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ORIGINAL PAPER

Syntheses, Structural and Nonlinear Optical Characteristics of ZnO Films Using Z-Scan Technique

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Abstract

ZnO films were deposited on two substrates Silicon (Si) and glass using RF magnetron sputtering. Our aim is to characterize the structural and the nonlinear optical (NLO) properties of the new ZnO films. Both of XRD and EDX analysis were utilized to reveal some information about the structural improvements and composition of our new films. Also, morphology and thickness of the films have been acquired from a scanning electron microscope (SEM). The nonlinear absorption (NLA) coefficients of the new films were estimated from the experimental data. Our observations suggest that the present grains on the films surface could be as clusters of crystallites. The optical band gaps (Eg) of the new ZnO prepared films were found about 3.25 eV for film thickness of 500 nm and 3.29 eV for the other film thickness of 1200 nm. It was found that the two films thickness have a good quality with (002) prefer orientation, as well as compared with (002) single crystal ZnO using z-scan method. The NLA coefficient (β) of the film is inversely proportional with the films thickness.

Keywords Thin films · Zinc oxide · Structure properties · Z-scan · Morphology

1 Introduction

ZnO is very interesting wurtzitic II-VI wide band gap semiconductor. So, it may be useful as a transparent electrodes in solar cells manufacturing [1]. It can be used in various applications, as well as a thin film transistor (TFT), and important protection element in electronic circuitry [2], piezoelectric transducer, surface acoustic wave device [3], and combined with high excitonics gain as well as large excitonic binding energy [4]. Also, new thin films were prepared by DC magnetron sputtering, it was found that the films have a corrosion resistance with high microhardness value [5]. The NLO properties of ZnO films are currently subject to specific work, in response to satisfy the industrial need for optoelectronic devices, it could be operated at a short wavelengths range [6]. Pure and doped nanocrystalline ZnO films have shown high second-harmonic efficiency and this makes the ZnO to be used as efficient optical modulator [7]. Although, a majority of the optical devices depend on higher order susceptibility of the materials (χ^3), ZnO as well as ZnS have been considered to be good candidate for potential optical applications in the field of nonlinear optical modulators [8] [5].

The nonlinear optical properties were measured for undoped ZnO and Mn doped ZnO thin films [9]. The percentage of the transmittance and band gap have been modified by plasma parameters (Magnetron Sputtering) such as oxygen element effect, and the thickness effect on structural and NLO properties of ZnO thin film [4] [10], as well as the metal doped SnO_2 films [11]. A compounds containing the linkage C-N=N-C called AZO dye thin films were prepared by different methods, where high quality ZnO films produced with a thickness controlled by using DC or RF magnetron sputtering in the semiconductor high technology industry [12]. Also, it has been demonstrated that the increased in substrate temperature accompanied with improvement of ZnO film quality, could be led to extract the band gap of 3.2 eV at 400 °C by recording the UV-Vis transmittance spectra. The C-V and I-V measurements on the basis of the heterojunction thermal emission model have confirmed that the domination of high-density grain boundary layer existing at the region of interfacing [6].

In this article, we have deposited ZnO films on two substrates of Si and glass, for investigating the optical properties and structural of ZnO films. For the first time, the NLO

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response of ZnO thin films is measured and compare with study on ZnO single Crystal. Such study will be useful in optoelectronic applications. Different techniques were used to characterize the new prepared ZnO films, such as X-ray diffraction (XRD), Dispersive X-ray Spectroscopy (EDX), photo-luminesces (PL), UV-Vis, SEM, and z-scan technique.

2 Experimental Details

ZnO films were deposited using PLASSYS-MP600S coating system at power close to 600 W. The Si (100) and glass substrates were exploited to prepare the new films. The purity of the used target "ZnO" was 99.99%, and the diameter of the target disk is 15 cm. SEM TSCAN Vega\\XMU (Czech Republic) equipped with EDX was employed to find both the morphology and composition of the ZnO films. The thicknesses of the newly prepared films were measured to be 500 and 1200 nm. The structure of the film was analyzed by XRD (Stoe transmission X-ray diffractometer Stadi P (Germany)) using the Cu Kα with λ = 0.15405 nm at "θ–2θ scan configuration". The Optical transmittance spectra have been recorded using the UV-310PC Spectrophotometer from Shimadzu. PL spectra were recorded using He-Cd laser at λ = 325 nm (a 1 m Spex monochromator and a multialkali photomultiplier). All the deposition mentioned parameters were summarized in Ref [4]. Micro-Raman spectra of ZnO films were observed with 514 nm laser line from Argon ion laser (Jobin–Yvon (LabRAM HR) MicroRaman).

