Effect of La doping on ZnO thin films by spray pyrolysis

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Abstract— **Zinc oxide (ZnO) undoped and Lanthanum doped (ZnO: La) thin films were deposited on 400°C heated glass using spray pyrolysis technique with moving nozzle . (Zn (CH_3COO)2, $2H_2O$) and ($LaCl_3$, $7H_2O$) were used as sources of ZnO and Lanthanum respectively. Effects of dopant on the optical, structural and opto-electrical properties of undoped and 2,4,6 wt. % Lanthanum doped ZnO thin films .Optical transmittance spectra of the films showed high transparency of about 98% in visible region. The optical gap,for ZnO and 0,2,4wt. % La doped ZnO thin films ,were found to be in 3.25-3.28 eV range . X-ray diffraction showed that the thin films have hexagonal wurtzite structure with a strong (*002*) as preferred orientation, whereas the crystalline size was ranged in 15.89-33.45 nm.. ZnO thin films are promising to be used a light emitting diodes ,gas sensor and UV detectors.**

***Keywords—Zinc Oxide, thin films, XRD, La doped,Uv-visible*.**

Introduction

Zinc oxide (ZnO) nanostructures show considerable interest in the scientific community due to their unique optical, electronic and piezoelectric properties. ZnO offers a wide range of applications such as solar cells [1], diluted magnetic semiconductors [2] nanopiezotronics [3], UV detectors [4], gas sensors[5], light emitting diodes [6], etc. ZnO is a direct band gap semiconductor (Eg = 3.37 eV at room temperature), and has a large exciton binding energy (60 meV) [7]. ZnO is an n-type II–VI semiconductor most stable when crystallized in wurtzite structure. ZnO has the richest range of morphologies. Additionally, it has been found to display good photoconductivity and high transparency in the visible region.

Various physical and chemical routes were used to synthesize RE^{+3}-doped nanostructure material: electrochemical deposition [8], hydrothermal method [2, 4, 6], chemical vapor deposition (CVD) [3], sol–gel method [5, 10, 11], precipitation [9], solution combustion [12], and magnetron sputtering [13]. In this research, a facile route of spray pyrolysis of La-doped ZnO thin films at low temperature was created. A possible mechanism on the growth of La-doped ZnO thin films was explained. In the end, the photocatalytic performance of pure ZnO and La-doped ZnO was investigated. It was found that La-doped ZnO showed better photocatalytic performance than pure ZnO

Experimental methods

A. Solutions and thin films preparation

By dissolving (1M) zinc acetate dihydrate (Zn (CH3COO)2, $2H_2O$) in the solvent containing equal volumes of double distilled water and absolute methanol solution (purity: 99.995%), undoped ZnO thin films solution was ready. Few drops of concentrated acetic acid solution were added to the prepared solution as a stabilizer. The mixture solution was stirred at 50°C for 2 hours to have a clear and transparent solution. For Lanthanum doping, ($LaCl_3$, $7H_2O$) with appropriated ratio of La/Zn (0, 2 and 4wt. %) was added to the precedent solution. Each solution, with appropriated ratio of La/Zn, became homogeneous and clear after stirring for 2 hours too. For non-doped and La-doped ZnO thin films, the resulting solutions were sprayed on 400°C heated glass substrates. The deposition of ZnO thin films was performed for 10 min with keeping the moving nozzle-substrate distance equal to 7cm. The substrates are microscope glass with compressed air.

B. Characterization

Optical transmittance spectra were carried out using a UV-Visible spectrophotometer (Shimadzu, Model 1800) operating in the range of 200-900 nm. Structural characterizations are implemented using X-ray diffractometer (BRUKER - AXS type D8) under Cu Kα (λ = 1.5405 A˚) radiation while the full scanning range of (2θ) was between 10° and 80°. Fourier transform infrared (FTIR) spectra of the powders (were recorded using a Fourier transform infrared spectrometer (Perkin Elmer) in the range of 4000–400 cm^{-1} with a resolution of 1 cm^{-1}.

II. RESULTS AND DISCUSSION

A. Optical properties

All the ZnO films were n-type and films have an optical transmission about 95% in the visible region Fig. 1a shows transmission spectrum of a ZnO thin film with different dopant. The optical energy band gap (Eg) of ZnO thin films was 3.25-3.28 eV (inset of Fig. 1a) as estimated from Tauc plot (Eq. (1)). Fig. 1b shows a plot of the variation in band gap energy with with different dopant and it is observed increases the band gap energy of ZnO after doping. The increase in the values of band gap energy with different dopant is attributed to the decrease in crystallinity and grain size of ZnO films [14].

$$(\alpha h\upsilon)^2 = A(h\upsilon - E_g) \quad (1)$$

where α is absorption coefficient,hν is the photon energy , A is a constant, E_g is the optical band gap. For E_g values were deduced from the transmission by extrapolating $(\alpha h\nu)^2 = 0$.The optical band gap values as in Table I.

