J. Nano- Electron. Phys.
3 (2011) No1, P. 601-609

PACS numbers: 61.72.Uj, 78.20.Ci, 78.30.FS, 78.55.Et

LASER INDUCED NONLINEAR OPTICAL PROPERTIES OF ZINC OXIDE THIN FILM PREPARED BY SOL-GEL METHOD

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Optical nonlinearities of spin coated ZnO *thin film have been investigated by using single beam Z-Scan technique in the visible region. X- ray diffraction shows that all films are oriented along the c-axis direction of the hexagonal crystal structure. The average optical transmittance of all films is higher than* 80 %. *The nonlinear optical parameters viz. nonlinear absorption coefficient* (β), *nonlinear index of refraction* (η_2), *nonlinear susceptibility* (χ^3), *have been estimated using nanosecond laser pulses of second harmonic of* Nd:YAG *Laser. The value of nonlinear absorption coefficient* β *is estimated to be greater than the already reported value. The films clearly exhibit a – ve value of nonlinear refraction at* 532 *nm which is attributed to the two photon absorption and free carrier absorption. The presence of RSA in* ZnO *thin films inferes that* ZnO *is a potential material for the development of optical limiter.*

Keywords: ZnO, *NONLINEAR ABSORPTION, NONLINEAR INDEX OF REFRACTION, OPTICAL LIMITING, NONLINEAR SUSCEPTIBILITY, Z-SCAN.*

(Received 04 February 2011, in final form 18 June 2011)

1. INTRODUCTION

ZnO thin films have attracted much attention because of its versatile nature. It is less expensive, n-type direct band gap semiconductor with E_g value of ~ 3.3 eV. It is widely studied as it possesses excellent electro-optic, piezoelectric, acousto-optic properties which allow us to fabricate electro optic modulators, surface acoustic wave devices, gas sensors and solar cell windows [1, 2] and room temperature UV lasers [3]. There is always a demand for thin film nonlinear optical materials and recent studies have found that ZnO has a strong nonlinear second order susceptibility χ^2, which results in second harmonic generation [4, 5].

Nanostructures of ZnO are fabricated using various thin film techniques as spray pyrolysis [6], molecular beam epitaxy [7], chemical vapor deposition (CVD) [8], vacuum evaporation [9], pulsed laser deposition [10], RF Sputtering [11] and sol-gel processing [12, 13]. All these processes are associated with complicated methodologies except sol-gel. Sol-gel allows us to fabricate large area coating at relatively low cost. It controls the microstructure of the films and the optical and electrical properties can be tailored easily by adding suitable dopant.

During the present course of investigation, we have estimated the nonlinear optical properties of ZnO thin films deposited on corning (1737) glass substrate by sol. gel method using spin coating technique. The films have been characterized by a single beam Z-scan technique under illumination of Nd:YAG laser at 532 nm.

2. EXPERIMENTAL DETAIL

In order to obtain good quality ZnO thin film from sol-gel technique, the precursor sols for the films were prepared from zinc acetate dihydrate [(Zn $(CH_3COO)_2$ $2H_2O$), purity 99.95 %], methanol and monoethanolamine (MEA). The solution was stirred magnetically for about 120 minutes to obtain clear and homogeneous solution and was kept for aging for 48 hours before the deposition of the films [14]. Corning glass (1737) slides were used as substrate for spin coating of the film. These glass substrates were cleaned ultrasonically by acetone, methanol and deionised water for 15 minutes and at last were dried in nitrogen atmosphere. The spinning speed and time were optimized to 2500 rpm and 30 seconds respectively, so that each spun layer is thin enough for evaporation of all solvents and thus preventing the films from cracking. The films were then dried in air at 300 °C for 10 min. The spin coating process was repeated fifteen times in order to get a film thickness of ~ 300 nm. The finally deposited films were annealed at optimized temperature of 450 °C for 1 hour [15]. The structural properties of the annealed film were investigated by X-ray diffractometer (Rigaku Corporation) using CuKα radiations.