3 Results and Discussion

3.1 Structural Study

The XRD patterns of ZnO films at the two thicknesses of 500 and 1200 nm were shown in Fig. 1a. A preferential orientation peak (002) at 34.42° is found with the c-axis perpendicular with the substrate surface. This peak at (002) may be assigned to the "hexagonal" ZnO würtzite phase [13], JCPDS card no. 36–1451. The stoichiometry (O/Zn about 1) was confirmed by EDX analysis.

The grain size for orientation peak (002) of ZnO films was calculated using Scherrer's formula [14] and it was found to be close to 20 nm and 26 nm for 500 nm and 1200 nm films thickness, respectively. Fig. 1b shows the Rocking curve of the two films thicknesses. The full width half-maximum (FWHM) can be determined for each the peak, it is equal to 5.6° for film of 500 nm, and to 2.9° for the film of 1200 nm. The rocking value is consistent with XRD results (θ–2θ mode) and confirmed the preferential orientation (002).

3.2 SEM and AFM Study

The new films deposited on Si (100) substrates were charactrized by SEM to reveal some information regarding to the thickness of the films and their surface morphology. The thicknesses of the ZnO films were esitemated from SEM cross section images close to 500 nm and 1200 nm as shown in Figs. 2 a and b, respcitivily.

From Fig. (2c), one can recognise the nano-crystallite size from the top-view of SEM image of the film surface of 1200 nm thickness. The morphology of the film contains grains that average size increases as the film thickness increases. However, the grain sizes were found quite large average between 60 nm and 70 nm (in the film with thickness of 1200 nm), when it is compared to that obtained by XRD analysis in the preceding section. It was caused by the different grain size criteria, underlying the different techniques. While via SEM, the size of grain is determined by the distances between the visible grain boundaries, the XRD method measures the extension of the crystalline regions that diffract the X-rays coherently, which is a more stringent criterion, leading to smaller XRD grain size. This observation suggests

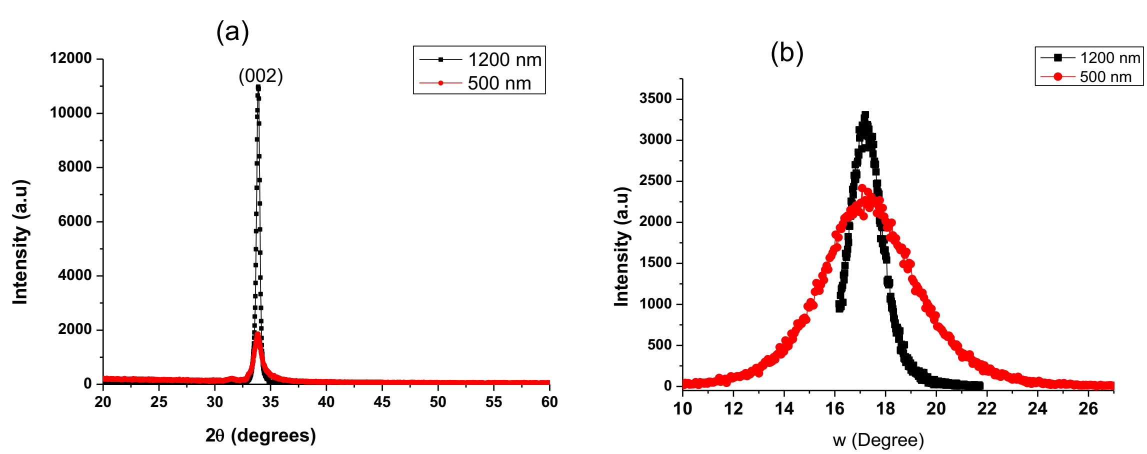


Fig. 1 **a** XRD patterns and **b** X-ray rocking curves for both newly prepared films of ZnO on Si(100) substrate

