

## STRUCTURAL AND SIMS STUDY OF ZnO: Er, Yb THIN FILMS GROWN BY SOL-GEL SPIN COATING

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### ABSTRACT

The use of ZnO thin films have been proposed for the design of multilayer optical storage disks, photo luminescent screens for optically written displays and photovoltaic cells that capture sub-band gap solar radiation. ZnO is a promising material for optoelectronic devices and solar cells. ZnO thin films doped with rare earth materials (Er<sup>3+</sup>/Yb<sup>3+</sup>) were deposited on Si (100) substrates using the sol-gel spin coating technique. The effect of Yb<sup>3+</sup> concentration on the structure and particle morphology of the films was examined. These thin films may find applications in optoelectronic devices and to the increase in the efficiency of solar cells.

**KEYWORDS:** ZnO, Rare Earths, Thin Films

Polycrystalline films may also have different luminescence mechanisms as compared to the bulk material. The II-VI compounds, such as transparent and conducting oxides films, have been attracting as starting material for electro-luminescent devices because of their high visible transmittance and low electrical resistivity in the visible region. In the past decade, ZnO has been explored for new device applications when extra functionalities are intentionally introduced through proper doping or alloying with impurity ions despite the considerable challenges [1-4]. It is worth noting that much effort has also been made through doping rare earth (RE) ions (e.g. Er<sup>3+</sup>, Eu<sup>3+</sup> and Yb<sup>3+</sup>) into the ZnO host lattice, which undergoes upconversion (UC) luminescence and/or energy transfer, in realizing new optoelectronic and photonic device applications, such as solid-state full-colour displays, infrared detectors, solar cells, biological fluorescent labels and all-solid compact lasers [5-7]. The preparation of zinc oxide thin films has been the subject of continuous research for different field of application. Many techniques are used for preparing this transparent conductive ZnO such as: RF sputtering [8], evaporation [9], chemical vapour deposition [10], ion beam sputtering [11], spray pyrolysis [12] and spin coating technique [13-15]. Among these methods spin coating method has attracted considerable attention due to its simplicity and large scale with low-cost fabrication. Additionally, by using this technique one can produce large area coatings without the need of ultrahigh vacuum.

In this work, we report the fabrication, structural, morphological and luminescent properties of a multifunctional ZnO transparent hybrid material by additionally doping Er<sup>3+</sup> and Yb<sup>3+</sup> ions. The Er<sup>3+</sup> concentration made constant (3 mol %) and Yb<sup>3+</sup> concentration varied from 6 to 12 mol%. The experimental results considerably increase the possibilities of this ZnO hybrid material for various potential applications.

### METHODOLOGY OF THIN FILMS DEPOSITION

For the synthesis of ZnO sol, zinc acetate dihydrate [Zn (CH<sub>3</sub>COO)<sub>2</sub> · 2H<sub>2</sub>O, Alfa Aesar] was used as the zinc source. 2-methoxy ethanol [(CH<sub>3</sub>)<sub>2</sub>CHOH (AR, Merck)] and monoethanolamine (MEA) [H<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>OH, Merck], were used as solvent and stabilizer, respectively. The zinc precursor solution of concentration 0.2 mol/l was prepared by dissolving zinc acetate dihydrate in methanol. MEA was then added into the solution. The molar ratio of the MEA/zinc solution was fixed at 1. The sol-gel technique was used to prepare a transparent solution that was obtained after stirring the mixture for 1 h. The concentration of Yb<sup>3+</sup> was varied from 6 to 12 mol% by changing the amount of Yb (NO<sub>3</sub>)<sub>3</sub> in the solution, while that Er<sup>3+</sup> concentration was fixed at 3 mol%. Thin films of ZnO synthesized via the sol-gel method were spin coated on Si (100) substrates. The solution was spin-coated onto Si (100) substrates at 2500 rpm for 30 s. The as-deposited films were dried at 230 °C for 10 min on a hot plate to evaporate the solvent. This was

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repeated several times to obtain the required thin films. Finally, the samples were annealed at 1000 °C for 2 h to make the thin films optical active. A schematic representation of the sol-gel synthesis and spin-coating procedure is shown in Fig. 1.