The optical transmittance measurements were done in the wavelength range 200-800 nm by using a double beam SHIMADZU - 330 spectrophotometer (Solidspec-3700). Surface morphology of the films was analyzed by scanning electron microscopy (SEM). Photoluminescence measurements were carried by photoluminescence spectrometer (S7000, Hitachi Corporation) and the nonlinear optical properties measurements were estimated by single beam Z-scan technique. The experimental set up of a single beam Z-scan experiment used for the present measurements is shown in Fig. 1. The experiment was carried with nanosecond laser pulses (5 ns) illuminated by second harmonic of a Q-switched Nd:YAG Laser (Quanta System, HYL-101) at room temperature. The beam was focused to a small spot using a lens and the sample was moved in the direction of light incident near the focus of the lens having focal length 150 mm along the z-axis. The transmitted light in the far field passed through the aperture and the beam intensity was recorded by a photodiode detector (Thorlabs, DET-110) and then was read by an oscilloscope (Tektronics, TDS-2024). For open aperture Z-scan measurements the aperture was removed ($S = 1$) completely. The radius of the beam waist ω_0 was calculated to be 24.3 µm. The Rayleigh length (z_0) was found to satisfy the criterion of a Z-scan experiment. The obtained data was analyzed by the procedure described by the pioneer worker Sheik Bahae et al. [16].

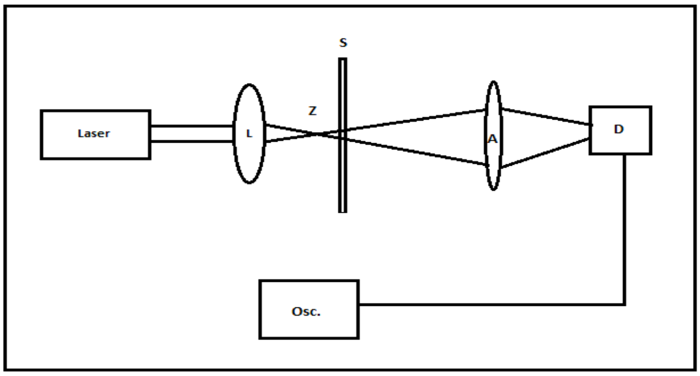

Fig.1 *– Shematic representation of a single beam Z-scan experiment setup: lens (L); focal point of lens (Z); Sample (S); Aperture (A); Detector (D); Oscilloscope (O)*

3. RESULTS

3.1 Structural properties

The structural properties of the film were investigated by X-ray diffraction studies. The X-ray 2θ scan pattern of ZnO thin films deposited on a glass substrate at an annealing temperature of 450 °C are shown in Fig. 2. One can clearly observe a diffraction peak at ~ 34.47 °C corresponding to the (002) plane of ZnO exhibiting the hexagonal wurtzite structure corresponding to the preferential c-axis orientation in the film due to lowest surface free energy of this plane.

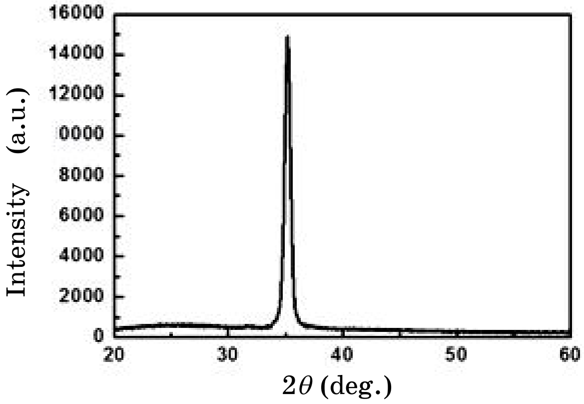

Fig.2 *– XRD pattern of ZnO thin film*

3.2 Surface Morphology

Surface morphology of ZnO thin films were investigated by scanning electron microscopy. SEM micrograph of ZnO film is shown in Fig. 3 with presence of tightly packed grains. All films show smooth surface with a fine structure without cracks and voids. The grain size of ZnO is observed approximately 16 nm.