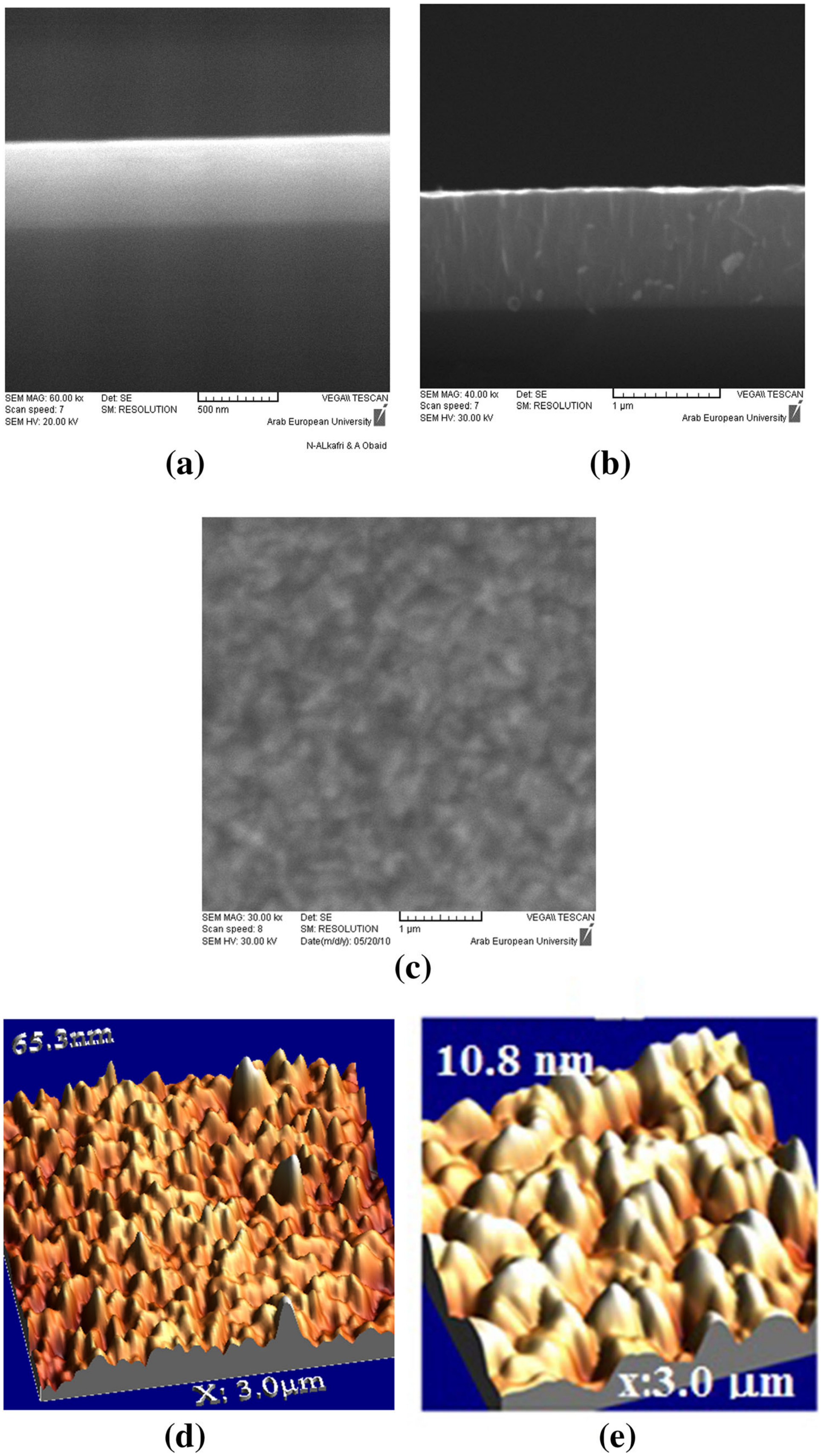


Fig. 2 images of ZnO films, (**a**) SEM images cross section for ZnO 500 nm thickness, and (**b**) cross section for ZnO 1200 nm thickness, (**c**) surface for ZnO film at 1200 nm thickness on Si substrates, (**d**) AFM image of 500 nm thickness, and (**e**) AFM image of 1200 nm thickness.

Table 1 Atomic and Weight percentage for the ZnO film of thickness of 1200 nm

Element	Weight %	Atomic %
O K	19.17	49.21
Zn L	80.83	50.79

that the present grains on the films surface could be as clusters of crystallites [10]. These kinds of texture and growth were found in (all samples) our investigations and confirm the present analysis.

