption coefficient (α) can be calculated from the transmittance (T) values from the Lambert law.

$$\alpha = \frac{In(1/T)}{t} \qquad (9)$$

The variation of absorption coefficient with photon energy ($h\nu$) 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, (αhν)2 vs. (hν) and (αhν)1/2 vs. (hν) plots are drawn. Since better linearity is obtained in the (αhν)2 vs. (hν) plot, the direct band gap values are determined by extrapolating the linear portion of this plot to the energy axis (Figure 7).

$$\alpha = A(h\nu - Eg)^{n/2} \qquad (10)$$

The variation in Mg doping concentration of deposited ZnO showed energy band gap of

ZnO film increases with increase in concentration. The energy band gap increases from 3.93 eV for 0% Mg level to 3.955 eV for 15% Mg doped films uniformly. The uniform increase in absorbance and energy band gap value represents the formation of optically active ZnO.

The obtained E_g values for the studied ZnO films are higher than the values obtained that method, which might be due to decreased crystallite size and thickness of the films with higher Mg doping concentration. This indicates that the optical band gap of the ZnO film can be enhanced by Mg doping concentration.

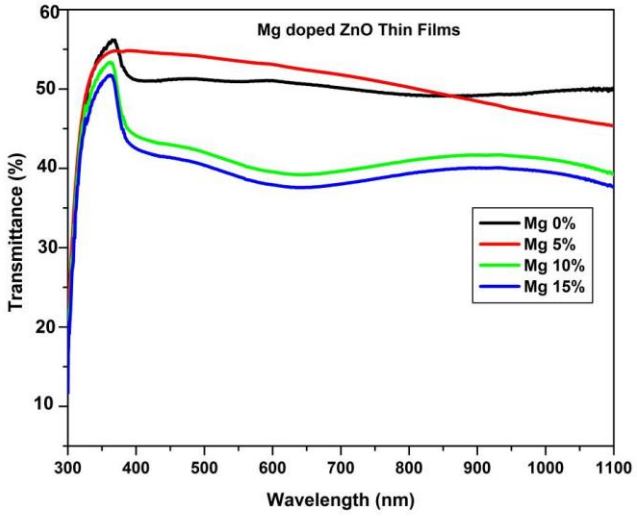

Figure 6. Transmission spectra of Mg doped ZnO thin films

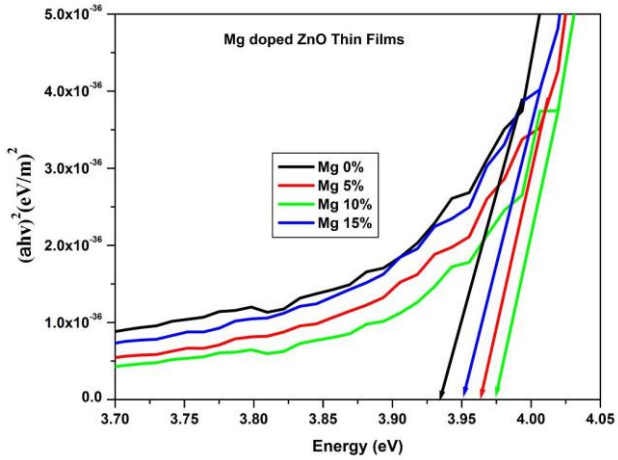

Figure 7. Tauc's plot of Mg doped ZnO thin films

Conclusions

Nanocrystalline ZnO thin films were fabricated by modified SILAR method by altering Mg doping concentration. XRD studies show that all the films are polycrystalline in nature with hexagonal structure having preferential orientation along (002) plane. It is observed from the SEM images and XRD patterns that the grain sizes of the structures were decreased with Mg doping concentration. The optical transmittance in the visible range is greater than 55%. The optical band gap of the coated ZnO films increase with the increase in solution concentration. Both optical band gap and morphological properties could be controlled and calibrated by adjusting the Mg doping concentration. This controlling mechanism might be instrumental for different optoelectronic device applications where tunable material properties including band gap and crystalline quality are of critical importance. We believe that our proposed SILAR based nano structured Mg doped ZnO film coating technique is promising for tunable opto electronic materials synthesis.

Conflict of interest

Authors declared no conflict of interests.

References

[1] Krunks M, Enn M. Zinc oxide thin films by the spray pyrolysis method. Thin Solid Films 1995;270(1-2):33-6.

[2] Lee C, Koengsu L, Jinsoo S. Highly textured ZnO thin films doped with indium prepared by the pyrosol method. Solar Energy Materials and Solar Cells 1996;43(1):37-45.

[3] Lucio-Lopez MA, Luna-Arias A, Maldonado M, de la L, Olvera, Acosta DR. Preparation of conducting and transparent indium-doped ZnO thin films by chemical spray. Solar Energy Materials and Solar Cells 2006;90(6):733-41.

[4] Major S, Satyendra K, Bhatnagar M, Chopra KL. Effect of hydrogen plasma treatment on transparent conducting oxides. Applied Physics Letters 1986;49(7):394-6.

[5] Ohtomo YA, Kawasaki M, Koinuma H KTZ, Tang ZK, Yu P, Wong GKL. Growth of ZnO thin film by laser MBE: lasing of exciton at room temperature. Physica Status Solidi (B) 1997;202(2):669-72.