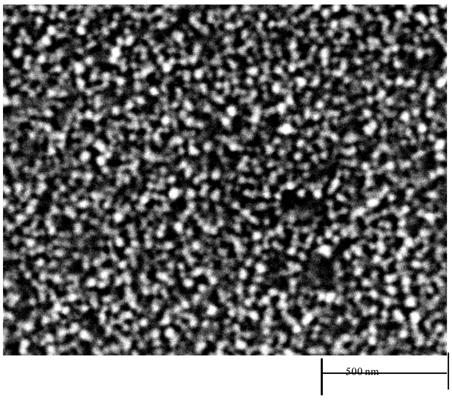

***Fig. 3** – SEM image of* ZnO *thin films annealed at* 450 *°C*

3.3 Optical Properties

Transmittance measurements were carried out in the range 200-800 nm to estimate the band gap of the films and are shown in Fig. 4. The average transmission within the visible wavelength region for all the films was higher then 80 %. The firings in transmittance spectra show that ZnO films have good homogeneity.

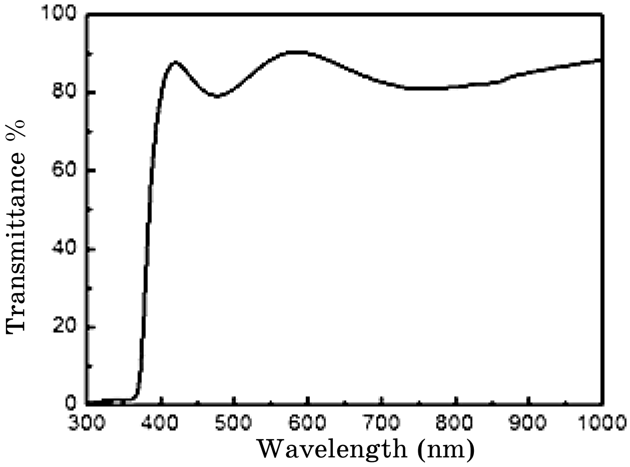

***Fig.4** – Optical Transmittance spectra of* ZnO *films*

In the direct transition semiconductor, the absorption coefficient, obeys the following relationship with optical energy band gap (E_g) [17]:

$$\alpha h\nu = (h\nu - E_g)^{1/2}$$

where h is Planck's constant and ν is the frequency of incident photon. So the band gap of ZnO film is estimated by plotting graph of $h\nu$ vs $(\alpha h\nu)^2$ for the linear absorption coefficient α. Extrapolation of the linear part until it intersects the $h\nu$ axis gives us the value of band gap (E_g).The value optical band gap (E_g) is found to be shifted from that of the bulk as shown in Fig. 5. The total change in the band gap of the material is simultaneously contributed by shifts of the valence and the conduction band edges with respect to each other [18]. Generally the shift of the top of the valance band (TVB) is not the same as that of the bottom of the conduction band (BCB). A larger shift for the BCB is expected in view of the fact that the band edge shifts are related inversely to the corresponding effective masses of electron and hole. The effective mass of the electron is always much smaller than that of the hole in these II-VI semiconductors [19].

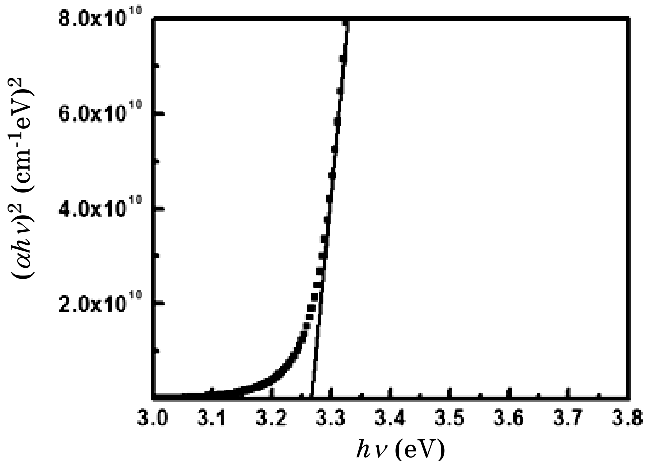

***Fig.*5** – *Plot of* $(\alpha h\nu)^2$ *on* $(h\nu)$ *of* ZnO *films*

Photoluminescence spectrum of ZnO films are shown in Fig. 6 exhibiting emission peak at 385 nm.This peak lie in UV region and corresponds to band to band transition [20].

Typical results of the open aperture Z-scan measurements of the film that corresponds to the far-field normalized tranmittance, $T(z)$ as a function of the distance from the lens focus at an intensity of 2.1 TW/cm^2 are shown in Fig. 7. The open aperture curve exhibits a normalized transmitted valley, indicating the presence of reverse saturable absorption (RSA) in the films.