Figures (2-d) and (2-e) show 3D AFM image with 3 × 3 μm dimension. This figure presents the typical texture line for ZnO film deposited with 500 nm thickness and 1200 nm thickness, respectively. It explains the existence of nanostructure in spherical forms with low roughness (in order few nanometers) the particle size increase with increase the thickness, which is consistent with XRD grain size study (last paragraphs).

3.3 EDX and Raman Study

The atomic compositions and the stoichiometry of the ZnO films have been checked via EDX, as shown Fig. (3a), the ratios of O/Zn (49.21/50.79) and the film stoichiometry are tabulated in Table 1.

The Raman scattering spectra of the films have bands atE_2(low) mode at 99 $cm^{-1}$is assigned to Zn sub-lattice (Fig. 3b) and characterized wurtzite ZnO structure, where it was sharper for the film of 1200 nm and wider for the film of 500 nm. The other mode E_2(high) at 467 cm^{-1} is assigned to oxygen atoms, it was observed for both films [15].

Exarhos et al [16] have investigated the influence of the processing on the structure and optical properties of ZnO films, they have studied the Raman spectra for the thin films, even under non-resonance excitation, features characteristic of the wurtzite phase (particularly the appearance of the 437 cm^{-1} E_2 mode) are easily discernible. The thick sputtered film also exhibits features characteristic to the wurtzite phase. The E_2 mode at 434 cm^{-1} appeared in Fig. 3b. The phonon modes were already found in the Raman spectra of studying the ZnO bulk [17].

3.4 Optical Properties

3.4.1 UV-Vis Study

Fig. (4a) shows the UV-Vis transmissions spectra of the ZnO films, and Fig. (4b) depicted the optical band gap (Eg) of the same films. The present result is indicated that the ZnO film has high optical transmittance 90% in the visible spectrum area. The optical transmittance (OT) gives more information about the Eg of the semiconductor [6] as shown in Fig. (4b), which is demonstrated a plot of "α^2 versus hν" that it is expected to be linear. We can extend the linear part of "α^2 "as a straight asymptotic line which intercepts the X- axis, α^2= 0, yielding the value of Eg from the term of "hν" [4, 18]. It was found that the average OT in the visible area is estimated around the 95% as shown in the spectra of the ZnO films.

The Eg of the ZnO films (Fig. 4b) were about 3.25 eV and 3.29 eV for 500 nm and 1200 nm films thickness, respectively. The dependence of Eg and crystalline quality were investigated earlier in previous work, that the study was concluded the concept of better quality leads larger of Eg [12]**.** That's in contrary with our previous work on ZnO films, where the Eg increases with decrease the grain size with the Oxygen percentage increase, where the Eg depends on the deposition methods and surface morphology [4].

The refractive index n_0 of ZnO films were deduced from the optical transmittance measurement using Manifacier's envelop method [19]. The quality of sputtered prepared ZnO film shows strong influence on the refractive index. Our value of the refractive index (n_0) is 2.0430 at the wavelength of λ = 550 nm for thickness of 500 nm film and n_0 = 2.0425 for thicker film, that value is similar to value of the ZnO bulk, n_0 = 2.006 [20].

