

Photoluminescence Study of Sol-Gel Derived Hf-/In- Doped ZnO Thick Films

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Abstract

Thick films of undoped ZnO and Hf/In doped ZnO were synthesized by sol-gel process followed by screen-printing. The microstructural and optical properties of prepared thick films were studied in order to study the effects of variation in dopant ions. Microstructural studies by X-ray diffraction analysis revealed the hexagonal ZnO formation in undoped as well as in Hf-/In-doped ZnO thick films. Both of the dopants induced lowering of the transmittance and also the optical band-gap. The photoluminescence spectra of undoped sample as well as doped samples show one emission peak in UV region, and a broad-band emission in visible region. The sample doped with Hf-/In- showed significant reduction in luminescence as compared to undoped ZnO.

Keywords: ZnO; Photoluminescence; XRD; Thick films; Screen printing

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1. Introduction

Zinc oxide (ZnO) is a widely studied semiconductor material due to its unique physical, optical and chemical properties. Owing to these peculiar combinations of properties, ZnO has emerged as a choice of material for various electronics, optoelectronics, and energy harvesting applications [1 – 4]. The wide versatility of ZnO stems from several intrinsic/extrinsic advantages as a functional material; low cost, high electron mobility, transparency, and easy fabrication into various forms including pellets, thin films and various nanostructures. ZnO exhibits a stable wurtzite crystal structure under ambient conditions, and possesses band-gap as 3.37 eV in bulk form. With a variety of dopants (i.e. Al, Ga, In, Ni, Hf, Zr, Ti etc) the electrical and optical properties of ZnO can be enhanced for the desired use [5–13]. Transparent conductive characteristics of ZnO films are reported to be controlled by the dopants' concentration and defects creation by O vacancies [9]. The doping with group IIIa elements (such as In, Al) in ZnO are reported in order to produce n-type semiconductor [7, 9, 10, 13]. Doping of IVb group elements (such as Hf, Zr and Ti) improved the intrinsic defects and over high interface trap density in ZnO [11]. The optical properties of doped-ZnO are substantially different from its undoped form and also depends on the crystallite size and form (nanostructure, thin film, bulk). Such variation can tune the band-gap and luminescent properties of ZnO in the near ultra violet and visible regions. The emission properties of ZnO in the visible region widely depend on their synthesis method and also depend on surface defects [14]. Nanostructures emit visible luminescence stronger than bulk crystals due to the concentration of oscillator strength into just a few transitions. Therefore, obtaining reasonable luminescence in thick layers/bulk ZnO pellets is considered challenging.

For the growth of ZnO, number of deposition methods have been employed such as molecular beam epitaxy [15], magnetron sputtering [16], chemical vapour deposition [17], metal-organic chemical vapor deposition [18] and solution-based chemical methods such as sol-gel [12 – 14, 19, 20], hydrothermal [21] and electrochemical deposition [22] methods.

Requirement of vacuum system makes vacuum-based methods expensive for large scale deposition [23]. On the other hand, the popularity of sol-gel methods comprising of techniques such as spin coating [19], dip coating [24], spray pyrolysis [25] etc. have increased mainly due to their promising advantages i.e. low cost, high throughput, and large area coverage. In comparison to widely reported works in nanoparticle, thin film and bulk form, reports on thick film form of undoped and doped ZnO are sparsely available [26]. Development of thick films with an economic method paves their potential use in fabrication of low-cost devices.

This work presents an economic sol-gel based synthesis to yield micron sized layers of undoped and Hf/In doped ZnO deposited by screen-printing method. The microstructural and optical properties are presented and correlated to elucidate the role of doping and dopant type.