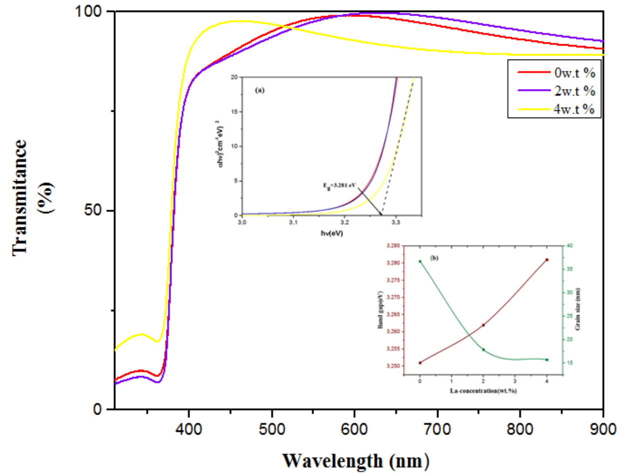

Fig1. *Optical transmission spectra of spray pyrolysis doped and undoped La-ZnO thin films at 400C°. Inset shows the Tauc plots (a) $(\alpha h\nu)^2$ versus hν showing direct band gap and (b) Plot of grain size and band gap versus La-concentration of ZnO thin films.*

TABLE I. *Optical parameters of 0-4wt % La-ZnO thin films: optical transmittance, band gap and Urbach energy*

Material	***Transmittance T (%)***	***E_g (eV)***	***E_{Urbach} (meV)***
ZnO: La (0 wt. %)	96	3.251	84.85
ZnO: La (2 wt. %)	97	3.262	80.42
ZnO: La (4 wt. %)	97	3.281	76.35

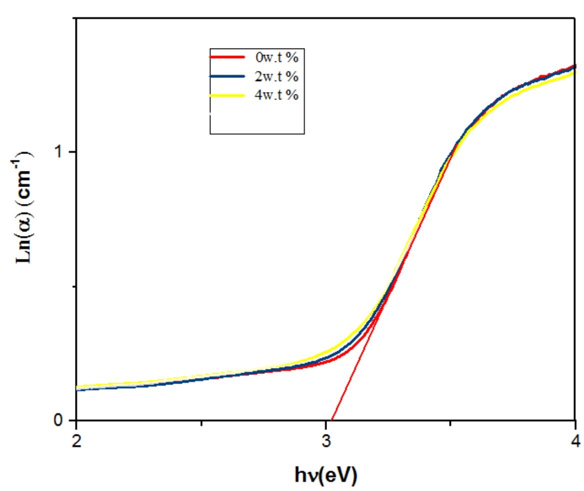

Fig2.*Urbach energy (E_g) of La doped ZnO thin films*

B. Structural properties

The XRD patterns of ZnO thin films with different dopant are shown in Fig. 2a. The diffraction peaks corresponds to the wurtzite ZnO having hexagonal structure (JCPDS No. 36-1451) [15]. The crystallinity of the films decreases afte rdoping . The average crystallite size as calculated from XRD by Scherer equation (Eq. (2)) [16] is found to increase a doping (Fig. 3).

$$D = \frac{k\lambda}{\beta \cos\theta} \tag{2}$$

where, D is the crystallite size, k is the shape factor lying between 0.95 and 1.15 depending on the shape of the crystals and in the present study the value is assumed to be 1, b is the full width at half maximum (FWHM) of the diffraction peak in radians, h is the Bragg angle of the diffraction peak and k is the wavelength of X-rays [16]. The average crystallite size was found to be 33, 17 and 15 nm respectively for the La-ZnO films at 0, 2and 4 wt%.

The texture coefficients TC(hkl) have been based on following formula [17]:

$$TC(hkl) = \frac{I(hkl)/I_0(hkl)}{N^{-1}\sum_n^N I(hkl)/I_0(hkl)} \tag{3}$$

where TC(hkl) is the texture coefficient of the plane (hkl), I(hkl) is the measured intensity , I_0(hkl) is the standard intensity, N is the reflection number and n is the number of diffraction peaks. The preferred crystallographic orientation of the undoped and La doped thin film was along (200) .

