Structural and Optical Properties of Mn-Doped ZnO Thin Films Prepared by SILAR Method

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Abstract. The growth of highly textured Mn doped Zinc oxide (ZnO) thin films with a preferred (002) orientation has been reported by employing successive ionic layer growth by adsorption reaction (SILAR) using a sodium zincate bath on glass substrates has been reported. The prepared films were characterized by X-ray diffraction (XRD), optical spectroscopy and scanning electron microscopy (SEM) measurement. The XRD analysis reveals that the films were polycrystalline. Morphology of the films was found to be uniform with smaller grains and exhibits a structure with porous. The calculated Band gap value was found to be 3.21 eV prepared at 15 mM MnSO₄ concentration.

1. Introduction

Thin films of transparent conducting oxides (TCO) such as doped metal oxide thin films like zinc oxide, indium oxide, tin oxide and cadmium oxide have attracted considerable attention because of their low resistivity and high optical transmittance [1-4]. They are widely used for many applications such as flat panel display, light emitting diodes and photovoltaic cells [5-7]. Among these TCO, Zinc oxide (ZnO) has received considerable attention for optoelectronic application due to its low electrical resistivity and high transparency in the visible range of solar spectrum [8]. Zinc oxide based films have attracted more attention due to the various advantages they have over others. The multifunctional ZnO material is one of the most promising candidates for the fabrication of the next generation of optoelectronic devices. Besides being a wide band gap semiconductor with gap energy of 3.37 eV, ZnO has several desirable characteristics such as high transmittance in the visible region, low electrical resistivity and non toxicity [9, 10]. More interest has been shown on TCOs based on doped ZnO films with cationic dopants such as Al, Ga, or B. In recent days, several investigations in which fluorine was used as anionic dopant can be found in the literature, due to the stability of Manganese doped ZnO films (MZO) which makes them a potential candidate for solar cell technology.

The ZnO thin films can be prepared by a variety of methods such as chemical vapour deposition (CVD), RF magnetron sputtering [11], DC reactive magnetron sputtering [12], metal organic chemical vapour deposition (MOCVD), molecular beam epitaxy (MBE) [13], pulsed laser deposition [14], sol–gel process [15], chemical bath deposition, etc. Of these methods, SILAR technique has several advantages over the others such as low cost, safety and easy handling. This technique does not require vacuum conditions, and by employing different deposition parameters, one can control the microstructure and surface features of the films [16, 17]. In the present work, Mn doped ZnO films are fabricated by employing a further simplified chemical bath SILAR technique.
2. Experimental procedure

2.1. Materials

All the precursors namely, zinc sulphate, manganese sulphate and sodium hydroxide that were 99.9% pure were purchased from Merck Chemical Co., Germany and used without further purification.

2.1. Methods

ZnO thin films were grown using a two-step chemical bath deposition technique using a solution comprising 0.1 M zinc sulphate, 0.2 M sodium hydroxide with a pH value of 9±0.2 deposited at bath temperature of 90 °C under optimized condition [18]. Before deposition, the glass substrates were cleaned by chromic acid followed by cleaning with 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 known number of 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 equations, 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 following equations.

\[
\text{ZnSO}_4 + 2 \text{NaOH} \rightarrow \text{Na}_2\text{ZnO}_2 + \text{H}_2\text{SO}_4 \quad \uparrow
\]

\[
\text{Na}_2\text{ZnO}_2 + \text{H}_2\text{O} \rightarrow \text{ZnO} + 2 \text{NaOH}
\]

Part of the ZnO so formed was deposited onto the substrate as a strongly adherent film and the remainder formed as a precipitate. For Mn doping MSO₄ were used.

2.2. Characterization Studies

The structural properties of various solution Mn molar doped films prepared zinc oxide was investigated by X-ray diffraction using X’ pert PRO (PAN analytical) diffractometer with CuKα radiation (\(\lambda = 0.15405 \text{ nm}\)) and employing a scanning rate of 5° min⁻¹ over a range of 10°–80° at the room temperature. The morphological characteristics of the thin film after calcination 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.
3. Results and discussion

3.1. Thickness Studies

Figure 1. Film thickness variation of MZO thin films prepared at various MnSO$_4$ concentrations.