2. Materials and Methods

Zinc acetate dehydrated [$\text{Zn}(\text{CH}_3\text{COOH})_2 \cdot 2\text{H}_2\text{O}$] ($\geq 98\%$ Sigma Aldrich), Hafnium (IV) chloride (HfCl_4) ($>98\%$ Sigma Aldrich), Indium (III) chloride (anhydrous powder, $\geq 99.99\%$ Sigma Aldrich), Ethanolamine (MEA) and Ethylene glycol (AR 99%) were procured. Undoped ZnO gel was prepared by sol-gel processing. For preparation of undoped ZnO, primary sol of 0.50 M was prepared by dissolving appropriate amount of zinc acetate in 20 ml ethylene glycol solvent. Subsequently, 15 ml ethanolamine was added as a stabilizer. For preparation of Hf-/In-doped gel, the appropriate amount of Zinc acetate dehydrated and $\text{HfCl}_4/\text{InCl}_3$ were dissolved in ethylene glycol to keep the effective molarity of primary sol as 0.50 M, and at % of Hf/In as 5%. The prepared sol was magnetically stirred at 60 °C for 1 h on the hot plate, and then diluted by adding 20 ml ethylene glycol. Further, the sol was stirred at 60 °C for another 1 h. During the gel formation pH was maintained between 7 – 8 by adding appropriate amount of ammonia solution. The gel was kept at room temperature for 72 h.

The films were deposited on glass substrate by using screen-printing method in which above mentioned gels were used as ink. Deposition process in screen-printing is based on the principle of squeezing the ink through open area of the mesh that have not been hardening and allow ink through. As ink is squeezed by squeegee from the inside of the mesh, it exits through the open mesh on the substrate. The mesh size, used in this work, was 1.50×1.50 cm. Deposited films were pre-heated inside oven for 1 h at 100 °C and finally annealed at 400 °C for 15 min in muffle furnace.

The thickness of deposited films was determined by Digital Microscope (Carl Zeiss: Model Smart Zoom 5). The microstructural information of the films was studied using grazing incidence x-ray diffraction (XRD; Rigaku, Smart Lab) with a Cu K α ($\lambda = 1.5418$ Å) source. The X-ray source was operated at 9kW, and data was collected at the interval of 0.02 deg. Ultraviolet (UV)–visible spectra of the films were obtained using a Cary 5000 UV-Vis-NIR spectrophotometer in the range of 300 – 900 nm. The room-temperature photoluminescence spectroscopy experiments have been conducted using the RIMS spectrometer with UV light emitting diode (LED) source of 275 nm with a long pass filter of 370 nm.

3. Results and Discussions

XRD is carried out to determine microstructural information of the undoped and doped ZnO thick films. Samples having thickness ~ 20 μm were selected to be studied by using XRD. The effect of doping on the microstructure of undoped ZnO films, Hf-doped ZnO and In-doped ZnO thick films is presented in Fig. 1. It is evident that all films show well-defined crystalline planes of ZnO. The main XRD peaks are observed at 2θ values as 33.60, 38.50, 49.30, 58.60, 64.30 and 69.30. These are assigned to be due to the reflection planes (002), (101), (102), (110), (103) and (112), respectively, corresponding to the wurtzite hexagonal phase of ZnO. The broader full width at half maxima (FWHM) of the most prominent (200) diffraction peak is an indication that the crystallite sizes of evolved ZnO crystals are in nanosized domain. The mean crystallite sizes (r) were estimated in the range of 57 – 108 nm from the value of FWHM ($\beta_{1/2}$) of the most intense XRD peak, by using the Scherrer's formula [27];

Absence of other peaks indicates the purity of samples, and successful doping. Diffraction patterns also show that crystallinity remains in same phase and Hf-doping does not induce any additional metallic Hf or Hafnium oxide characteristic peaks. This implies that Hf atoms can substitute Zn in the lattice because their ionic radius ($\sim 0.76 - 0.83$ Å) is close to Zn^{2+} (0.76 Å). Such substitution can occur effectively without leading to crystal distortion and changing the wurtzite structure. Here, it is important to note that the shift in peak position can be based on the dopant size. If the dopant size is smaller than the base metal it occupies the interstitial position leading to the change in the lattice structure and the d-spacing between the

atoms become less and there is an increase in the XRD resulting in higher angles. Applying the same analogy, when the dopant size is bigger than the base metal, XRD peaks may shift towards lower angles. Considering that ionic size as 0.80 Å of In with respect to that as 0.76 Å of Zn, the peak shift towards lower angles can be justified. The lattice strain (ϵ) is calculated using [28];