X-ray diffraction (XRD) patterns of the films were recorded using a Bruker D8 diffractometer. The surface

topography of the films were examined using a Shimadzu SPM-9600 atomic force microscope (AFM). Time of flight secondary ion mass spectroscopy (TOF-SIMS) measurements were performed using IONTOF TOF-SIMS. All measurements were performed at room temperature.

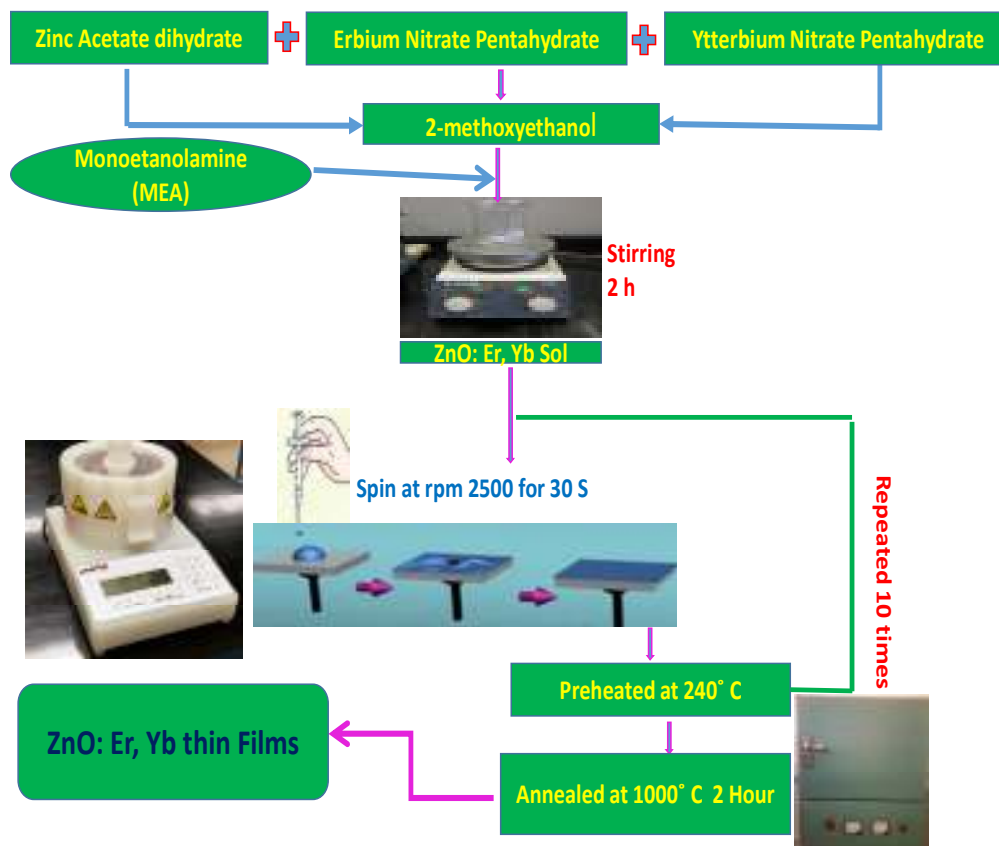


Figure 1: A schematic representation of the sol-gel synthesis ZnO thin films

## RESULTS AND DISCUSSION

### X-ray Diffraction

X-ray diffraction is used to determine the crystal structure of the microcrystalline materials and to determine if they are single phase. X-rays with a wavelength of 0.154 nm (Cu - K $\alpha$  radiation) are diffracted by the sample. The XRD patterns of the thin film samples (ZnO: Er<sup>3+</sup>3% /Yb<sup>3+</sup> x %) are shown in Fig. 2. The patterns indicate that all the films were preferentially orientated along the (002) direction and crystallized in a hexagonal wurtzite structure of ZnO (JCPDS card no: 36-1451). The non-varying

