Linear and Non Linear Optical Parameters of TZO Thin Films Prepared by Spray Pyrolysis Technique

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Abstract- In doped zinc oxide (TZO) thin film was deposited on heated glass substrates at 450 °C using Spray pyrolysis method. Linear and nonlinear optical properties were studied in detail. Prepared films were characterized by X-ray diffraction (XRD). The optical parameters such as optical energy gap, the refractive index, the first and third order nonlinear optical properties of the transparent films were investigated. All films were polycrystalline; crystallized in a hexagonal wurtzite structure with a preferred orientation along the direction (002), tin doped ZnO films with a transmittance greater than 85% were obtained. Based on spectroscopic method, the analyzing linear refractive index (n) and optical susceptibility $\chi^{(1)}$ were used thereafter for calculation of non-linear refractive index (n2) and the third order non-linear optical susceptibility $\chi^{(3)}$ parameters. Sn-doped ZnO thin films is a suitable material for optoelectronic applications.

I INTRODUCTION

Transparent conducting oxides (TCOs) are considered as a promising oxides material in electronic and optoelectronic devices [1]. The nonlinear optical proprieties of TCOs thin film have a great attraction because it alters the optical properties of the light during its propagation. TCOs thin film can be used in different application such as optical communication network, optical, wave guides [2].

Among various (TCOs), Zinc oxide is one of the most promising materials for the next generation of optoelectronic manufacturing devices which derived from wide band gap semiconductors ~3.37 eV with low resistivity, his free excitation energy 60MeV and its good third order nonlinear generation reported by x [3].Tin doped zinc oxide (TZO) thin films can be prepared by various deposition techniques, such as sputtering [4], MOCVD [5], vapor transport [6], pulsed laser deposition [7], spray pyrolysis [8]. Each deposition method has its advantages and disadvantages suitable to their use. Among the various deposition techniques spray pyrolysis is considered as a feasible one due to its (simplicity, low cost, low temperature and process yield. Assia bougrine et al [9] reported the preparation of ZnO: Sn thin films using the spray pyrolysis method on a glass substrate and analyzed the structural, optical and electrical properties of tin-doped zinc oxide thin films.

In this paper, we have focused to mainly investigated the linear/ nonlinear optical properties of Sn-doped ZnO using the spectroscopic method employed to calculate this linear and nonlinear optical parameters. the spectroscopic method is a simple method to obtain some information about using such films and/or other materials in non-linear optical without extra devices such as: third harmonic generation (THG) experimental or other nonlinear design systems[10].

II EXPERIMENTAL DETAILS

Tin-doped zinc oxide thin films were deposited on glass substrate by using Spray pyrolysis system. The optimum conditions of preparation have been reported [9]. 0.05M was used as starting solution of zinc chloride ($ZnCl_2$) in a mixture of deionised water. The compound source of dopant was tin chloride ($SnCl_2$, $2H_2O$). The crystallinity of the thin films was studied by X-ray diffraction using Cu (Kα) radiation. The optical transmission measurements were performed with a Shimadzu 3101 PC UV-Vis-NIR spectrophotometer.

III RESULTS AND DISCUSSION

A. Structural analysis

Fig.1 shows the results of X-ray diffraction analysis of TZO films deposited at different tin doping ratio at a substrate temperature of Ts = 450°C. These patterns show that the doped layers crystallize in a hexagonal wurtzite structure with space group P63 mc and following the same preferential (002) direction of ZnO undoped. As seen in the diffraction peaks the location of the measured diffraction peaks do not change with increasing doping concentration, but the peak intensities become more intense and sharper at doping ratio of 2 wt. %, this indicates a good crystallinity of doped films .same behavior was observed by Paraguay et al [11]

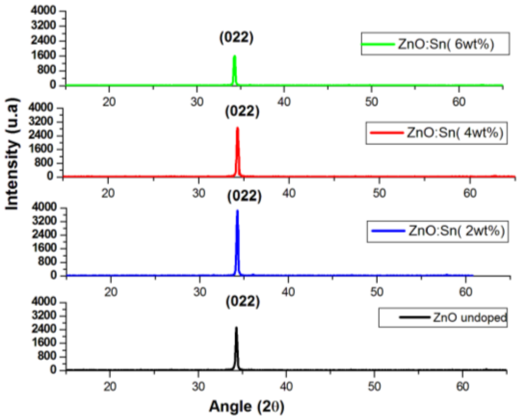

Figure 1: XRD spectra of Sn doped ZnO films prepared at different doping rates

B. Linear optical properties

The study of the optical transmission of the ZnO and Sn-doped ZnO films (TZO) produced at different doping levels are shown in figure (2). We have remarked that the transmission of thin films is decreasing at high doping levels Same behavior was observed by Ganesh et al [12] reported that the increasing the thickness of sample with doping may affect the transmittance, many investigations on several thin films with different dopants they had the same observations [13].