$$\epsilon = \frac{\beta_{1/2}}{4 \tan \theta} \quad (2)$$

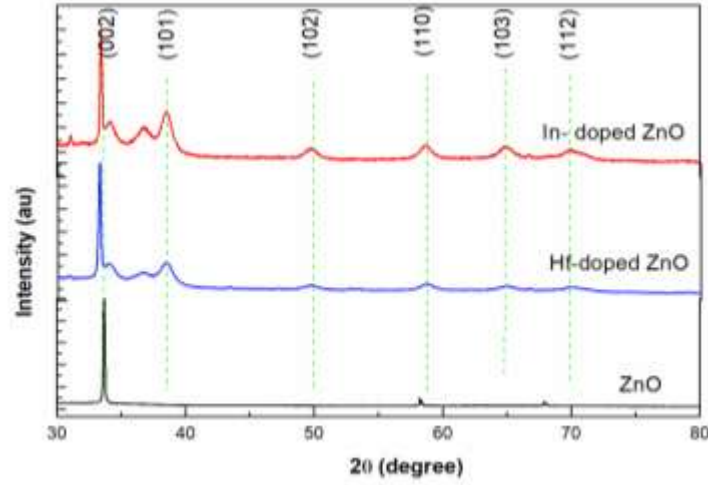


Fig. 1 X-ray diffraction patterns of undoped ZnO, Hf-doped ZnO and In-doped ZnO films.

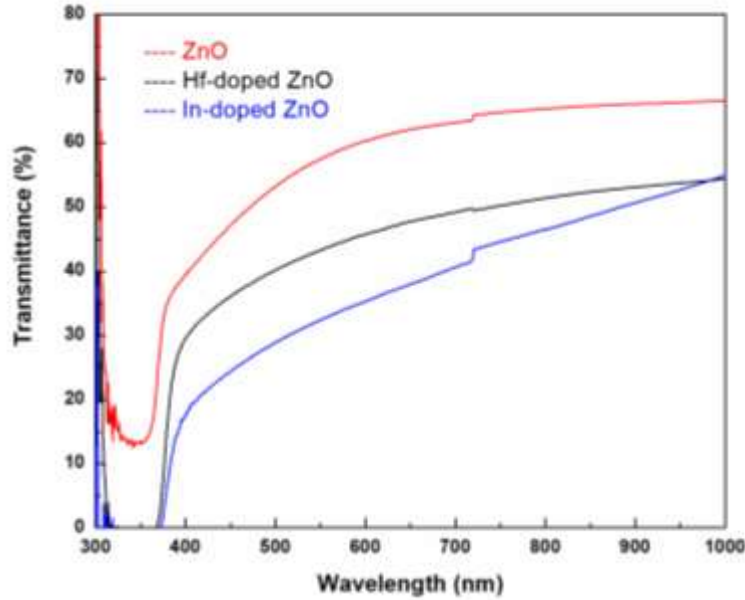


Fig. 2 UV-Visible transmittance spectra of undoped, Hf-doped and In-doped ZnO films.

Table 1 shows the variation of crystallite size and lattice strain in undoped and doped ZnO thick films.

Table 1 Variation of crystallite size and lattice strain in undoped and doped ZnO thick films

Thick Film	r (nm)	ϵ
ZnO	108	0.019
Hf doped ZnO	57	0.065
In doped ZnO	61	0.057

Optical properties are studied using UV-Visible spectrophotometer recorded in wavelength region of 300 – 1000 nm. Optical transmittance of undoped ZnO, Hf-doped ZnO and In-doped ZnO films are shown in Fig. 2. It is evident from the plots that despite having thickness in μm region, all the thick films demonstrate fair transmittance in entire visible region. Transmittance values of Hf-doped ZnO is lower than that of undoped ZnO thick film. If transmittance of In-doped ZnO is considered, it is showing the lowest values of transmittance. Further, the steep fall in transmittance of all samples near 370 – 390 nm range is because of the band-gap induced absorption. The absorption edges shift towards higher wavelength side is an indication of band gap lowering on doping of ZnO with Hf and In dopants.