hexagonal structure and lack of any impurity peaks in the XRD patterns suggest that Er and Yb atoms were homogeneously distributed within the ZnO lattice [16]. The X-ray diffraction pattern of ZnO thin films deposited on Si substrate using ZnO: Er<sup>3+</sup>/Yb<sup>3+</sup> powder solution with different Yb concentration and annealed at 1000 °C (Fig. 2). Yttrium oxide (Yb<sub>2</sub>O<sub>3</sub>) and Zinc oxide peak are observed in the powder XRD pattern matched with the JCPDS 01-077-0457 and 01-079-0208 respectively. The (002) preferential orientation was observed for all the ZnO: Er<sup>3+</sup>/Yb<sup>3+</sup> thin films. The (002) peak intensity increased from 6 to 10 mol%. This indicates that a higher Yb

contribution led to a decrease in the crystallinity of the ZnO, as has been reported for other additive elements such as La and Pb [17]. It is clearly observed that no other phase of Yb<sub>2</sub>O<sub>3</sub> and Er<sub>2</sub>O<sub>3</sub> appeared in XRD patterns, indicating a well incorporation of Er<sup>3+</sup> and Yb<sup>3+</sup> ions into ZnO matrix during deposition process. Actually, the Er<sup>3+</sup> and Yb<sup>3+</sup> ions were incorporated in the matrix by the substitution of Zn<sup>2+</sup> ions [18]. Kumar et al. [19] observed that Si only diffused up to a certain concentration into the ZnO matrix. The crystallite size was determined by using the Scherrer's equation [20];

$$D = \frac{K\lambda}{\beta \cos\theta}$$

where K is a constant (0.94), λ is the wavelength (λ = 0.154 nm for Cu Kα X-rays) and β is the full width at half maximum (FWHM). Using the (002) peaks, this gives the minimum crystallite size of 19 nm obtained for 10 mol% Yb doped ZnO.

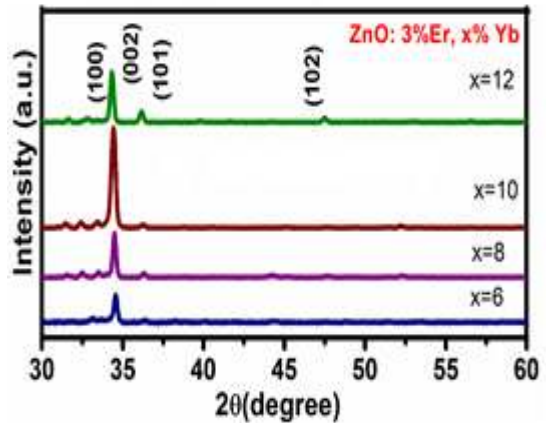


Figure 2: X-ray diffraction pattern ZnO: Er<sup>3+</sup>3% /Yb<sup>3+</sup> x% thin films within 20 to 80 diffraction angle

### Atomic Force Microscopy

The AFM 3D images of ZnO: Er<sup>3+</sup>/Yb<sup>3+</sup> thin films annealed at 1000°C (Er 3 mol%, Yb 6→12 mol%) are presented in Fig. 3. It is clear that the Yb<sup>3+</sup> and Er<sup>3+</sup> incorporated films consisted of nano-sized ZnO particles. The particle distribution of the ZnO films are all very homogeneous. The surface roughness (RMS) particle size were slightly affected with the addition of the Yb ion concentration into the ZnO thin films.