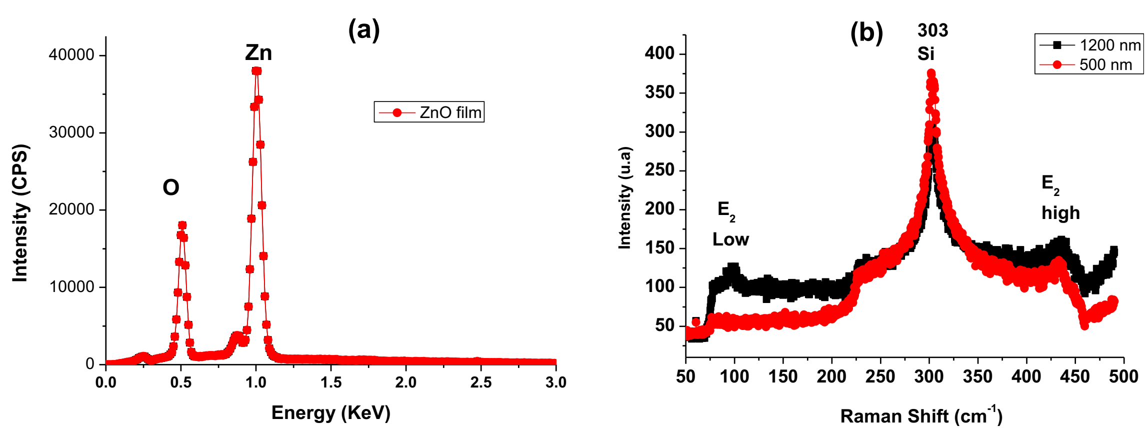


Fig. 3 **a** EDX spectra for 1200 nm film and **b** Raman spectra of 500 nm and 1200 nm ZnO films deposited on Si substrate

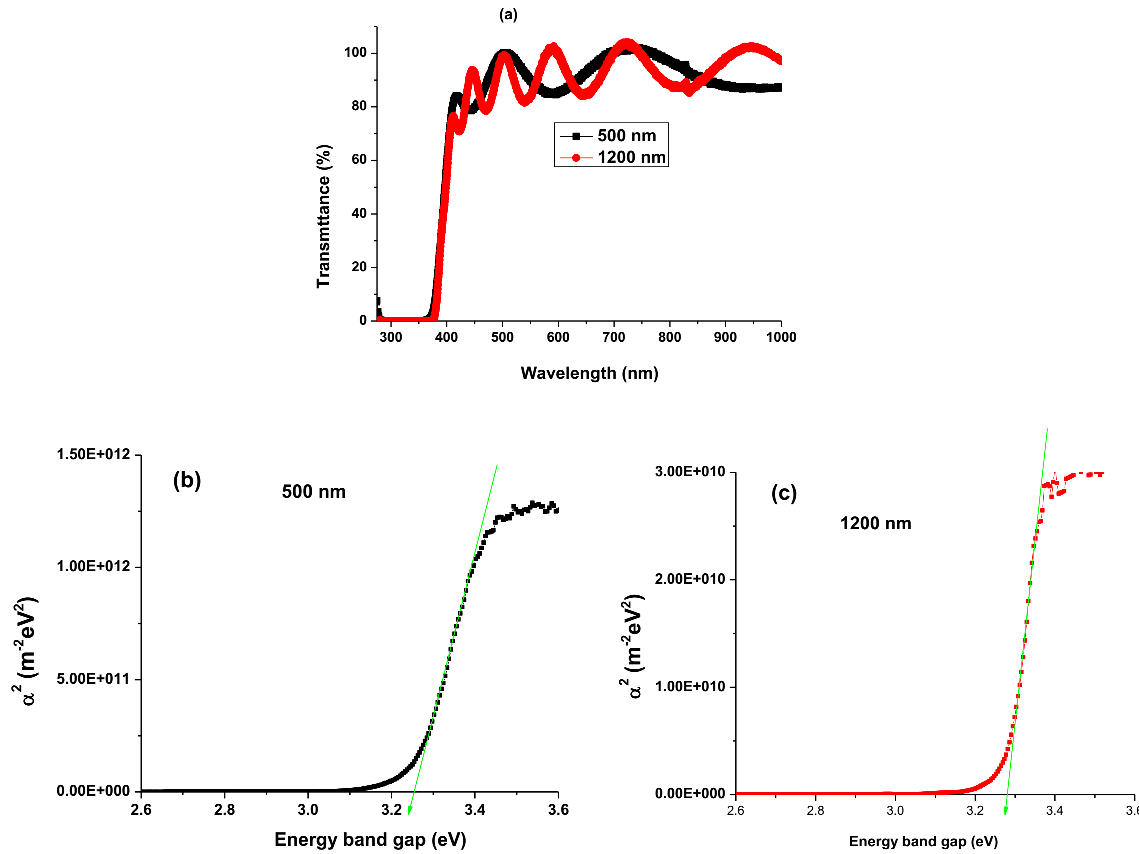


Fig. 4 **a** Optical transmittance spectra and the corresponding (Eg) for **b** ZnO film at 500 nm and **c** ZnO film at 1200 nm deposited on glass substrate

3.4.2 Photoluminesce Spectra

Photoluminesce (PL) spectra show one peak at 382 nm (~3.25 eV) for direct E_g and the two peaks nearby 404 and 435 nm. The two peaks could be attributed to Zn vacancy in addition to interstitial, respectively [21], and the broad peak close to 530 nm which might be attributed to oxygen vacancies or interstitials [4]. The intensity (I) of the band gap emission increases with thickness as seen in Fig. 5, this is in consistent with Fig. 4(b), which indicates to better quality, i.e. The crystalline quality is improved, while, the stress factor decreased with increasing the thickness.