In the presence of RSA, transmittance $T(z)$ of the films is calculated as:

$$T(z) = 1 - \frac{q_0}{2\sqrt{2\left(1 - z^2/z_0^2\right)}}, \tag{1}$$

where $q_0 = \beta I_0 L_{\text{eff}}$, I_0 is the irradiance of laser beam at focus, L_{eff} is the

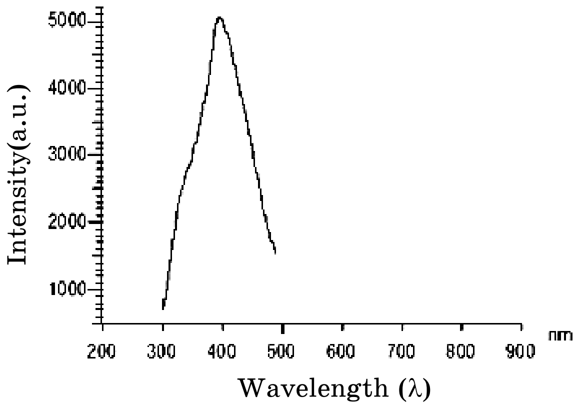

Fig.6 *– Photoluminescence spectrum of* ZnO *films*

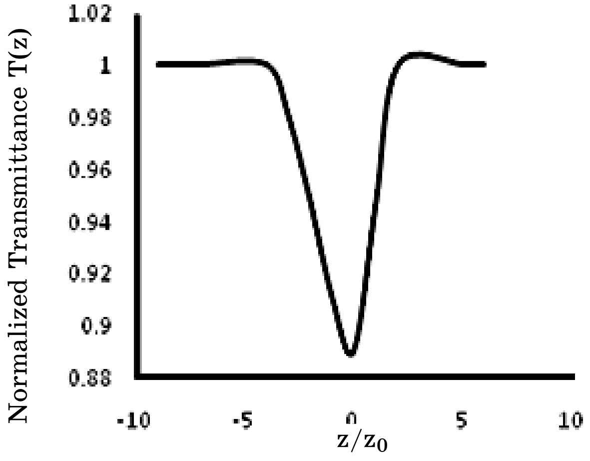

Fig.7 *– Open aperture Z-scan measurements*

effective thickness of the sample, which is defined as:

$$L_{eff} = \frac{\left(1 - e^{-\alpha L}\right)}{\alpha}, \tag{2}$$

where L is the real thickness.

From Fig. 7 the value of q_0 is obtained to get the value of β. The value of β, gives us directly the value of imaginary part of susceptibility (Im$\chi^{(3)}$)through the relation:

$$\operatorname{Im} \chi^{(3)} = \frac{\lambda \varepsilon_0 \eta_0^2 \varepsilon \beta}{4\pi}, \tag{3}$$

where, λ is the excitation wavelength, n_0 is the linear refractive index of ZnO, ε_0 is the permittivity of free space and c the velocity of light in vacuum.

In general, induced absorption can occur due to a verity of processes. The theory of two photon absorption (TPA) process fitted well with the experimental curve and two photons of 532 nm radiation lie below the absorption band-edge of the samples under investigation infers that TPA is the basic mechanism. There is possibility of higher order nonlinear processes such as free carrier absorption (FCA) contributing to induced absorption. It is already reported that carrier lifetime of ZnO is 2.8 s [21] plot as we are using 5 ns pulses to excite the free carriers generated by TPA so we can say that TPA and FCA are the two important mechanism responsible for RSA in our sol-gel thin films. RSA is also responsible for optical limiting effects, so the sample can also be used as an optical limiter.