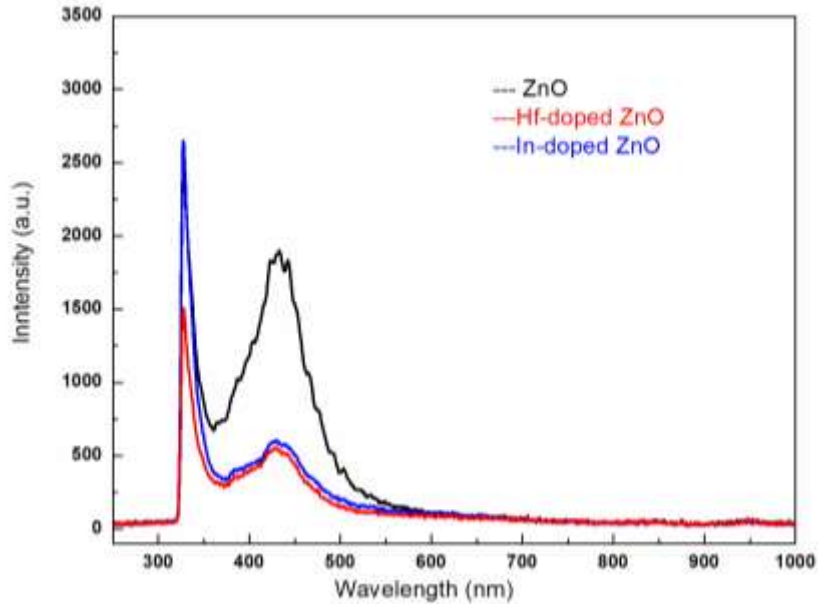


Fig. 3 Photoluminescence spectra of undoped, Hf-doped and In-doped ZnO films.

The characteristic of UV band edges against the optimum value of PL intensity for undoped and doped ZnO is shown in Fig. 3. The first peak, which gives strong UV emission is obtained centered at 327 nm. Further, the PL intensity of the In-doped ZnO is increased with respect to that of undoped ZnO, whereas the PL intensity of the Hf-doped ZnO is decreased with respect to that of undoped ZnO. The second broad peak is found in visible region centered at 430 nm. These peaks agree well with the reported ultraviolet energy-gap of ZnO. The band edge emission at ~ 430 nm should be attributed to the recombination of excitons from the localized level below the conduction band to the valance band. Hf and In dopants significantly influence the PL of host materials like Zinc Oxide by modulating carrier concentration and passivating or inducing specific lattice defects. Hf acts primarily as a defect suppressor and a luminescent center in oxide semiconductors. Hf effectively passivates oxygen vacancies, reducing non-radiative recombination. In Hf-doped ZnO, Hf^{4+} ions can create local energy levels that act as luminescent centers. This leads to the enhanced ultraviolet (UV) emission peaks rather than standard near-band-edge emission, as observed in the present case. In is a classic n-type dopant providing extra electrons to the conduction band of ZnO. Because the ionic radius of In often differs from the host (e.g., Zn^{2+}), it introduces lattice strain that can shift PL emission peaks. In ZnO systems, In-doping can create shallow donor levels below the conduction band, facilitating excitonic recombination that enhances UV emission intensity.

In general, visible emission in ZnO is attributed to some of the intrinsic defects such as oxygen vacancies, zinc vacancies, oxygen interstitials, zinc interstitials, and oxygen antisites. The observed bandgap in doped ZnO can be justified by the Burstein–Moss shift and bandgap shrinkage. The Burstein–Moss band-filling effect shifts the measured bandgap to the positive side with increasing carrier concentration. Bandgap shrinkage is a kind of renormalization due to a change in the nature and strength of interaction potentials between donors and the host crystal. In heavily doped semiconductors, these two phenomena compete and decide the location of the absorption edge. Considering these contributing factors, the dominance of band-gap shrinkage over the Burstein-Moss shift can be the possible reason for the observed lower band-gap in the Hf-/In-doped ZnO thick films. The broad emission of samples reported in present work can be utilized for optoelectronic and photocatalytic applications.