The intensity (I) of the first peak and its broadening could be a good proof to crystallinity of ZnO film, according to reference [22], the higher crystallinity possesses higher intensity. The broadening decreases which indicates to better quality thin film, i.e. The quality of crystalline was found to be better, while

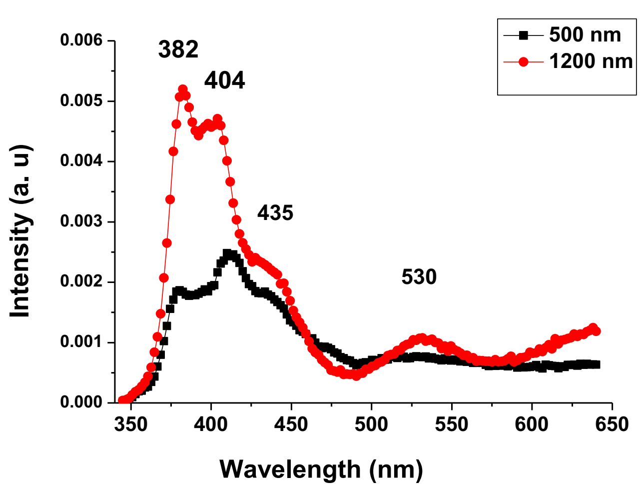


Fig. 5 Photoluminesce spectra of ZnO films on Si substrate

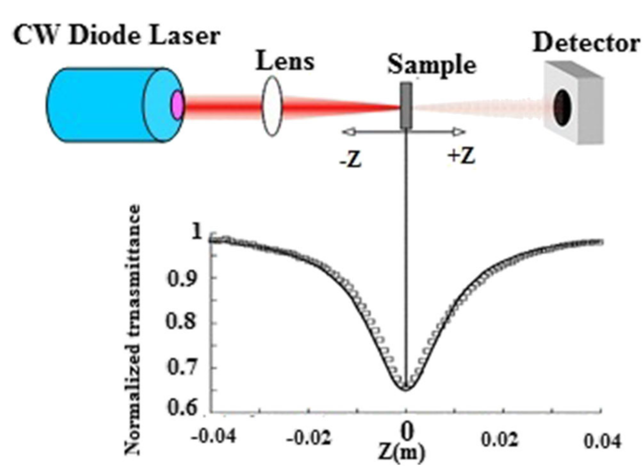


Fig. 6 the z-scan experimental setup

the stress rate decreased with increasing the thickness of the film [20], This concept is agreed with our work.