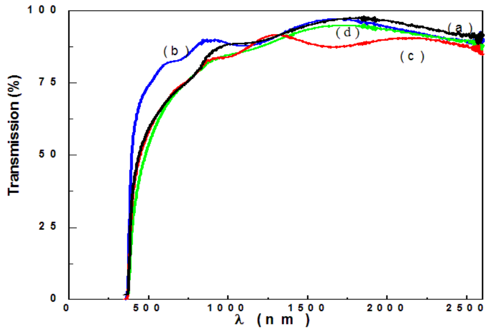

Figure 2: Optical transmission of the ZnO:Sn as function Sn/Zn ratio: (a) 0 at.%, (b) 2 at.%, (c) 4 at.% and (d) 6 at.%.

Among the optical parameters of linear optical materials, the refractive index plays an important role in giving the importance of polarization and structural changes in a material during his interaction with light radiation. Figures 4 depicts the plot of refractive index as a function of wavelength for different concentrations of Sn-doped ZnO films. The transmission performance was related to the refraction index (n) was evaluated from the measured transmittance versus wavelength using well-known Swanepoel method [14] several researchers have used this technique to calculate the refractive index of thin films |[15].

$$n = \left[M + (M^2 - n_s^2)^{1/2}\right]^{1/2} \quad (1)$$

$$M = 2n_s \frac{T_M - T_m}{T_m T_M} + \frac{n_s^2 + 1}{2} \quad (2)$$

Where T_m and T_M are the experimental values of transmission at minimum or maximum points of a particular fringe and ns is the refractive index of the substrate,

Thin films with high transparency are best used in optics [10]. The better transmission with well-contrasted interference fringes have remarked for a doping rate of 2% with the average transmission of about 85% and 76% for undoped ZnO film in the visible range .This results is correlated with the good crystalinity observed by the X-ray diffraction, Jilani et al[10] reports that the presence of oscillations in the transmission of deposited thin films could be due to the interference of light arising from the difference in refractive indexes of thin films and the substrate.

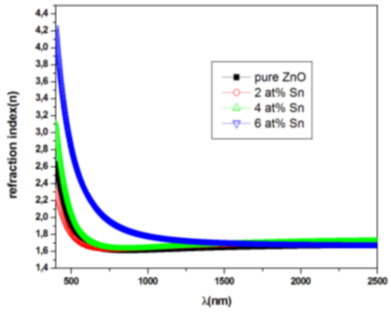

Figure 3 : Variaton refractive index with wavelength in lineear of pure and Sn-doped ZnO thin films (a) 0at%, (b) 2at%, (c) 4at%, et (d) 6at%

From the spectra giving in figure 4 .it is found that the refractive index n vary with The wavelength show a dispersion normal in the spectral region (400-800) nm. also It is clearly observed that n decreases first at 2 at % Sn addition ,and with again addition of 4at% and 6 at% Sn n increases. the similar type of behavior is observed by several researchers. P.yadav [15], Shaaban et al [16] and V.Ganesh et al [12]. T. Nakada et al [17] and M. S. Ashour A et al [18] were reported respectively that the refractive index decrease with Sn addition of 2 atomic% Sn thin film is due to change in density and probably by deviation from stoichiometry. Concerning the increase of n in higher concentration is attributed to increasing in polarization due to the incorporation of highly Sn dopant in ZnO matrix in accordance with Lorentz –Lorenz equation, highly doped system with Sn lead to increase in refractive index due to increase in polarization [19].

