Structural properties of pure and Sn doped ZnO thin film prepared using sol-gel method

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Abstract. In this work, the pure ZnO and Sn doped ZnO thin films with different volume ratios (2, 4, 6, and 8V/V) of tin chloride have been successfully prepared by using sol-gel method. The structural properties were investigated by using X-ray diffraction (XRD), Scanning electron microscope (SEM), and Atomic force microscope (AFM). The results showed that, pure ZnO and Sn doped ZnO thin films have polycrystalline in nature with hexagonal structure. The structure have different plane at (1 1 1),(0 0 2),(1 0 1),(1 0 2),(1 1 0),(1 0 3),(1 1 2) belong to $2\theta$ of 31.64, 34.30, 36.13, 47.43, 56.49, 62.73, 67.83 respectively. The orientation of (002) at $2\theta = 34.30$ has a narrow FWHM, low strain, and crystalline size equal to 4.913, 3.683, 3.686, 2.455, and 4.911 respectively for pure, Sn doped ZnO. Particle shapes were spherical granules morphology for all samples. The AFM images showed that the size of the grains on the surface of thin films increases with the increase in the concentration of impurity which agreement with the SEM results.

Keywords: zinc oxide, Tin impurities, sol gel, Roughness characterization, structural characterization.

1. Introduction

Thin films of transparent conducting oxides (TCOs) have gained a lot of significance because of their possible applications in photovoltaic and optoelectronic devices. Among the TCOs, the ZnO compound that belongs to the (II–IV) group of semiconductor[1], which has a direct broad energy band gap of 3.37 eV and big excitation binding energy of 60 meV [2]. ZnO thin film has a great interest due to their typical properties, such as abundant in nature, nontoxicity, thermal stability, high chemical[3]. ZnO thin films have a wide range of the applications including gas sensors, solar cells, laser systems, light emitting diodes (LED’s), transparent electrodes, antibacterial activities [4-9], and so on. Furthermore, (ZnO) may be used in a variety of applications as a pure material such as display and optical devices or it may be doped with elements like (Al, Ag, or Sn) to be a high conductivity or elements of Magnet (Mn, Co, or Ni) as the diluted magnetic materials [10]. Moreover, zinc oxid may be prepared by a various techniques, such as chemical vapour deposition (CVD), magnetron sputtering, pulsed laser deposition (PLD), reactive evaporation, spray pyrolysis, piezoelectrical, sol-gel [11-19], and so on. The sol-gel method has some advantages in compare with other techniques because of excellent compositional control, and homogeneity level because of the lower
crystallization temperature and mixing of liquid precursor simultaneously, the sol-gel method shows the possibility to prepare a large and small area coating of the zinc oxide thin film with a low cost for technology applications [20]. In this work, the interest was focused on Sn doped ZnO thin films prepared by sol-gel spin coating method.

2. Experimental part

In order to prepare Pure and Sn doped ZnO thin film using sol-gel spin coating method, zinc acetate dehydrate(Zn(CH₃COO)₂·2H₂O), tin chloride with 2-methoxyethanol as a solvent and monoethanolamine (MEA) as a stabilizer which add to the solution have been employed. The molar ratio of zinc acetate to MEA is 1.

First, zinc acetate in 2-Methoxyethanol with 1M of HCL and MEA were dissolved to produce pure ZnO, then the solution were stirred at 60°C for 1 hour to get transparent yellow solution in color. Then add of tin to ZnO solution with volume ratio (V/V) of 2%, 4%, 6% and 8% with stirred at 60°C for 30 minutes to obtain a homogenous ZnO aqueous solution which leaved to 24 hours at room temperature before deposition process. Secondly, Pure and Sn, doped ZnO were deposition on glass substrate using spin coating technique with spin speed of 2000 rpm for 60 sec and then dried on hot plate for 20 min at 200°C. Finally, the films annealed with furnace for 1 hours at 400°C to obtain crystallization of ZnO. These steps have been shown in Figure (1).