The film thickness is estimated against various MnSO$_4$ concentrations ranging from 5 to 15 mM in shown in Fig. 1. The film thickness was estimated by the weight gain method using the formula

$$t = \frac{m}{A \rho} \quad (1)$$

where ‘t’ is the thickness of the film, ‘m’ is the weight gain, ‘A’ is the area of the coated film and ‘$\rho$’ is the density of the film (6.055 gm/cm$^3$). Fig. 1 shows that the growth rate linearly increases with increased deposition time. The fastest growth is observed up to 15 sec rinsing time and the film grows to a thickness at 631 nm at 5 mM MnSO$_4$. The maximum value of the film thickness is obtained at 685 nm at 15 mM MnSO$_4$ concentrations.

3.2. Structural Studies

X-ray diffraction patterns recorded for the SILAR prepared Mn doped ZnO thin films onto glass substrates at various doping concentrations such as 5, 10 and 15 mM MnSO$_4$ are shown in Fig. 2(a)–(c). The XRD studies revealed that the films exhibited polycrystalline nature of MZO thin films, whose c-axis was preferentially, oriented normal to the glass substrate. The predominant orientation of the film is (002) and its corresponding Bragg’s angle 34.48°. The 5 mM manganese sulphate concentration prepared film possesses the polycrystalline nature of XRD patterns as shown in Fig. 2(a).
The diffraction peaks are observed at an angle 31.62°, 34.43°, 36.23°, 47.37°, 56.38°, 62.95°, and 68.01° and corresponding crystallographical planes are (100), (002), (101), (102), (110), (103) and (112), respectively. The peak intensities are increases with increase of doping molar concentration of manganese sulphate for MZO thin films. The peak intensities are increases for increase of zinc sulphate concentrations from 10 to 15mM prepared MZO film as shown in Fig. 2(c). However, no other new peaks emerged due to the variation of doping molar concentration.

The crystallite sizes of all the prepared samples were calculated using Debye-Scherrer formula [19-22].

\[
D = \frac{k\lambda}{\beta \cos \theta} \quad (2)
\]

where the constant ‘k’ is the shape factor = 0.94, ‘\(\lambda\)’ is the wavelength of X-rays (1.5406 ÅCuK\(_{\alpha}\)) ‘\(\theta\)’ is the Bragg’s angle and ‘\(\beta\)’ is FWHM. Crystallite size increases with respect to the molar concentration of manganese sulphate. The maximum value of crystallite size is achieved at 32.1 nm and it may be due to the Mn atoms incorporate with ZnO matrix.

\[
\delta = \frac{1}{D^2} \quad (3)
\]

The dislocation density values are linearly decreases with molar concentrations which may be due to increase of crystallite size. The microstrain (\(\varepsilon\)) developed in thin films can be evaluated from the relation (4). Microstrain values are linearly decreases with manganese sulphate concentrations. The lower value of microstrain is observed at 1.09 x 10\(^{-3}\) lines\(^{-2}\).m\(^{-4}\).

\[
\varepsilon = \left(\frac{\lambda}{D \cos \theta} - \beta\right) \frac{1}{\tan \theta} \quad (4)
\]
The relation connecting stacking fault probability ($\alpha$) with peak shift $\Delta (2\theta)$ was given by

$$\alpha = \frac{2\pi^2}{45\sqrt{3}} \left[ \frac{\Delta(2\theta)}{\tan \theta} \right]$$

(5)

where $D$ is crystallite size, $\beta$ is full width at half maximum, $\alpha$ stacking fault probability and $\lambda$ wavelength of the X-ray diffraction respectively. The stacking fault probability values are rapidly increases with increase of molar concentrations. The predominant peak is shift towards higher values due to incorporation of Mn atoms in ZnO matrix.