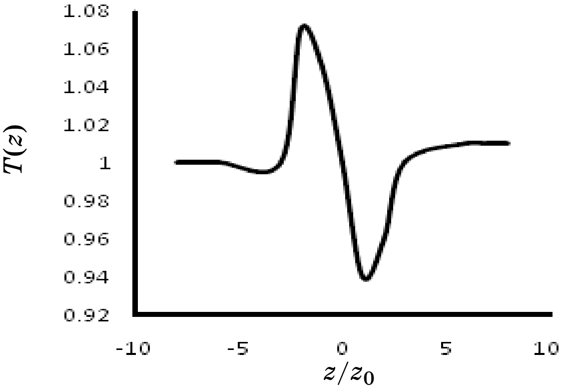

***Fig. 8** – Normalised transmittance with closed-aperture as a function of the position*

The closed aperture Z-scan plot is shown in Fig. 8 at an intensity of 2.1 TW/cm^2 .The graph clearly exhibits the presence of a peak followed by a valley, which indicates a –ve value of coefficient of nonlinear refraction η_2 and can be estimated as:

$$\eta_2\left(esu\right)=\frac{c\eta_0}{40\pi^2}\frac{\lambda\Delta T_{p-v}}{0,812\cdot\left(1-S\right)^{0,25}I_0L_{eff}}. \tag{4}$$

The value of $\Delta T_{\text{p-v}}$ is the difference between peak and valley transmittance and it can be determined by the best theoretical fit from the Z-scan curve. The value of η_2 is associated with the real part of nonlinear susceptibility Re $\chi^{(3)}$ as:

$$\operatorname{Re}\chi^{(3)}\left(esu\right)=\frac{\eta_0\eta_2\left(esu\right)}{3\pi}. \tag{5}$$

The absolute value of $\chi^{(3)}$ can be obtained by using formula:

$$\chi^{(3)}(esu) = \{\ [\text{Im}\chi^{(3)}]^2 + [\text{Re}\ \chi^{(3)}]^2\ \}^{1/2}. \tag{6}$$

The value of nonlinear absorption coefficient β is estimated to be greater than the already reported values because of good crystalinity of the film free from any voids shown our XRD and SEM data. The results are in good agreement as that of reported by various research workers. It is observed

Table 1 *– Measured values of absorption coefficient, nonlinear refractive index, real and imaginary Parts of third order nonlinear susceptibility* $\chi^{(3)}$*and total value of* $\chi^{(3)}$ *of* ZnO *films at* $I_0 = 2.1$ *TW/cm*^{2} *and wavelength of* 532 *nm*

Sample	Nonlinear absorption coefficient (β) (cm/W)	Nonlinear refractive index (η_2) (cm^2/W)	Img. $\chi^{(3)}$ (esu)	Real $\chi^{(3)}$ (esu)	$\chi^{(3)}$ (esu)
ZnO Thin film sample	1.46×10^{-6}	-1.54×10^{-10}	3.149×10^{-5}	-1.57×10^{-4}	2.5×10^{-4}

that the real part of $\chi^{(3)}$ is larger than the imaginary part of $\chi^{(3)}$ that implies stronger refraction effect. By comparing the work done by various researchers we found that the nonlinear absorption coefficient (β) values are quiet high indicating that ZnO thin film sample has good nonlinear response and are therefore potential candidate for Optoelectronic devices.

Table 2 *– Comparison of work done about the values of* β *and* $\chi^{(3)}$ *for* ZnO *samples measured by Z-Scan technique*

Method of preparation of sample	Laser Wavelength h	Laser Intensity (I_0)	β (cm/GW)	$\chi^{(3)}$(esu)	Reference No.
Sol-gel	532 nm	220 MW/cm^2	4.59×10^6	5.86×10^{-6}	22
bulk	532 nm	-	4.2 ± 0.9	-	21,23
Laser beam molecular epitaxy	390 nm	154 GW/cm^2	3000	-	24
Laser Deposition	745 nm	1.6 GW/cm^2	297	-	25
Electro deposition method	800 nm	--	$5.9 \cdot 10^2$	-	26
Sol-gel	532 nm	2.1 TW/cm^2	1.46×10^7	2.5×10^{-4}	Pres. Work

4. CONCLUSIONS

The nonlinear optical properties of ZnO thin film developed by spin coating sol-gel technique have been investigated. The sample exhibits a negative nonlinear index of refraction at 532 nm and the observed nonlinear refraction is attributed to two photon absorption. The real part of $\chi^{(3)}$ is found to be larger than the imaginary part. Further the RSA behavior implies that ZnO is a good candidate for optical limiting.

The authors acknowledge UGC and DST for financial support under SAP and FIST program, respectively. The authors also acknowledge Prof. Avinashi Kapoor, Head, Department of Electronic Science, University of Delhi (South Campus) for permitting to use research facilities in the department.

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