![Figure 1. Experimental process of prepared pure and Sn doped ZnO thin film.](image-url)
3. Results and discussion

3.1. Structural characterization

The XRD pattern was achieved through the use of the (Cu Kα) radiation (λ = 1.54056 Å) within the 2θ range from (20° to 80°) and as an X-ray detector has been Panalytical PIXcel3D. The X-ray diffraction pattern evolution for pure and Sn doped ZnO thin film as shown in Figure (2). All of the observed peaks may be indexed within (ZnO) wurtzite hexagonal structure by using (JCPDS data card No= 36-1451). Considering the XRD patterns, pure ZnO thin film has polycrystalline in nature and the peaks with the highest intensity were found at 2θ= 31.64, 34.30, 36.13, 47.43, 56.49, 62.73, 67.83 at plane (111), (002), (101), (102), (110), (103), (112) respectively shown in Figure (2-a). Moreover, Sn doped ZnO thin films have been reflected the some peaks as appearing in pure ZnO belong to Sn elements at 2θ=30.645, 44.903, 55.332, and 72.416 at plane (200), (211), (301), (420) respectively shown in Figure (2-b), which suggested that, the Sn doping has good linked with ZnO lattice; the other new peaks and shifted peaks to small distance due to fabrication of ZnSn(OH) which is become as result of ion exchange between the chlorides and HCl acid [21-22].

![Figure 2. XRD pattern for (a) Pure ZnO (b) Pure and Sn doped ZnO.](image-url)
The average crystallite size (C.S) of these samples were estimated by using Scherrer's formula[23]:

\[
C.S = \frac{0.9\lambda}{B\cos\theta}
\]  

(1)

Where:
\[
\lambda : \text{is the wavelength of X-ray equal to (1.54 Å), } \theta : \text{is the angle of Bragg diffraction and } B: \text{is the full width at half maximum (FWHM) of } \theta.
\]

The determined of crystallite sizes were changed, when Sn doping was varied from (2 to 8)%. In Table (1) it is obviously that after doping with Sn, (C.S) decreases significantly, with increasing Sn concentration, (C.S) increases slightly, in 8% Sn. The value of dislocation density (δ) determined by the formula:[24]

\[
\delta = \frac{1}{D^2}
\]  

(2)

The dislocation density (δ) is increased with increased doping concentration except doped Sn (8)% is decreased. The smaller dislocation density value (Parameters of defects) indicate that the films levels for crystallization are good. The decrease in crystallite size and relative increase in other parameters (dislocation density) with increasing Sn doping concentration clearly show that the deterioration of crystallinity.

| Sample       | 2θ    | FWHM  | D(nm)  | d (Å)   | δ *10^4 (nm)^2 |
|--------------|-------|-------|--------|---------|----------------|
| ZnO          | 34.3065 | 0.2952 | 4.915  | 2.61405 | 414            |
| ZnO-Sn2%     | 34.0709 | 0.3936 | 3.683  | 2.36151 | 737            |
| ZnO-Sn4%     | 34.3498 | 0.3936 | 3.686  | 2.61079 | 736            |
| ZnO-Sn6%     | 34.0926 | 0.5904 | 2.455  | 2.62989 | 1659           |
| ZnO-Sn8%     | 34.1379 | 0.2952 | 4.911  | 2.62651 | 415            |

3.2. morphological characterization

Surface morphology of thin films is very important tool to investigate microstructure of thin films. SEM micrograph of pure ZnO and doped Sn in a volume concentration (2, 4, 6 and 8)% thin films in Fig.2 (a-e) shows a homogeneous spherical granules spread over the surface of the film and it's similar size, and we note that the size of the granules increases with the increase in the concentration of impurity.
Figure 3. SEM images for pure & doped a) Pure ZnO b)ZnO-Sn 2% c)ZnO-Sn 4% d)ZnO-Sn 6% e)ZnO-Sn 8%.

AFM image showed that the samples have homogeneous spherical granular shapes a uniform distribution of the grains and the roughness increased with increasing the concentration reached the concentration of 8 percentage the roughness is decrease sharply as show in fig (4). These results including the roughness, RMS, and the average diameter were summarized in table (2).
Figure 4. AFM images of (a) pure ZnO, (b) ZnO-Sn 2%, (c) ZnO-Sn 4%, (d) ZnO-Sn 6%, and (e) ZnO-Sn 8%.