For the calculation of lattice parameter *c* and the inter-planer spacing *dhkl*, we have used the following formulas [13]:

$$\frac{1}{d_{hkl}^2} = \frac{4}{3}\left(\frac{h^2 + hk + k^2}{a^2}\right) + \frac{l^2}{c^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots(4)$$

where d_{hkl} is the distance between two adjacent parallel planes of the family hkl, (hkl) are the Miller indexes and 'a', 'b' and 'c' are the lattice parameters. The standard and calculated lattice parameters have been summarized in Table II . The increase in lattice parameter *c* of La-doped ZnO may be due to the large difference between the substitute ionic radius of La^{+3} (1.15 Å) with Zn^{+2} (0.74 Å) into the ZnO lattice and its decrease may be attributed to the loss in the substitutional position of La^{+3} ion in the ZnO lattice [19].

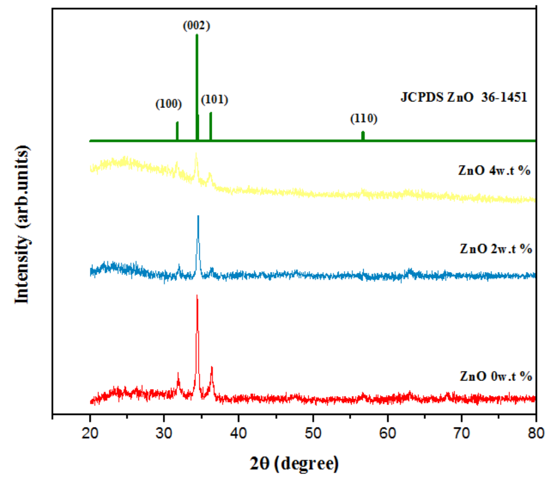

Fig3. *XRD patterns of 0, 2 and 4 wt. % La doped ZnO films .*

TABLE II. *Lattice parameters a, c, of 0, 2 and 4 wt. % La doped ZnO.*

ZnO: La	LATTICE PARAMETERS			
	a=b(A°)	*c(A°)*	*D(nm)*	*Stress(10^9 Pa)*
0 wt. %	3.246	5.202	33.12	- 0.28
2 wt. %	3.262	5.213	17.43	- 1.32
4 wt. %	3.268	5.244	15.21	-1.57

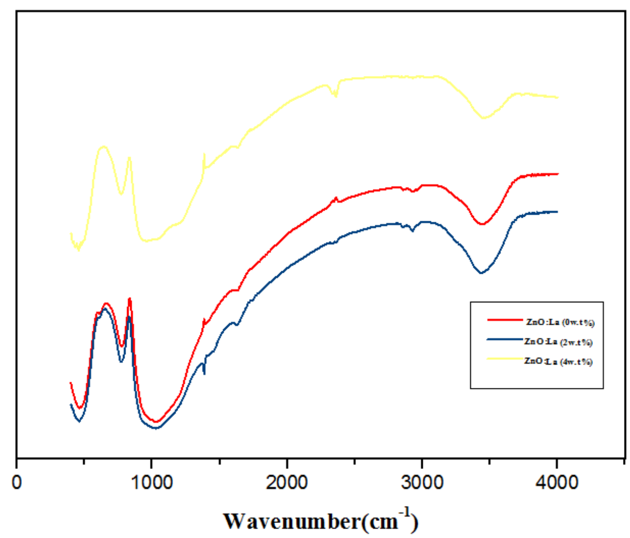

Fig4. *FTIR spectra of pure ZnO and La-doped ZnO thin films by spray pyrolysis*

shows FTIR spectra of 0 wt%,2.0 wt% and 4wt% La-doped ZnO products. The strong absorption bands at 426 and 565 cm^{-1} are attributed to the Zn–O stretching vibration of wurtzite hexagonal type ZnO crystal [20, 21], belonging to the oxygen sublattice (E_{2H}) vibration and oxygen vacancies of wurtzite ZnO crystal, respectively [22]. The broad absorption bands at 3013–3633 cm^{-1} are the O–H stretching vibration of adsorbed water on ZnO Surface [23]

III. CONCLUSION

La-doped ZnO with different dopant rates were deposit by spry pyrolysis on heated glass substrates. Effects of dopant on the structural ,optical of 0, 2 and 4 wt. % lanthanum doped ZnO thin films. The optical transmittance in the visible region was more than 96% for all thin films .The optical band gap for undoped ZnO and La-doped ZnO thin films increases from 3.25eV to 3.28 eV. X-ray diffraction appeared that all the thin films the wurtzite ZnO having hexagonal structure.The preferential orientations of undoped and doped ZnO was along (200) planes,. The crystalline sizes, for undoped and La doped ZnO thin films were in the range between 33.63 nm and 15 nm. La-doped ZnO has an excellent photocatalytic activity than pure ZnO for degradation of MB under UV irradiation. This research may provide guidance for the treatment of organic pollutants.

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