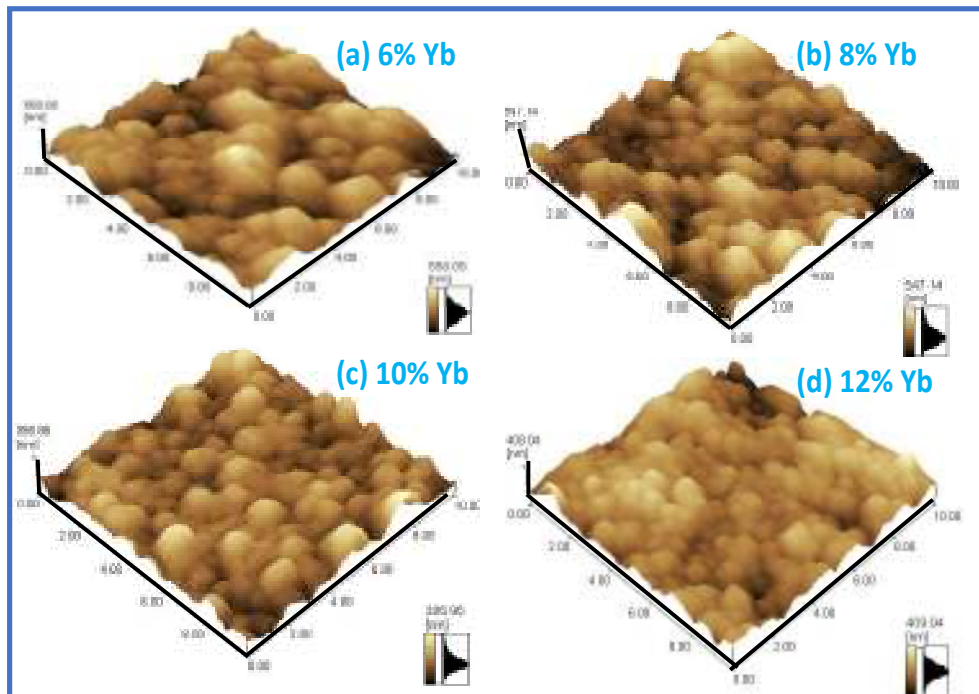


Figure 3(a-d): AFM 3D images of ZnO:Er<sup>3+</sup>/Yb<sup>3+</sup> thin films annealed at 1000°C (Er 3 mol%, Yb 6→12 mol%).

### Secondary Ion Mass Spectroscopy (SIMS)

TOF-SIMS is one of the most significant surface sensitive techniques for identifying the elemental, isotopic or molecular composition of the surface of the thin film samples. TOF-SIMS was performed on all the different Yb<sup>3+</sup> ion (Yb 8%, Yb 10%) co-doped ZnO:Er<sup>3+</sup> thin films to analyze the elemental composition of the films as a function

of depth. These elements were Zn, Si, Er and Yb show positive ion spectroscopy was performed using a base pressure of  $1.2 \times 10^{-8}$  mbar. The elemental analysis, measured over the total analyzed area, as a function of depth of the ZnO: Er<sup>3+</sup>/Yb<sup>3+</sup> (8 mol%) and ZnO:Er<sup>3+</sup>/Yb<sup>3+</sup> (10 mol%) are shown in Fig. 4. As expected, the Yb<sup>3+</sup> ion content was more in the Yb<sup>3+</sup> (10 mol%) thin films as compared to the Yb<sup>3+</sup> (8 mol%) film.

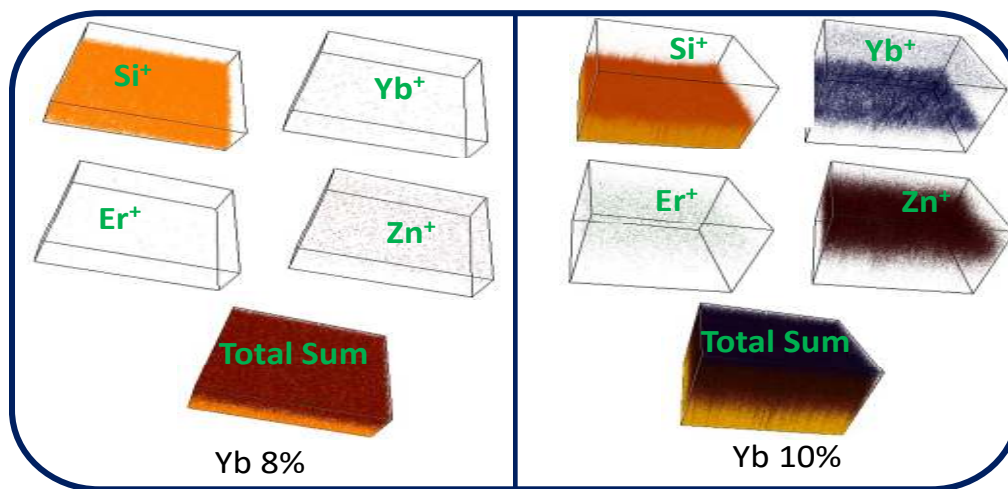


Figure 4: TOF-SIMS of ZnO:Er<sup>3+</sup>/Yb<sup>3+</sup> thin films for different Yb<sup>3+</sup> ion (Yb 8%, Yb 10%)

