Optical Materials 62 (2016) 64–71

Contents lists available at ScienceDirect

Optical Materials

journal homepage: www.elsevier.com/locate/optmat

# Influence of electron beam irradiation on nonlinear optical properties of Al doped ZnO thin films for optoelectronic device applications in the cw laser regime

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ARTICLE INFO

*Article history:*
Received 29 July 2016
Received in revised form
2 September 2016
Accepted 19 September 2016

*Keywords:*
AZO thin films
Z-scan
Electron beam
NLO
Optical limiting

ABSTRACT

We present the studies on third-order nonlinear optical properties of Al doped ZnO thin films irradiated with electron beam at different dose rate. Al doped ZnO thin films were deposited on a glass substrate by spray pyrolysis deposition technique. The thin films were irradiated using the 8 MeV electron beam from microtron ranging from 1 kG y to 5 kG y. Nonlinear optical studies were carried out by employing the single beam Z-scan technique to determine the sign and magnitude of absorptive and refractive nonlinearities of the irradiated thin films. Continuous wave He–Ne laser operating at 633 nm was used as source of excitation. The open aperture Z-scan measurements indicated the sample displays reverse saturable absorption (RSA) process. The negative sign of the nonlinear refractive index $n_2$ was noted from the closed aperture Z-scan measurements indicates, the films exhibit self-defocusing property due to thermal nonlinearity. The third-order nonlinear optical susceptibility $\chi(3)$ varies from $8.17 \times 10^{-5}$ esu to $1.39 \times 10^{-3}$ esu with increase in electron beam irradiation. The present study reveals that the irradiation of electron beam leads to significant changes in the third-order optical nonlinearity. Al doped ZnO displays good optical power handling capability with optical clamping of about ~5 mW. The irradiation study endorses that the Al doped ZnO under investigation is a promising candidate photonic device applications such as all-optical power limiting.



## 1. Introduction

Semiconductor materials are of great importance as they play a vital role in nonlinear optics due to their applications in optical switching, optical information storage, all optical signal processing, optical limiting, optical waveguides and high speed optical communication networks [1]. Zinc oxide (ZnO) a well-known II–VI semiconductor possess a direct band gap of 3.37eV and high exciton binding energy of 60 meV. It has emerged as one of the promising materials due to its high mechanical and chemical stability, excellent electrical and optical properties together with its natural abundance [2,3]. ZnO thin films have potential application in electronics, spintronics, optoelectronics, solar cells and information technology devices [4]. Doped ZnO thin films have been investigated widely for many practical applications like light emitting diodes and laser diodes [5]. Doping into ZnO lattice increases the functionality of the ZnO. Dopants such as aluminum, gallium etc. significantly enhances the conductivity of ZnO due to the presence of excess electrons in the trivalent metal ions [6–10]. Several thin film deposition techniques are employed to obtain the ZnO thin films such as molecular beam epitaxy (MBE), metal organic chemical vapor deposition (MOCVD) sputtering, pulsed laser deposition (PLD) and spray pyrolysis. Kityk et al. [15] established the use of simple spray deposition technology may be of interest for the nonlinear optical properties when the external photoinduced

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http://dx.doi.org/10.1016/j.optmat.2016.09.053
0925-3467/

beam is used.

Radiation sources such as γ −rays, UV radiation, pulsed lasers, microwaves, and ultrasonic waves [10–13] are used to modify the desired properties by irradiation. Electron beam irradiation has been utilized to synthesize nanoclusters and nanowires. Mechanical, electronic and magnetic properties can be tailored using electron beam irradiation. However, a little is known about the effects arises due to electron beam irradiation on third-order nonlinear optical parameters [14]. Hence, it is necessary to investigate the possibility of tuning the third-optical nonlinearity in a controlled manner by electron beam irradiation for use in photonic device applications. To the best of our knowledge, the third order nonlinear optical properties of electron beam irradiated ZnO thin films have not been investigated till now. In this context, we present the third-order nonlinear optical and optical power limiting studies on electron beam irradiated Al doped ZnO (AZO) thin films by Z-scan technique under cw regime.

## 2. Experimental

### 2.1. Preparation of Al doped ZnO thin films

The samples of Aluminum doped ZnO thin films were deposited on glass substrates by spray pyrolysis technique. The starting solution consisted of zinc chloride ($ZnCl_2$) at a concentration of 0.1 M, dissolved in distilled water. The doping was achieved by the addition of Aluminum nitrate (Al(NO3)3) in distilled water at room temperature. The [Al]/[Zn] atomic percent ratio were 3%. The substrate temperature was fixed to 350 °C and the solution was sprayed at a flow rate of 2.6 ml/min.

### 2.2. Electron beam irradiation

The electron beam irradiation of AZO thin films were carried out using the electron beam from a variable energy Microtron accelerator at Mangalore University, India. The energy of the electron beam was 8 MeV. The samples were irradiated with 1, 2, 3,4 and 5 kGy doses.