The X-ray diffraction peak of films corresponding texture coefficient ($T_c$) is estimated using an expression (6). The crystallite shape of the Mn doped ZnO film is strongly related to the texture coefficient of the film. The doping molar variation of texture coefficient values for different lattice plane Mn doped ZnO thin films are shown in Fig. 5.

$$T_c (h_kl_i) = \frac{I(h_kl_i)}{I_0(h_kl_i)} \left[ \frac{1}{n} \sum \frac{I(h_kl_i)}{I_0(h_kl_i)} \right]^{-1}$$

(6)

where $I_0$ represents the standard intensity, $I$ is the observed intensity of $(h_kl_i)$ plane and $n$ is the reflection number. The (002) predominant plane orientation of the film has high texture coefficient value in 5 mM prepared MZO thin film. The texture coefficient of (002) predominant peak value is increases with increase of doping concentrations from 5 to 15 mM MnSO$_4$. Also other peaks texture coefficient value of (100), (101), (110), (102), (103) and (112) planes are increases with doping concentrations. The maximum value of predominant peak orientation of (002) is estimated at 2.66.

Table 1. Microstructural properties of various MnSO$_4$ concentrations prepared MZO thin films.

| Manganese sulphate concentrations (mM) | Crystallite size (nm) | Micro strain ($\varepsilon$) | Dislocation density ($\delta$) x 10$^{14}$ lines/m$^2$ | Stacking fault probability ($\alpha x 10^{-4}$) |
|--------------------------------------|-----------------------|----------------------------|---------------------------------------------|---------------------------------------------|
| 5                                    | 32.1                  | 0.00154                    | 9.69                                        | 9.91                                        |
| 10                                   | 40.9                  | 0.00127                    | 5.95                                        | 10.2                                        |
| 15                                   | 47.8                  | 0.00109                    | 4.36                                        | 10.5                                        |

Figure 3. Crystallite size and microstrain values variation of MZO thin films prepared at various molar concentrations of MnSO$_4$. 

3.3. Morphological Studies

The surface morphology Mn doped ZnO thin films were examined by scanning electron microscopy (SEM). Fig. 6 shows the SEM picture of Mn doped ZnO thin film prepared at 15 mM concentration of MnSO₄ concentration. The 15 mM concentration grown Mn doped ZnO films appear to be uniform with smaller grains and exhibits a structure with pores. The hexagonal shaped rod like grains with protruding of nano wires. This result is due to the increase in nucleation over-growth and the deposits are more compact with uniform grain structure. It is observed from the scanning electron micrograph of Mn doped ZnO film where average grain size about 250nm.
3.4. Optical Studies

Fig. 7 shows the variation of $(\alpha h \nu)^2$ with the photon energy for Mn doped ZnO thin films deposited on glass substrate. The absorption coefficient ($\alpha$) and incident photon energy ($h \nu$) can be related as

$$\alpha = \frac{A(h \nu - E_g)^n}{h \nu}$$  \hspace{1cm} (7)

where $A$ is a constant and $E_g$ is the band gap of the material. From the Tauc’s plot, the band gap value is found to be 3.20 eV prepared at 15 mM MnSO$_4$ concentration.

4. Conclusions

Mn doped zinc oxide thin films were coated onto glass substrates by using low cost SILAR technique. Thickness of the film increase with increasing ZnSO$_4$ molar concentration. The microstructural parameters were estimated. The preparation conditions were optimized for the growth of Mn doped ZnO thin films with excellent crystallites. From the SEM results the 15 mM
concentration grown Mn doped ZnO films appear to be uniform with smaller grains and exhibits a structure with pores. The hexagonal shaped rod like grains with protruding of nano wires and also observed from the scanning electron micrograph of Mn doped ZnO film where average grain size about 250nm. The calculated direct band gap of energy was 3.20 eV for Mn doped film.

References

[1] A. Hongsingthong et al., Preparation of ZnO thin films using MOCVD technique with D2O/H2O gas mixture for use as TCO in silicon-based thin film solar cells, Sol. Energ. Mat. Sol. Cells. 95(1) (2011) 171–174.

