Morphological And Compositional Variations of Zno/Mg Thin Films Prepared By SILAR Method

M. Karunakaran[1], K. Radhi Devi[2], G.Selvan[3], G.Rajesh Kanna[4], K. Kasirajan[5], V. Annalakshmi[6]
[1, 2, 3, 5, 6] Dept of Physics
[4]Dept of Electronics
[1, 5, 6] Alagappa Government Arts College, Karaikudi – 630 003, India
[2]Sethupathy Govt. Arts College, Ramanathapuram-623 502, India
[3]Thanthai Hans Roever College, Perambalur - 621 220, India.
[4]Government. Arts College for Women, Ramanathapuram- 623 502, India.

Abstract- *Mg doped zinc oxide (ZnO/Mg) thin films have been successfully grown onto glass substrates by Low cost SILAR method by varying doping concentration as well as dipping cycle. The prepared films structural, morphological, compositional properties were studied using X-ray diffraction (XRD), scanning electron microscope (SEM) and EDAX spectrophotometer respectively. The structure of the films were found to be hexagonal structure with polycrystalline in nature with preferential orientation along (002) plane. Morphological results showed that the 'Mg' doping concentration and dipping cycle has a marked effect on morphology of the 'Mg' doped ZnO thin films. EDAX studies showed that the presence of Zinc and oxygen content and also a doping metal Mg ions.*

Keywords- Thin Films, XRD, Morphological Studies, Compositional Analysis,

I. INTRODUCTION

A great deal of attentions has been paid to the Transparent Conductive Oxide (TCO) thin films due to their plenty applications such as transparent electrodes in flat panel displays, touch panels and solar cells. Zinc oxide (ZnO) is one of the most promising TCO materials because ZnO is an abundant, low-cost, and non-toxic material [1]. The intrinsic n-type semi-conductivity of ZnO arises from such structural defects as oxygen vacancies and zinc interstitials [2]. For improving its electrical conductivity, ZnO was doped with other metal elements such as boron, aluminum, gallium, magnesium etc. The resistivity of MZO thin films are over 105 Ω cm and nearly equivalent to the resistivity of intrinsic ZnO. To promote the electrical conductivity of MZO films, it was suggested that extra dopant be added to the MZO thin films such as gallium [3]. There are few limitations in the application of pure ZnO for integrated optical devices which require a much wider band gap [4]. The band gap of ZnO can be tailored by alloying ZnO with group II elements e.g. Be, Mg, Ca, Cd, and Sr [5]. Moreover, the radius of the Mg^{2+} ion (0.57 Å) closely matches with the radius of Zn^{2+} ion (0.60 Å), so the incorporation of Mg^{2+} ion into ZnO lattice is quite favorable, thus forming MZO. Mg-doped ZnO thin films have been prepared using various methods, such as spray pyrolysis [6], pulsed laser deposition [7], chemical vapor deposition [8], radio frequency (rf) magnetron sputtering [9,10], electro-deposition [11], SILAR method [12], the sol–gel method technique [13]. It is also experimentally established that the structural and optical properties of these thin films are very sensitive to the deposition conditions [14]. Among these deposition techniques, SILAR has many advantages such as simplicity, low cost and reproducibility. 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. In this study, Mg doped ZnO thin films were deposited by SILAR technique on amorphous glass substrates. The variation in the influence of Mg doping concentration and dipping cycle of ZnO thin films is investigated.

II. EXPERIMENTAL PROCEDURE

2.1. Synthesis

In this study Mg doped ZnO thin films were prepared using a cost effective modified SILAR method. Mg doped ZnO thin films were grown using a two-step successive immersion of a precleaned glass substrate using a solution comprising 0.1 M Zinc sulphate (99% e-Merck), 0.2 M sodium hydroxide with a pH value of 9±0.2 and suitable amount of Magnesium sulphate deposited at bath temperature of 90^0C under optimized condition. 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 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. In the present study, the doping concentration of Magnesium sulphate is varied such as 5, 10 and 15 (at wt %) and also change the dipping cycle like 60, 80 and 100 cycles.