### CONCLUSION

Er<sup>3+</sup> and Yb<sup>3+</sup> co-doped ZnO thin films were successfully deposited by a conventional sol-gel spin coating technique. The XRD results conclude that it contains wurtzite hexagonal structure. The XPS results confirmed that the defect concentration in the films also effected with Yb concentration. The AFM analysis revealed that the films consisted of nano-sized particles. Mapping of the thin film shows the uniform distribution of atoms. The RMS surface roughness values were varied with increasing Yb<sup>3+</sup> concentration. The SIMS study confirm the doping of Yb<sup>3+</sup> and Er<sup>3+</sup> ions in the ZnO thin films, and these results lead to high luminescence efficiency and may be considered as potentially active components in new optoelectronic devices.

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### REFERENCES

- Ozgur U., Alivov Y.I., Liu C., Teke A., Reshchikov M.A., Dogan S., Avrutin V., Cho S.J. and Morkoc H., 2005. *J. Appl. Phys.*, **98**: 041301.
- Schmidt-Mende L. and MacManus-Driscoll J.L., 2007. *Mater. Today*, **10**: 40.
- Karlsson T. and Ross A., 1984. *Sol. Energy Mater.*, **10**: 105-119.
- Jebril S., Kuhlmann H., Muller S., Ronning C., Kienle L., Duppel V., Mishra Y.K., Adelung R., 2010. *Cryst. Growth Deg. Commun.*, **10**: 2842-2845.
- Pathak T.K., Kumar V., Swart H.C. and Purohit L.P., 2016. *Physica E77*: 1-6.
- Zeng X.Y., Yuan J.L., Wang Z.Y. and Zhang L.D. 2007. *Adv. Mater.*, **19**: 4510.

- Liu Y.X., Yang Q.B. and Xu C.F., 2008. *J. Appl. Phys.*, **104**: 064701.
- Trilok K. Pathak, Vinod Kumar, L.P. Purohit, H.C. Swart, R.E. Kroon, *Physica E* 84 (2016) 530–536.
- K. Haga, F. Katahira, H. Watanabe, *Thin Solid Films* 344 (1999) 145.
- Y. Natsume, H. Sakata, T. Hirayama, H. Yanigida, *J. Appl. Phys.* 72 (1992) 4203.
- M. Ruth, J. Tuttle, J. Goral, R. Noufi, *J. Crystal Growth* 96 (1989) 363.
- A. Ortiz, C. Falcony, J. Hernandez, M. Garcia, J.C. Alonso, *Thin Solid Films* 293 (1997) 103.
- Trilok Kumar Pathak, Vinod Kumar, H.C. Swart, L.P. Purohit, *Physica B* 480 (2016) 31–35.
- Z.R. Khan, M.S. Khan, M. Zulfequar, M.S. Khan, *Mater. Sci. Appl.* 2 (2011) 340–345.
- M. Zaharescu, S. Mihaiu, A. Toader, I. Atkinson, J. Calderon-Moreno, M. Anastasescu, M. Nicolescu, M. Duta, M. Gartner, K. Vojisavljevic, B. Malic, V. A. Ivanov, E.P. Zaretskaya, *Thin Solid Film* 571(3)(2014)727–734.
- G. Turgut, E. Sonmez, *Metall. Mater. Trans. A* 45 (2014) 3675–3685.
- F. Cai, L. Zhu, H. He, J. Li, Y. Yang, X. Chen, Z. Ye, *J. Alloys Compd.* 509 (2011) 316–320.
- R. Elleuch, R. Salhi, N. Maalej, J. L. Deschanvres, and R. Maalej, *Mater. Sci. Eng., B* 178, 1124 (2013).
- Vinod Kumar, Odireleng M. Ntwaeaborwa, Hendrik C. Swart, *J. Colloid Interface, Sci.* 465 (2016) 295–303.
- Trilok K. Pathak, Ashwini Kumar, C. W. Swart, H. C. Swart and R. E. Kroon, *RSC Adv.* 6 (2016) 97770.