Figure 5. Roughness as function of concentration for: (a) pure ZnO, (b) ZnO-Sn 2%, (c) ZnO-Sn 4%, (d) ZnO-Sn 6%, and (e) ZnO-Sn 8%.
Table 2. Roughness parameters and Avg. Diameter.

| sample          | Roughness Average (nm) | Root Mean Square (nm) | Avg. Diameter (nm) |
|-----------------|------------------------|-----------------------|-------------------|
| p-ZnO           | 5.18                   | 6.62                  | 43.51             |
| ZnO-Sn2%        | 7.33                   | 9.29                  | 63.27             |
| ZnO-Sn4%        | 14.2                   | 18                    | 64.08             |
| ZnO-Sn6%        | 42.1                   | 56.1                  | 26.02             |
| ZnO-Sn8%        | 21.2                   | 27.9                  | 75.67             |

Conclusion

In this paper, pure ZnO and Sn doped ZnO in a various volume concentration (2, 4, 6 and 8)% thin films were successfully prepared by using simple and low cost sol-gel method. The prepared films have spherical granules morphology with uniform distribution of the grains. The size of the grains on the surface of thin films increases with the increase in the concentration of impurity. This result is agrees with the results of SEM images. The concentration of Sn elements play an important role on the structural properties of ZnO thin films. Sn dopes ZnO have consider as promising structure for optic limiting.

References

[1] H. Aydin, H. M. El-Nasser, C. Aydin, A. A. Al-Ghamdi, and F. Yakuphanoglu, Synthesis and characterization of nanostructured undoped and Sn-doped ZnO thin films via sol-gel approach, Appl. Surf. Sci., vol. 350, pp. 109–114, 2015.

[2] A. Karthick, G. Umadevi, and D. Pradhabhan, Structural, Optical and Antibacterial Activity Studies of Sn Doped Zno Thin Films Prepared By Chemical Spray Pyrolysis Technique, Int. J. Res. Anal. Rev., vol. 5, no. 4, 2018.

[3] M. Özgür et al., Sn doped ZnO thin film deposition using thermionic vacuum arc technique,” J. Alloys Compd., vol. 774, pp. 1017–1023, 2019.

[4] L. Wang, Y. Kang, X. Liu, S. Zhang, W. Huang, and S. Wang, ZnO nanorod gas sensor for ethanol detection, Sensors Actuators, B Chem., vol. 162, no. 1, pp. 237–243, 2012.

[5] L. Lu, J. Chen, L. Li, and W. Wang, Direct synthesis of vertically aligned ZnO nanowires on FTO substrates using a CVD method and the improvement of photovoltaic performance, Nanoscale Res. Lett., vol. 7, pp. 1–8, 2012.

[6] J. M. Szarko et al., Optical injection probing of single ZnO tetrapod lasers,” Chem. Phys.
Let., vol. 404, no. 1–3, pp. 171–176, 2005.

[7] K. M. Sandeep, S. Bhat, and S. M. Dharmaparaksh, Structural, optical, and LED characteristics of ZnO and Al doped ZnO thin films, *J. Phys. Chem. Solids*, vol. 104, pp. 36–44, 2017.

[8] T. Ootsuka *et al.*, Studies on aluminum-doped ZnO films for transparent electrode and antireflection coating of β-FeSi2 optoelectronic devices, *Thin Solid Films*, vol. 476, no. 1, pp. 30–34, 2005.

[9] Salam Hussein Ewaid *et al* 2021 IOP Conf. Ser.: Earth Environ. Sci. 722 012008

[10] B. Lallo da Silva, B. L. Caetano, B. G. Chiari-Andréo, R. C. L. R. Pietro, and L. A. Chiavacci, Increased antibacterial activity of ZnO nanoparticles: Influence of size and surface modification, *Colloids Surfaces B: Biointerfaces*, vol. 177, no. September 2018, pp. 440–447, 2019.

[11] Salam Hussein Ewaid *et al* 2021 IOP Conf. Ser.: Earth Environ. Sci. 790 012075

[12] A. A. G. Farrag and M. R. Balboul, Nano ZnO thin films synthesis by sol–gel spin coating method as a transparent layer for solar cell applications, *J. Sol-Gel Sci. Technol.*, vol. 82, no. 1, pp. 269–279, 2017.

[13] Z. Chen, K. Shum, T. Salagaj, W. Zhang, and K. Strobl, ZnO thin films synthesized by chemical vapor deposition, *2010 Long Isl. Syst. Appl. Technol. Conf. LISAT 10*, no. April 2015, 2010.

[14] P. Y. Dave, K. H. Patel, K. V. Chauhan, A. K. Chawla, and S. K. Rawal, Examination of Zinc Oxide Films Prepared by Magnetron Sputtering, *Procedia Technol.*, vol. 23, pp. 328–335, 2016.