2.2. 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) with EDAX

III. RESULTS AND DISCUSSION

3.1. XRD Analysis:

Figure 1 (a) shows the XRD pattern of various concentration of Mg such as (Mg=5%, 10% and 15%) doped ZnO thin films. The XRD studies revealed that the SILAR coated ZnO/Mg films exhibited hexagonal structure with polycrystalline in nature. The observed'd' spacing values were indexed with JCPDS standards [36-1451]. The XRD results revealed that the (002) lattice orientation is preferentially oriented for prepared at various doping level of Mg doped zinc oxide thin films. Also other peaks corresponding to planes (100), (101), (102), (110), (103) and (112) lattice orientations were present for prepared films. The intensity of (002) plane decreases with increases of Mg percentage. The various dipping cycle like 60, 80 and 100 prepared XRD pattern is shows in Figure 1 (b). In this XRD also same peaks are appeared. From figure 2 (b) we observed that, the high major peaks (100), (002) and (101) increases when the dipping cycle increases. This clearly indicated that the crystalline quality of the sample increases with dipping cycle.

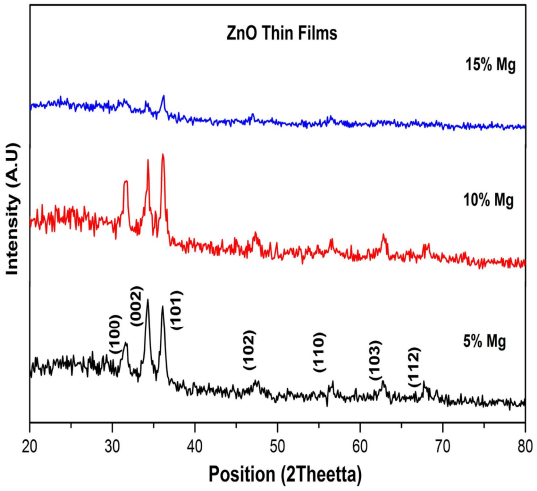

Figure 1 (a): XRD pattern of ZnO/Mg Thin films (at Mg doping level 5%, 10% and 15%)

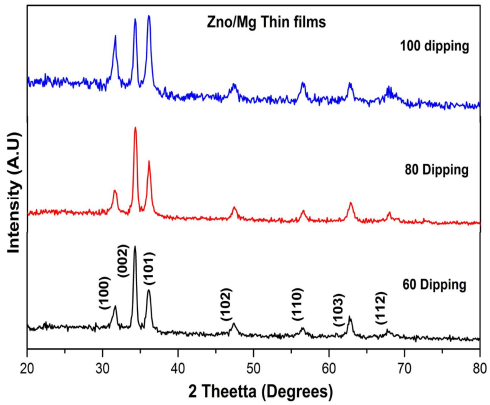

Figure 1(b): XRD pattern of ZnO/Mg Thin films (at various dipping cycle)

3.2. SEM and EDAX Analysis:

Figure 2 (a-c) shows the morphology as obtained from SEM images of prepared Mg doped ZnO thin films with the Mg doping level of 5%, 10% and 15% respectively. Typical magnifications around 1–20K were employed for the samples. At low magnification, samples appear very homogeneous and compact. However, at high magnifications (5 µm), the differences observed in terms of chemical composition are reflected also in the morphology of films. It is also possible to observe that these large grains are made up of many smaller crystallites within them. It is observed that the films are continuously formed and consists of some spherical shapes. The size of the spherical particles are reduces and more vacancies are created with increasing a Mg doping content. For 15% Mg doping, we observed that tha particles are small in size and also it has more voids. It is clearly reflect from XRD pattern recorded for higher Mg doping level (15 %) in figure 1 (a).