[2] I. Hotovy et al., Structural Characterization of sputtered indium oxide films deposited at room temperature, Thin Solid Films. 518(16) (2010) 4508–4511.

[3] J. Yang et al., Preparation of high quality indium tin oxide film on a microbial cellulose membrane using radio frequency magnetron sputtering, Chin. J. Chem. Eng. 19(2) (2011) 179–184.

[4] R. Kumaravel et al., Electrical, optical and structural properties of aluminum doped cadmium oxide thin films prepared by spray pyrolysis technique, Mater. Chem. Phys. 122(2) (2010) 444–448.

[5] B.G. Lewis, D.C. Paine, Applications and processing of transparent conducting oxides, MRS Bulletin. 25 (2000) 22–27.

[6] H. Kim et al., Electrical, Optical, and structural properties of indium-tin-oxide thin films for organic light-emitting devices, J. Appl. Phys. 86(11) (1999) 6451–6461.

[7] J.A.A. Selvan et al., A New light trapping TCO for nc-Si: H solar cells, Sol. Energ. Mat. Sol. Cells. 90(18) (2006) 3371–3376.

[8] Y. Yang et al., Highly transparent and conductive double-layer oxide thin films as anodes for organic light-emitting diodes, Appl. Phys. Lett. 89(5) (2006).

[9] C. Major et al., Optical and electrical characterization of aluminium doped ZnO layers, Appl. Surf. Sci. 255 (2009) 8907–8912.

[10] Y. Caglar et al., Crystalline structure and morphological properties of undoped and Sn doped ZnO thin films, Superlattices Microstruct. 46 (2009) 469–475.

[11] R.E. Treharne, K. Durose, Fluorine doped ZnO thin films by RF magnetron sputtering, Thin Solid Films. 519(21) (2011) 7579–7582.

[12] X. Noirfalise et al., Synthesis of fluorine doped zinc oxide by reactive magnetron sputtering, Acta Materialia. 59 (2011) 7521–7529.

[13] K. Ramamoorthy et al., Development of a novel high optical quality ZnO thin films by PLD for III–V opto-electronic devices, Curr. Appl. Phys. 6 (2006) 103–108.

[14] L. Cao et al., Highly transparent and conducting fluorine-doped ZnO thin films prepared by pulsed laser deposition, Sol. Energy Mater. Sol. Cells 95 (2011) 894–898.

[15] G. Srinivasan, J. Kumar, Optical and structural characterisation of zinc oxide thin films prepared by sol-gel process, Cryst. Res. Technol. 41 (2006) 893–896.

[16] M.T. Htay, Y. Hashimoto, K. Ito, Growth of ZnO submicron singlecrystalline platelets, wires, and rods by ultrasonic spray pyrolysis, Japanese Journal of Applied Physics. 46(1R) (2007) 440–446.

[17] M. Bizarro et al., Photocatalytic performance of ZnO: Al films under different light sources, International Journal of Photoenergy. 2012 (2012) 1–7.
[18] M. Karunakaran et al., The influence of Ni doping on the structural, optical and morphological properties of ZnO thin films grown by Silar method, Int. J. Curr Res. 4 (2012) 23–25.

[19] T.A. Vijayan et al., Comparative investigation on nanocrystal structure, optical, and electrical properties of ZnO and Sr-doped ZnO thin films using chemical bath deposition method, J. Mater. Sci. 43 (2008) 1776–1782.

[20] B.D. Cullity, Elements of X-ray diffraction, Addison-Wesley Publications Company Inc, Reading, Massachusetts, 1956.

[21] S. Valanarasu et al., Role of solution pH on the microstructural properties of spin coated cobalt oxide thin films, Journal of Nanoscience and Nanotechnology. 13 (2013) 1–6.

[22] V. Dhanasekaran, T. Mahalingam, Surface modifications and optical variations of (-111) lattice oriented CuO nano films for solar energy applications, Mater. Res. Bull. 48 (2013) 3585–3593.