4. Conclusion

This work presented the successful synthesis of undoped ZnO and Hf/In doped ZnO thick films by sol-gel process followed by screen-printing deposition method. Microstructural study carried out by XRD confirmed the hexagonal ZnO formation in undoped as well as in Hf-, and In-doped ZnO thick films. Optical transmittance of these thick films was fairly good. The band-gap edge shifted towards the higher wavelength side in doped ZnO revealed the lowering of band-gap values. The broad photoluminescence emission in visible region of present Hf-/In- doped ZnO films can be useful for potential application in photocatalytic sensing and optoelectronics.

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References

- [1] A. Boora, S. Duhan, B. Rohilla, P. Malik, S. Sehrawat, M.S. Goyat, Y.K. Mishra, V. Kumar, A three-dimensional ZnO/TUD-1 nanocomposite-based multifunctional sensor for humidity detection and wastewater remediation, *Mater. Adv.* 5 (2024) 4467 – 4479.
- [2] N. Tiwari, H.-P.D. Shieh, P.-T. Liu, Structural, optical, and photoluminescence study of ZnO/IGZO thin film for thin film transistor application, *Mater. Lett.* 151 (2015) 53 – 56.
- [3] Y. J. Chung, W. J. Choi, S. G. Kang, C. W. Lee, J. Lee, K.-J. Kong, Y. K. Lee, A study on the influence of local doping in atomic layer deposited Al:ZnO thin film transistors, *J. Mater. Chem. C* 2 (2014) 9274 – 9282.
- [4] Y. Kang, F. Yu, L. Zhang, W. Wang, L. Chen, Y. Li, Review of ZnO-based nanomaterials in gas sensors, *Solid State Ion.* 360 (2021) 115544.
- [5] A. Vora-ud, A.T.T. Pham, D.C. Truong, S. Thaowonkaew, H.T. Lai, T.B.N. Le, N.M.Q. Tran, M. Insawang, P. Muthitamongkol, M. Horprathum, M. Kumar, S. Park, G.J. Snyder, T. Seetawan, T.B. Phan, Transparent-flexible thermoelectric module from In/Ga co-doped ZnO thin films, *Chem. Eng. J.* 465 (2023) 142954.
- [6] D.C. Truong, S. Thaowonkaew, P. Muthitamongkol, M. Horprathum, M. Kumar, T.B.N. Le, A.T.T. Pham, T. Seetawan, A. Vora-ud, T.B. Phan, Relaxation of residual stress-controlled thermopower factor in transparent-flexible Ti-doped ZnO thin films, *Ceram. Int.* 48 (2022) 2605 – 2613.
- [7] L. Wen, M. Kumar, H.J. Cho, K. Leksakul, J.G. Han, Low band-gap highly c-axis oriented Al doped ZnO thin films, *J. Phys. D: Appl. Phys.* 50 (2017) 185206.
- [8] F. X. Xiu, Z. Yang, L. J. Mandalapu, D. T. Zhao, J. L. Liu, Photoluminescence study of Sb-doped p-type ZnO films by molecular beam epitaxy, *Appl. Phys. Lett.* 87 (2005) 252102.
- [9] M. Kumar, L. Wen, B.B. Sahu, J.G. Han, Simultaneous enhancement of carrier mobility and concentration via tailoring of Al-chemical states in Al-ZnO thin films, *Appl. Phys. Lett.* 106 (2015) 241903.