Figure 2 (d-f) shows the Mg doped ZnO morphology of various dipping such as 60, 80 and 100. For comparison, the SEM micrographs obtained for various dipping in higher magnifications are also included in figure 2 (d-f). The thickness improvement via additional dipping changes the morphology considerably as shown in figure 2 (d-f). This is understandable as the ionic and atomic radii of Mg are considerably larger and also addition of layers to the surfaces would alter the state considerably leading to different morphologies. The various morphologies like needle, rod and flower structure. The dopant atoms occupancy is one of the reasons for various morphology formations. This can be explained by the following kinetics. The voids in the structure may invite more atoms to make them as sites. Different number of dipping in SILAR not only produces more layers but also adds more atoms to these vacant sites and intertials. Due to the nucleation in these sites and subsequent growth of the layer initially the one dimensional growth is favored. This leads to a needle like grains and their spreading to entire surface. The continuous growth of these grains and agglomerations leads to a various morphology. Many rods may be joined together forming a typical spinal structure. With the increase of Mg content in the film, strain in the film also increases which tends to resist this growth.

The EDAX spectrum with elemental mapping of SILAR grown Mg doped ZnO film is shown in figure 3 (a-f). From figure 3 (a-) EDAX elemental mapping shows the uniform distribution of Mg and ZnO which confirms the formation of ZnO/Mg film. In this system no carbon contamination was present. However, the blocky particles present in the film surface are also found to be made of Mg and Zn with different composition as is evinced by the variation in Mg intensity seen in EDAX. At higher doping of Mg, these spherical grains tend to agglomerate and due to thermal energy associated become a layer adhering to the adjacent layers adhered to the substrate which before being crystallized becomes sites for the molecules which once again try to agglomerate. The difference in energy used in the film formation process required adhering to the substrate and the cohesive bonding required for subsequent layer group might have supplied the thermal energy needed for the agglomerates. Such process lead to a morphology as revealed in figure 3 (d-f). The islands of grains that can be used for various applications.

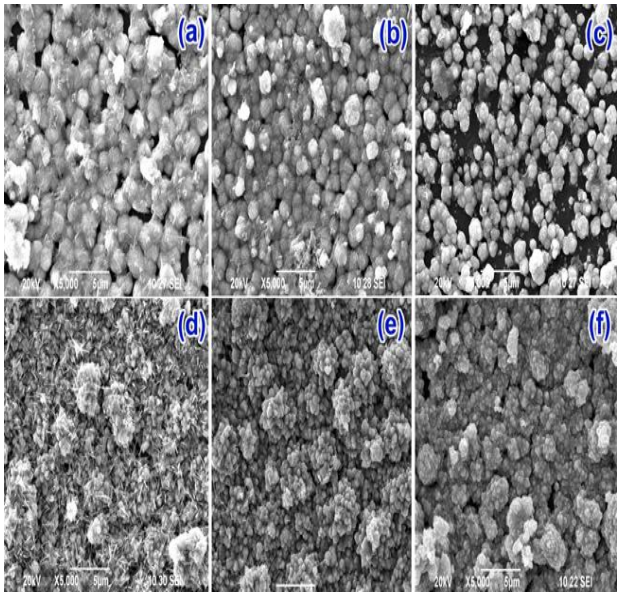

Figure 2: SEM images of ZnO/Mg thin films

Table 2: Compositional analysis of ZnO/Mg thin films

Element	Mn doping Concentration			No. of Dipping		
	5%	10%	15%	60	80	100
ZnK	61.04	63.84	66.12	60.49	56.64	55.07
OK	38.02	34.83	31.07	38.30	41.47	41.95
MgK	0.94	1.33	2.81	1.21	1.89	2.98