### 2.3. X-ray diffraction and surface morphology

X-ray Diffraction (XRD) patterns of the irradiated films were recorded using the Rigaku X-ray diffractometer with Cu Kα (λ = 1.54059 Å) radiation. Surface morphology of AZO thin films was characterized using commercially available Atomic Force Microscopy (AFM) system (Veeco, Innova) in contact mode.

### 2.4. Z-scan technique

The sign and magnitude of third-order nonlinear susceptibility χ(3) of electron beam irradiated AZO thin films was evaluated using z-scan technique. Sheik-Bahae et al. [16,17] developed the z-scan technique, with the help of this technique; one can obtain the nonlinear absorption and refraction nonlinearities simultaneously. The z-scan experiments were performed using CW He-Ne laser (Thor labs HRP350-EC-1) at 633 nm wavelength as an excitation source. The laser beam was focused to a spot size of 36.78 μm using a 5 cm focal length lens with input power 22 mW and the Rayleigh length $Z_R$ of 6.71 mm. The thickness of the AZO thin films were ~350 nm. Hence, the thin sample approximation is valid as the sample thickness is less than the Rayleigh length ZR [16,17]. The optical power limiting response of the films was studied by placing the films at the focus. The input power of the laser beam was varied by using neutral density filter and the resultant output power was recorded using a photo-detector fed to the power meter.

## 3. Results and discussions

### 3.1. Ultraviolet–visible characterization

The UV-VIS transmittance spectra and Tauc plots for electron beam irradiated AZO thin films are shown in Fig. 1 and Fig. 2 respectively. For a direct band gap semiconductor, the optical band gap $E_g$ can be estimated from absorption $\alpha(h\nu)$ using the following relation [18,19]:

$$\alpha = A(h\nu - Eg)^n / h\nu \quad (1)$$

Where $A$ is the proportionality constant and $h\nu$ is the photon energy. The absorption coefficient $\alpha(h\nu)$ can be calculated using the relation ln $(1/T)/d$, where $T$ is the total transmittance and $d$ is the thickness of the film. For a direct transition, n = 1/2. The optical band gap for the irradiated films were obtained by plotting $(\alpha h\nu)^2$ as a function of hν, and extrapolating the linear portion of $(\alpha h\nu)^2$ to the energy hν where $(\alpha h\nu)^2$corresponds to zero [18,19]. The optical band gap of the irradiated films were in the range of 2.72 eV −2.46 eV. The pincipal optical band energies are given in the Table 1.

### 3.2. Structure and surface morphology

Following ref [20] compound ZnO at higher pressure may possess a structural type ZnS (sphalerite), SG *F*-43 *m* (216), $a$ = 4.520 or NaCl, SG *Fm*-3*m* (225) $c$ = 4.223. Internal pressure − isoelectron replacement of Zn by larger atoms such as Nd [21] or Al [22] does not change structural type of resulting compounds. An existence of three maxima for irradiated ZnO:Al films leads to structural changes.

Fig. 3 shows XRD patterns of AZO thin films having thickness of about 350 nm. The films represent polycrystalline single phase, and the diffraction peaks identified in the films were found to be consistent with the diffraction planes of the sphalerite structure of ZnO. All the XRD patterns show a preferential oriented structure with the most intense peak being the (111, 2Θ = 34.56). There is also present a maximum at 222, 2Θ = 72.63. The cubic lattice parameter determined from these maxima is equal to $a$ = 4.51(2), which is in agreement with the data presented in ref [20] for structural ZnS type (sphalerite). Fig. 4 shows the second coordination of oxygen atoms for structures (a) $Zn_{1-3/2x}Al_xO$ (b)$ZnAl_2O_4$. The second coordination [23] of oxygen atoms will be in a form of cubooctahedral (sphalerite anion sub-lattice) in both of structures,

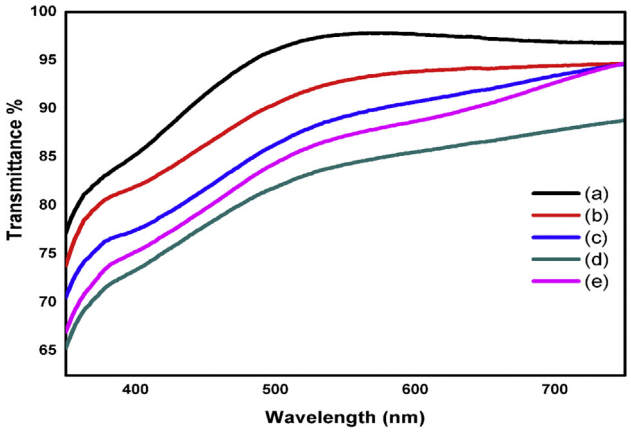


**Fig. 1.** Transmittance spectra of AZO thin film irradiated with (a) 1 kGy, (b) 2 kG y, (c) 3 kGy, (d) 4 kGy and (e) 5 kGy.