C.Nonlinear optical calculation of TZO Thin films

TCO materials have the promising optoelectronic application due to its good third order nonlinear generation attributed to the interaction of these materials with high intensity of radiation. the conversion of this radiation arises due to the interaction of induced polarization (P) with applied electric field(E) [20].The non-linear electron polarizability, P can be expressed by the following equation[21]:

$$p=\chi^{(1)}E + P_{NL} \qquad (3)$$

Where

$$P_{NL} = \chi^{(2)}E^2 + \chi^{(3)}E^3 \quad (4)$$

Where P is polarizability,$\chi^{(1)}$ is the linear optical susceptibility and $\chi^{(2)}$,$\chi^{(3)}$ are second and third order non–linear optical susceptibilities,respectively. The expression of refractive index n(λ) can be described as follows[21] .

$$n(\lambda) = n_0(\lambda) + n_2(E^2) \quad (5)$$

Where the components of n(λ) in Eq. 5 have such rule: $n_o(\lambda) \gg n_2(\lambda)$ i.e.,$n(\lambda) = n_o(\lambda)$ and (E^2) is the mean square of electric field.The linear optical susceptibility $\chi^{(1)}$ of a medium can given by the following equation [22]

$$\chi^{(1)}=\frac{(n^2-1)}{4\pi} \qquad (6)$$

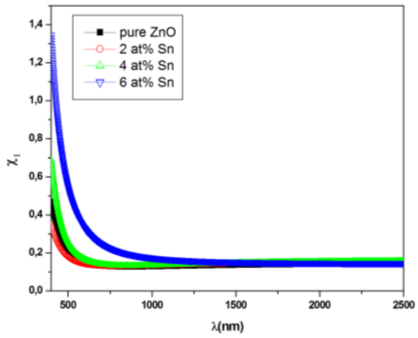

Figure 4 : Plotting of linear optical susceptibility as function of wavelength for TZO thin films

The expression of third order NLO susceptibility $\chi^{(3)}$ Based on the linear refractive index $n_0(\lambda)$ and linear optical susceptibility $\chi^{(1)}$ was showed as follows [23]–[25]

$$\chi^{(3)} = A\,((\chi^{(1)}))^4 \qquad (7)$$

By susbstitute from Eq(6) in Eq.(7), we obtaine the following equation [23]–[25]

$$\chi^{(3)}=\frac{A}{(4\pi)^4}(n_0^2-1)^4 \qquad (8)$$

Where (A) is a constant and it value is equals 1.7 × 10^{-10} [22].

It is showed in figure 5 the variation of linear optical susceptibility χ1 as function of wavelength for pure and Sn-doped ZnO and is it clearly seen that $\chi^{(1)}$ follows the same pattern as the linear refractive index [1] .further it is remarked that the linear optical susceptibility χ1 are increasing with high concentration of Sn–content compare to pure material. the values of $\chi^{(1)}$ are in the range (0.12 to 1.34).

Based on Eq .(8) the calculation of the third order non-linear optical susceptibility χ3 value has been made as a function of wavelengths and plotted in figure 5b. value of χ3 are in between (4.2210^{-14} -5.594 10^{-10}) [esu]. the values obtained are high compared with other techniques of elaboration of Sn-doped ZnO thin films[12] and other different materials[1], [10] in literature. Moreover, indicates that Sn doped ZnO thin films represent a promising material for non linear applications.

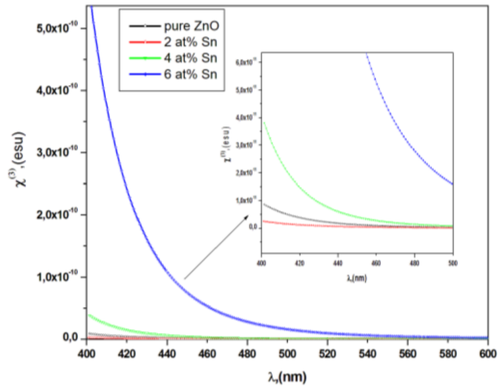

Figure 5 .Plotting of linear optical susceptibility as function of wavelength for TZO thin films

IV CONCLUSION

ZnO and Sn-doped thin films with different doping concentration (2,4,6 at%) were prepared by spray pyrolysis .X ray diffraction study exhibit hexagonal crystal structure with preferentially grown along (002) plane ,based on spectroscopic method in transmission spectral region 400-2500 nm.the linear index refractive , linear susceptibility , nonlinear susceptibility,and nonlinear index refractive .The dispersion normal was show in the spectral region (400-800) nm, also It is clearly observed that n decreases first at 2 at % Sn addition, and with the again addition of 4at% and 6 at% Sn n increases. the increase of n in higher concentration is related to increasing polarization due to the incorporation of highly Sn dopant in ZnO crystal matrix ..Te value of χ(3) are in the range from 4.2210^{-14} -5.594 10^{-10}) [esu].The obtained results indicate that Sn doped ZnO thin films are very suitable material for optoelectronic applications.

V. REFERENCES

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