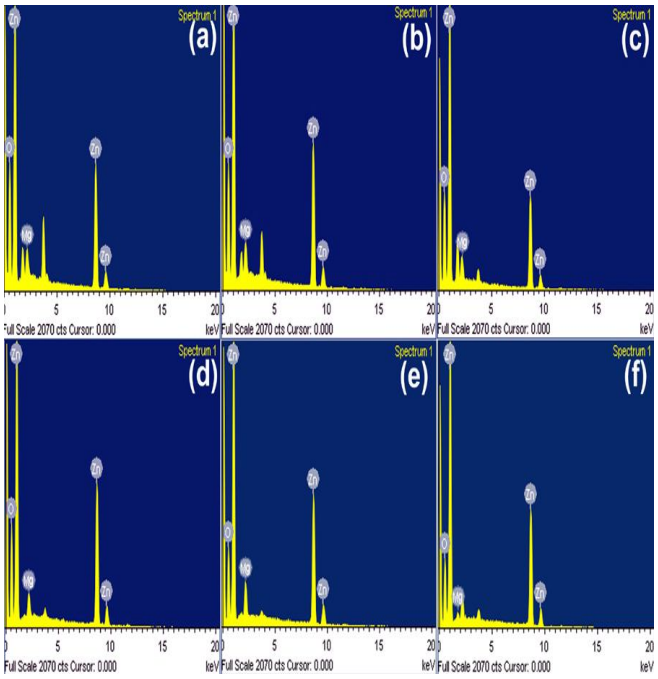

Figure 3: EDAX spectra of ZnO/Mg thin films

IV. CONCLUSION

Mg doped oxide thin films were coated onto glass substrates by using low cost SILAR method by varying Mg

doping concentrations (Mg=5%, 10% and 15%) and dipping numbers such as 60, 80 and 100. XRD studies revealed that the prepared samples were polycrystalline and hexagonal structure. From SEM and EDAX data we observed that by altering dipping condition we can alter thickness as well as morphology. We can change the morphology simply alter the doping concentration or change the dipping number. The change in morphology leads to the sample in numerous applications.

REFERENCES

[1] C. F. Yu, S. H. Chen, S. J. Sun, H. Chou, Appl. Surf. Sci. 257, 6498 (2011).
[2] X. L. Chen, X. H. Geng, J. M. Xue, L. N. Li, J. Cryst. Growth 299, 77 (2007).
[3] D.J. Cohen, K. C. Ruthe, S. A. Barnett, J. Appl. Phys. 96, 459 (2004).
[4] R. Hunger, K. Iwata, P. Fons, A. Yamada, K. Matsubara, S. Niki, MRS Proceedings 668(H2), 8 (2001).
[5] T. Makino, Y. Segawa, M. Kawasaki, A. Ohtomo, R. Shiroki, K. Tamura, Applied Physics Letters 78(1237), 1 (2001).
[6] P.P. Sahay, S. Tewari, R.K. Nath, Cryst. Res. Technol. 42 (2007) 723.
[7] E. Bellingeri, D. Marre, I. Pallecchi, L. Pellegrino, G. Canu, A.S. Siri, Thin Solid Films 486 (2005) 186.
[8] C.W. Lin, T.Y. Cheng, L. Chang, J.Y. Juang, Phys. Stat. Sol. (c) 1 (2004) 851.
[9] P. Wang, N. Chen, Z. Yin, R. Dai, Y. Bai, Appl. Phys. Lett. 89 (2006) 202102.
[10] M.K. Jayaraj, Bull. Mater. Sci. 25 (2002) 227.
[11] M. Fahoume, O. Maghfoul, M. Aggour, B. Hartiti, F. Chraibi, A. Ennaoni, Sol. Energy Mater. Sol. Cells 90 (2006) 1437.
[12] S. Dineshraj, M. Karunakaran, K. Kasirajan, V.Annalakshmi, S. Maheswari, International Journal for Research in Applied Science & Engineering Technology, 5(XII), 2017 464-469.
[13] G. Srinivasan, J. Kumar, Cryst. Res. Technol. 41 (2006) 893.
[14] K. Yoshino, T. Hata, T. Kakeno, H. Komaki, M. Yoneta, Y. Akaki, T. Ikari, Phys. Stat. Sol. (c) 2 (2003) 626.