[15] Salam Hussein Ewaid *et al* 2020 J. Phys.: Conf. Ser. 1664 012143.

[16] Ahmed Sabah Al-Jasimee *et al* 2020 J. Phys.: Conf. Ser. 1664 012141.

[17] Ahmed Alaa Kandoh *et al* 2021 IOP Conf. Ser.: Earth Environ. Sci. 790 012073

[18] E. H. H. Hasabeldaim, O. M. Ntwaeaborwa, R. E. Kroon, E. Coetsee, and H. C. Swart, Luminescence properties of Eu doped ZnO PLD thin films: The effect of oxygen partial pressure, *Superlattices Microstruct.*, vol. 139, no. February, p. 106432, 2020.

[19] A. J. Hashim, M. S. Jaafar, A. J. Ghazai, and N. M. Ahmed, “Fabrication and characterization of tetraleg zinc oxide nanostruture using evaporation methode, *Dig. J. Nanomater. Biostructures*, vol. 7, no. 2, pp. 487–491, 2012.

[20] F. Paraguay D., W. Estrada L., D. R. Acosta N., E. Andrade, and M. Miki-Yoshida, Growth, structure and optical characterization of high quality ZnO thin films obtained by spray pyrolysis, *Thin Solid Films*, vol. 350, no. 1, pp. 192–202, 1999.
[21] D. Bhatia, H. Sharma, R. S. Meena, and V. R. Palkar, A novel ZnO piezoelectric microcantilever energy scavenger: Fabrication and characterization, *Sens. Bio-Sensing Res.*, vol. 9, pp. 45–52, 2016.

[22] N. V. Kaneva and C. D. Dushkin, Preparation of nanocrystalline thin films of ZnO by sol-gel dip coating, *Bulg. Chem. Commun.*, vol. 43, no. 2, pp. 259–263, 2011.

[23] A. Mortezaali, O. Taheri, and Z. S. Hosseini, Thickness effect of nanostructured ZnO thin films prepared by spray method on structural, morphological and optical properties, *Microelectron. Eng.*, vol. 151, pp. 19–23, 2016.

[24] J. A. Alvarado, A. Maldonado, H. Juarez, and M. Pacio, Synthesis of colloidal ZnO nanoparticles and deposit of thin films by spin coating technique, *J. Nanomater.*, vol. 2013, 2013.

[25] Z. Pan *et al.*, Investigation of optical and electronic properties in Al-Sn co-doped ZnO thin films, *Mater. Sci. Semicond. Process.*, vol. 16, no. 3, pp. 587–592, 2013.

[26] M. García-Gabaldón, V. Pérez-Herranz, J. García-Antón, and J. L. Guñón, Effect of hydrochloric acid on the transport properties of tin through ion-exchange membranes, *Desalin. Water Treat.*, vol. 10, no. 1–3, pp. 73–79, 2009.

[27] G. Cifuentes, N. Guajardo, and J. Hernández, Recovery of hydrochloric acid from ion exchange processes by reactive electrodialysis, *J. Chil. Chem. Soc.*, vol. 60, no. 4, pp. 2711–2715, 2015.

[28] R. K. Fakher Alfahed, A. S. Al-Asadi, H. A. Badran, and K. I. Ajeel, Structural, morphological, and Z-scan technique for a temperature-controllable chemical reaction synthesis of zinc sulfide nanoparticles, *Appl. Phys. B Lasers Opt.*, vol. 125, no. 3, p. 0, 2019.

[29] N. Chahmat, T. Souier, A. Mokri, M. Bououdina, M. S. Aida, and M. Ghers, Structure, microstructure and optical properties of Sn-doped ZnO thin films, *J. Alloys Compd.*, vol. 593, pp. 148–153, 2014.

[30] Hamid Awad, S. (2019). EFFECT OF DEPOSITION PARAMETERS ON MECHANICAL PROPERTIES OF TIN FILMS COATED ON 2A12 ALUMINUM ALLOYS BY ARC ION PLATING (AIP). Al-Qadisiyah Journal Of Pure Science, 24(1), 1 - 6.

[31] Hameed Hamzah, S. (2019). Generalized Limit Sets. Al-Qadisiyah Journal Of Pure Science, 24(1), 7 - 12.