- [10] J.A. Sans, J.F. Sanchez-Royo, A. Segura, G. Tobias, E. Canadell, Chemical effects on the optical band-gap of heavily doped ZnO: MIII (M=Al, Ga, In): An investigation by means of photoelectron spectroscopy, optical measurements under pressure, and band structure calculation, *Phys. Rev. B* 79 (2009) 195105.
- [11] Y. Tang, P. Tan, Y. Luo, Z. Zhang, L. Luo, G. Duan, Hf-doped ZnO transistor with high bias stability and high field-effect mobility by modulation of oxygen vacancies and interfaces, *J. Mater. Sci. Technol.* 163 (2023) 59 – 68.
- [12] R. Bekkari, B. Jaber, L. Laânab, Effect of monovalent dopant ionic radius and concentration on the growth orientation and optical properties of the sol–gel-derived ZnO thin films, *J. Mater Sci: Mater. Electron.* 33 (2022) 12126 – 12136.
- [13] R. Bekkari, L. Laânab, B. Jaber, Effect of the bivalent dopant ionic radius, electronegativity and concentration on the physical properties of the sol–gel-derived ZnO thin films, *J Mater Sci: Mater Electron* 31 (2020) 15129 – 15139.
- [14] J.-H. Zhao, C.-J. Liu, Z.-H. Lv, Photoluminescence of ZnO nanoparticles and nanorods, *Optik* 127 (2016) 1421 – 1423.
- [15] H.J. Ko, Y. Chen, S.K. Hong, T. Yao, MBE growth of high-quality ZnO films on epi-GaN, *J. Cryst. Growth* 209 (4) (2000) 816 – 821.
- [16] M. Kumar, L. Wen, J.G. Han, Plasma diagnostic of cup-like magnetron source for transparent conductive oxide thin films, *Vacuum* 146 (2017) 517 – 523.
- [17] Y. Kashiwaba, F. Katahira, K. Haga, T. Sekiguchi, H. Watanabe, Hetero-epitaxial growth of ZnO thin films by atmospheric pressure CVD method, *J. Cryst. Growth* 221 (1-4) (2000) 431 – 434.
- [18] M.-C. Jeong, B.-Y. Oh, W. Lee, J.-M. Myoung, Comparative study on the growth characteristics of ZnO nanowires and thin films by metalorganic chemical vapor deposition, *J. Cryst. Growth* 268 (1) (2004) 149 – 154.
- [19] Y. Natsume, H. Sakata, Zinc oxide films prepared by sol-gel spin coating, *Thin solid films* 372 (1) (2000) 30 – 36.
- [20] M. Vafaee, M. S. Ghamsari, Preparation and characterization of ZnO nanoparticles by a novel sol–gel route, *Mater. Lett.* 61 (2007) 3265 – 3268.
- [21] E. Ohshima, H. Ogino, I. Niikura, K. Maeda, M. Sato, M. Ito, T. Fukuda, Growth of the 2-in-size bulk ZnO single crystals by the hydrothermal method, *J. Cryst. Growth* 260.1 (2004) 166 – 170.
- [22] D. Gal, G. Hodes, D. Lincot, H.-W. Schock, Electrochemical deposition of zinc oxide films from nonaqueous solution: a new buffer/window process for thin film solar cells, *Thin Solid Films* 361 (2000) 79 – 83.
- [23] A. Illiberi P. Poodt, P.-J. Bolt, F. Roozeboom, Recent Advances in Atmospheric Vapor-Phase Deposition of Transparent and Conductive Zinc Oxide, *Chem. Vap. Deposition* 20 (7-8-9) (2014) 234 – 242.
- [24] G.G. Valle, P. Hammer, S.H. Pulcinelli, C.V. Santilli, Transparent and conductive ZnO: Al thin films prepared by sol-gel dip-coating, *J. Eur. Ceram. Soc.* 24 (6) (2004) 1009 – 1013
- [25] S.A. Studenikin, N. Golego, M. Cocivera, Fabrication of green and orange photoluminescent, undoped ZnO films using spray pyrolysis, *J. Appl. Phys.* 84 (4) (1998) 2287 – 2294.
- [26] O. A. Azeez, R.S. Sabry, M.A.M. Hassan, S.F. Madlul, Synthesis and characteristics of screen printed ZnO thick films nanostructures grown using different methods, *J Mater Sci: Mater Electron* 26 (2015) 4051 – 4061.
- [27] C. Suryanarayan, M.G. Norton, *X-ray Diffraction: A Practical Approach*, Plenum Press New York (1998).
- [28] B.D. Cullity, *Elements of X-ray Diffraction*, Second Edition, Addison Wesley, Reading, MA, (1978).