[6] Devi, Radhi K, Selvan G, Karunakaran M, Kasirajan K, Mohd Shkir, AlFaify A. A SILAR fabrication of nanostructured ZnO thin films and their characterizations for gas sensing applications: An effect of Ag

concentration. Superlattices and Microstructures 2020;(2020):106547.
[7] Chopra KL, Major S, Pandya DK. Transparent conductors - a status review. Thin Solid Films 1983;102(1):1-46.
[8] Pati S, Banerji P, Majumder SB. Properties of indium doped nanocrystalline ZnO thin films and their enhanced gas sensing performance. RSC Advances 2015;5(75):61230-8.
[9] Ma QB, Zhi-Zhen Y, Hai-Ping H, Shao-Hua H, Jing-Rui W, Li-Ping Z, Yin-Zhu Z, Bing-Hui Z. Structural, electrical, and optical properties of transparent conductive ZnO: Ga films prepared by DC reactive magnetron sputtering. Journal of Crystal Growth 2007;304 (1):64-8.
[10] Ramakrishna Reddy KT, Reddy TBS, Ian F, Miles RW. Highly oriented and conducting ZnO: Ga layers grown by chemical spray pyrolysis. Surface and Coatings Technology 2002;151:110-113.
[11] Kaul AR, Yu Gorbenko O, Botev AN, Burova LI. MOCVD of pure and Ga-doped epitaxial ZnO. Superlattices and Microstructures 2005;38(4-6):272-82.
[12] Snure M, Ashutosh T. Structural, electrical, and optical characterizations of epitaxial Zn 1− x Ga x O films grown on sapphire (0001) substrate. Journal of Applied Physics 2007;101(12):124912.
[13] Wang Z, Xue-feng Q, Jie Y, Zi-kang Z. Large-scale fabrication of tower-like, flower-like, and tube-like ZnO arrays by a simple chemical solution route. Langmuir. 2004;20(8):3441-8.
[14] Fathollahi V, Mohammadpour Amini M. Sol–gel preparation of highly oriented gallium-doped zinc oxide thin films. Materials Letters 2001;50(4):235-9.
[15] Iwata K, Sakemi T, Yamada A, Fons P, Awai K, Yamamoto T, Matsubara M, Tampo H, Niki S. Growth and electrical properties of ZnO thin films deposited by novel ion plating method. Thin Solid Films 2003;445(2):274-7.
[16] Karunakaran M, Rubanancy K, Rajini M, Kavitha G, Chandramohan R. Influence of Dipping Cycle on Physical Properties of Nanocrystalline CdO Thin Films Prepared by SILAR Method. Int J Chem Tech Res 2016;2(01):84-9.
[17] Chandrasekar, Bruno L, Chandramohan R, Vijayalakshmi R, Chandrasekaran S. Preparation and characterization of Mn-doped ZnS nanoparticles. International Nano Letters 2015;5(2):71-5.
[18] Chandrasekar, Bruno L, Chandramohan R, Vijayalakshmi R. Effect of Mn doping on micro-structural and optical properties of cadmium sulfide nanoparticles. Journal of Nanoengineering and Nanomanufacturing 2013;3(3):253-7.
[19] Vijayan TA, Chandramohan R, Valanarasu S, Thirumalai J, Subramanian SP. Comparative investigation on nanocrystal structure, optical, and electrical properties of ZnO and Sr-doped ZnO thin films using chemical bath deposition method. Journal of Materials Science 2008;43(6):1776-82.
[20] Cullity BD. Elements of X-ray Diffraction. Addison-Wesley Publishing, 1956.
[21] Valanarasu S, Dhanasekaran V, Karunakaran M, Chandramohan R, Mahalingam T. Role of solution pH on the microstructural properties of spin coated cobalt oxide thin films. J Nanosci Nanotechnol 2013;13:1-6.
[22] Dhanasekaran V, Mahalingam T. Surface modifications and optical variations of (− 1 1 1) lattice oriented CuO nanofilms for solar energy applications. Materials Research Bulletin 2013;48(9):3585-93.
[23] Annalakshmi V, Kasirajan K, Maheswari S, Karunakaran M, Subbu C. International Journal for Science and Advanced Research in Technology 2018;4(1):382-6.
[24] Prabhu YT, Venkateswara Rao K, Sesha Sai Kumar V, Siva Kumari B. X-ray analysis of Fe doped ZnO nanoparticles by Williamson-Hall and size-strain plot. International Journal of Engineering and Advanced Technology 2013;2(4):268-74.
[25] Inbaraj P, Fermi H, Joseph Prince J. Optical and structural properties of Mg doped ZnO thin films by chemical bath deposition method. Journal of Materials Science: Materials in Electronics 2018;29(2):935-43.
[26] Alsaad Ahmad M, Ahmad A. Ahmad, Qais M. Al-Bataineh, Areen A. Bani-Salameh, Hadeel S. Abdullah, Issam A. Qattan, Zaid M. Albataineh, Ahmad D. Telfah. Optical, Structural, and Crystal Defects Characterizations of Dip Synthesized (Fe-

Ni) Co-Doped ZnO Thin Films. Materials 2020;13(7):1737.

[27] El Hallani G, Nasih S, Fazouan N, Liba A, Khuili M, Sajieddine M, Mabrouki M, Laanab L, Atmani EH. Comparative study for highly Al and Mg doped ZnO thin films elaborated by sol gel method for photovoltaic application. Journal of Applied Physics 2017;121(13):135103.

[28] Wang Z, Ziwei T, Dongmei H, Fubo G. Highly sensitive and selective ethanol sensor fabricated with In-doped 3DOM ZnO. ACS Applied Materials & Interfaces. 2016;8(8):5466-74.

[29] Znaidi L, Tahar T, Dominique V, Nacer S, Sana BY, Ovidiu B, Alexis F, Azzedine B. AZO thin films by sol-gel process for integrated optics. Coatings 2013;3(3):126-39.

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