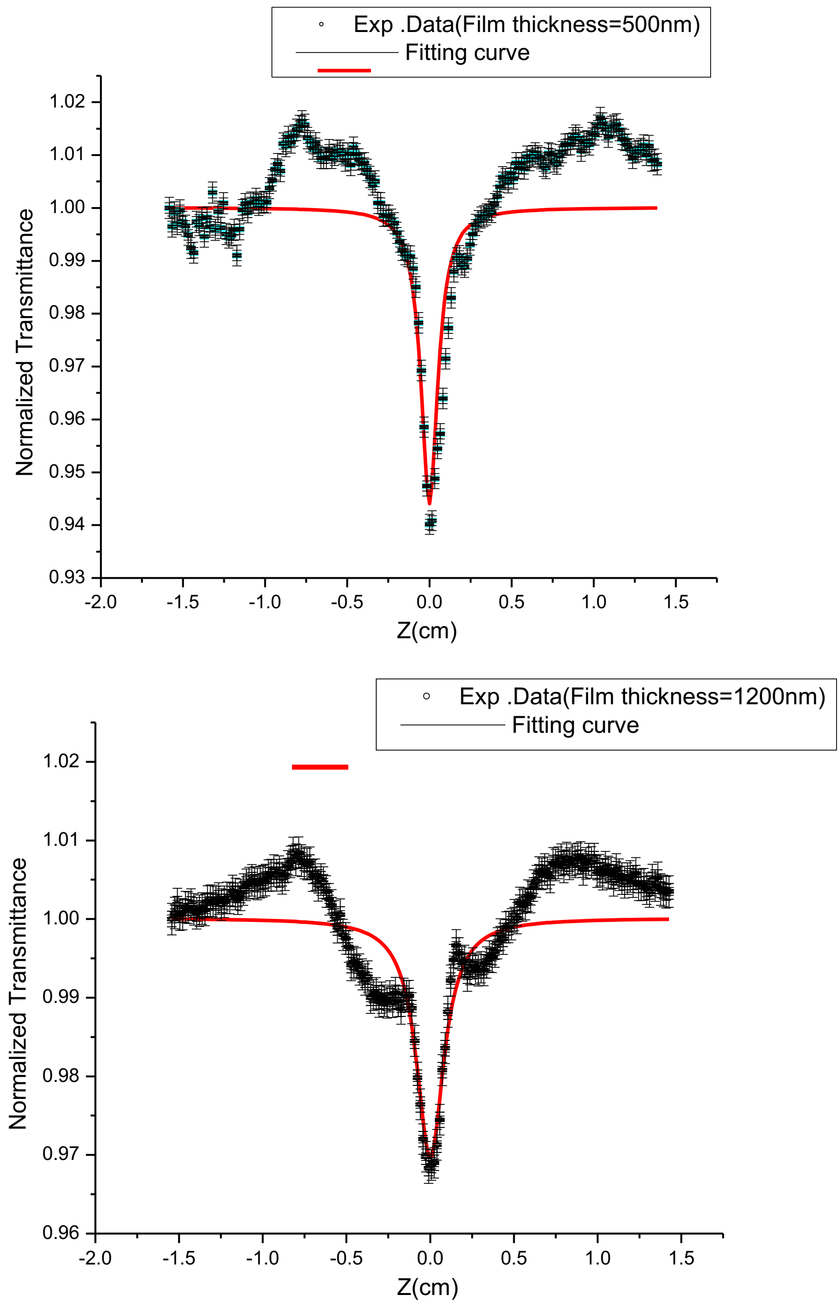
3.4.3 Nonlinear Optical Characteristics

The NLO coefficient β of the media was estimated via conducting OA *z*-scan experimental measurements (Fig. 6) using CW TEM_{00} Gaussian beam diode laser with power close to 26 mW [23]. The laser beam was focused on the film surface via a lens with focal point of 10 cm; the rate of transmittance intensity (I) was measured with pyro-electric power meter. Figs. 7 and 8 show the OA z-scan plots of a symmetrical, narrow dip at λ = 635 nm of the prepared the new deposited ZnO films on glass substrate, in addition to ZnO single crystal. At the Figs. 7 and 8, the symbols indicate to the experimental measurements, while the solid red lines are obtained by fitting the experimental data to Eq. 1 [24]:

$$\mathrm{T}\ (z) = 1 - \frac{\left(I_0 L_{eff}\ \beta\right)}{\left[2^{\frac{3}{2}}\left(1+\frac{z^2}{z_0^2}\right)\right]} \tag{1}$$

Here, $L_{eff} = (1\text{- exp. }(-\alpha_0 L))/\alpha_0$ is the effective thickness of the sample, L is the sample path length, α_0 is the LA

Fig. 7 the open-aperture z-scan data of ZnO films with two thicknesses



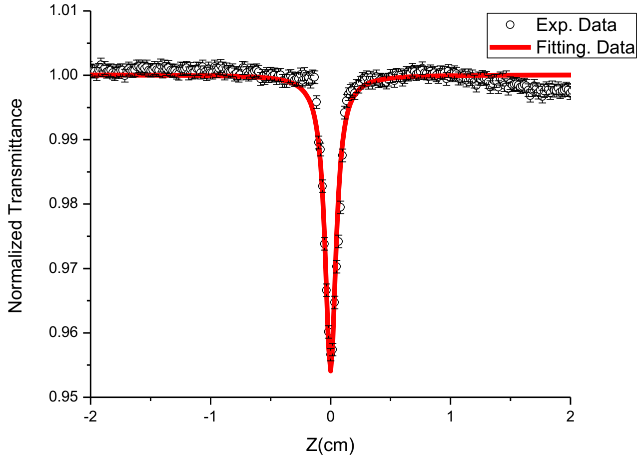


Fig. 8 the open-aperture z-scan data of ZnO single crystal

coefficient, $z_0 = \pi\omega^2{}_0/\lambda$ is diffraction range of the beam, $\boldsymbol{\lambda}$ is the laser wavelength, and the I_0 is the laser excitation intensity at z = 0. The value of the excitation intensity was determined with the relation of $\mathbf{I_0} = (2p\ /\ \pi\omega^2{}_0)$, it was equal to about 3342 W/cm^2. To determine the NLA coefficient, β, of both films at two thicknesses of 500 nm and 1200 nm, the fitting of the experimental data was performed using Eq.1. By calculating the NLA coefficient, β, we were able to estimate the imaginary part [Im(χ^3)] of the 3rd nonlinear optical susceptibility. All the deduced optical parameters, β, Im(χ^3), the linear absorption, α_0, and the linear refractive index,n_0, are listed in Table 2.

The OA z-scan smooth curve looks like a symmetrical; dip (valley) indicating that the ZnO films shows to the presence of NLO processes in our prepared films. It was reported that the two photon nonlinear absorption (TPA) in ZnO single crystal is the dominated around the λ = 635 nm [25].

The increasing of the NLA coefficient β in the prepared ZnO film with the thickness of 500 nm thickness was explain due to the presence of nano-crystallites. As seen from Table 2, the β coefficient of the film with the thickness of 500 nm is larger than to the 1200 nm thickness, and also to the ZnO single crystal. Our reported results agreed with reported value of ZnO study in ref. [26, 27]. It was found the NLA coefficient β of their ZnO thin films (20, 100, 300 nm) proportional to the film thickness. But, we have found in our study the opposite behavior, as our samples consider being thick films. Our results can be explain on the bases that the β of 500 nm ZnO film is large than the film thickness of 1200 nm because of the film of 500 nm has higher stress value, this leads to higher density, and the film of 1200 nm has less stress value, this means lower density [10]. The film of thickness 1200 nm contained large grain size which means that the NLA coefficient, β, is inversely proportional with grain size. The reported values of the NL optical parameters of our new prepared ZnO films which were acquired using z-scan with CW laser at λ = 635 nm can be compared with very similar reported work in ref. [9]. However, they have focused on studying the NLO properties of undoped and Mn doped ZnO films, with thickness of ZnO film is equal to 350 nm. But, we have conducted our measurements using two films thickness of 500 nm and 1200 nm. Table 2 summarizes the comparative study of our work with some results of Ref [9]. It is noted that there are some differences between the results of two works. However, we can justify that to the thickness of ZnO films coating of the two works. Moreover, we consider the novelty in our present work is the comparative study between the ZnO films and ZnO single crystal at λ = 635 nm. Such study could be advantage of the prepared ZnO films make it a good candidate for use in photonic applications.

4 Conclusions

ZnO films of thicknesses on silicon and glass substrates were prepared using RF magnetron sputtering system**.** The quality of the new prepared film has studied by XRD (grain size and orientation). The SEM images show the grain size is about the average of 60 nm. The band gaps values were obtained from the UV-Vis spectra of the new deposited films on glass substrates. Photoluminesce (PL) spectra show that the band gap increases with the thickness of the film. The NLA coefficients of the ZnO films with two thicknesses were estimated using z- scan technique. It was found that

Table 2 The calculated linear and NL parameters of ZnO films and ZnO single crystal at λ = 635 nm

ZnO form		β (cmW^{-1})	Im(χ^3) (esu)	Eg(ev)	Average Transmittance(%)	α_0 (cm^{-1})	n_0
ZnO single Crystal		**3.89 × 10^{-4}**	**2.57 × 10^{-5}**	–	–	**0.60**	**2.006**
ZnO Films	**Thickness 500 nm**	**4.74 × 10^{-4}**	**2.53 × 10^{-5}**	**3.25**	**95**	**0.68**	**2.041**
	1200 nm	**2.59 × 10^{-4}**	**1.39 × 10^{-5}**	**3.29**	**95**	**1.33**	**2.043**
Ref [9] ZnO	**350 nm**	**0.371 × 10^{-3}**	**1.4 × 10^{-5}**	**3.20**	**91**	–	–

the nonlinear absorption coefficient (β) of ZnO film of 500 nm is large than the film thickness of 1200 nm.

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