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Third-order nonlinear optical properties of Mn doped ZnO thin films under cw laser illumination

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ABSTRACT

We report the measurements of third-order nonlinear optical properties of undoped zinc oxide and manganese doped zinc oxide thin films with different doping concentrations investigated using z-scan technique. Thin films were prepared by radio frequency magnetron sputtering using a compound target on glass substrate at room temperature. The structural properties of the deposited films were analysed by X-ray diffraction studies. The atomic force microscope analysis of the deposited films reveals that the grain size and roughness of the films depend on the Mn concentration. The direct energy band gap of the deposited film increases with the increase in Mn concentration in the films. The nonlinear optical measurements were carried out using a cw He–Ne laser at 633 nm wavelength. The z-scan results reveal that the films exhibit self-defocusing nonlinearity. The third-order nonlinear optical susceptibility $\chi^{(3)}$ is found to be of the order of 10^{-3} esu. The films investigated here exhibit good optical power limiting at the experimental wavelength.

1. Introduction

Nonlinear optical semiconductor materials are of great importance, as they alter the optical properties of light propagating through them and hence used in many applications such as all-optical signal processing, optoelectronic devices, optical switching, optical image processing, optical information storage, optical limiting, optical waveguides, high speed optical communication networks, and future applications in biological and medical sciences [1]. Intense research has been devoted to the fabrication of nonlinear waveguides which are the integral part of electro-optic devices and efficient frequency doubling devices. Wideband gap semiconductors considered suitable for these types of devices as they can work in short wavelength region. Zinc oxide (ZnO) is II–VI compound semiconductor, having a wide band gap of 3.37 eV and high exciton binding energy of 60 meV at room temperature [2]. It has emerged as one of the promising materials due to its unique properties such as high mechanical and chemical stability, excellent electrical and optical properties together with its natural abundance and non-toxicity [3,4]. ZnO thin films have potential application in electronics, spintronics, optoelectronics, optical bistability, solar cells, gas sensors and information technology devices including displays and wavelength selective applications [4–6]. A key requirement for advancing the technological uses of ZnO is improved control of doping [7]. Doped ZnO thin films are studied widely for many practical applications like spintronics devices, light emitting diodes and diode lasers [7–10]. However, a little is known about the nonlinear optical properties of ZnO thin films [11].

Several deposition techniques such as molecular beam epitaxy (MBE), metal organic chemical vapor deposition (MOCVD), sputtering (DC reactive sputtering, RF magnetron sputtering), pulsed laser deposition (PLD) and spray pyrolysis [12–18], were employed to deposit ZnO thin films. Among these, RF magnetron sputtering is preferred because of its simplicity, low substrate temperatures, and as well as the reasonable quality of the resultant films. In RF magnetron sputtering, the growth of films takes place in an ambient of O_2/Ar + O_2 with ratios ranging from 0 to 1 at a pressure of 10^{-3}–10^{-2} mbar. O_2 serves as the reactive gas and Ar servers as the sputtering enhancement gas.

The second and third-order nonlinear optical properties of undoped ZnO thin films [19] and ZnO thin films doped with Ni, Zr, Ce, F, Er, Al, Sn, F:In [11,20–24] deposited using various techniques under pulsed lasers have been reported. The study of photo physical and optical characteristics such as nonlinearity, magnitude and response time, must be carried out to spot the material suitability for nonlinear applications [25]. The magnetic, optical and electrical properties of Manganese (Mn) doped ZnO thin films [13,14,18] have been studied. These results reveal that Mn doped ZnO films has good optical properties. To the best of our knowledge, the nonlinear optical properties of ZnO thin films doped with manganese

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(Mn) have not been investigated. Hence, it is necessary to investigate and study the nonlinear optical properties of Mn doped ZnO thin films for its future applications. The nonlinear optical response of thin films is of particular interest because of its application in integrated nonlinear optical devices [11]. Continuous wave (cw) lasers ranging from μW to kW are widely used in various applications [25]. This necessitates the need for protecting the optical sensors and human eyes from high intense laser beams. In this article, we report for first time the third-order optical nonlinearity and optical power limiting properties of Mn doped ZnO sputtered thin films under cw laser using z-scan technique. Under cw laser illuminations, the self-focusing and self-defocusing effects are usually associated with refractive nonlinearities of thermo-optic origin [26].

2. Experimental

2.1. Preparation of Mn doped ZnO thin films

Mn doped ZnO thin films were deposited on glass substrates by radio frequency (RF) magnetron sputtering. Glass substrates were ultrasonically cleaned in alcohol followed by distilled water rinse before mounting into the vacuum chamber. The compound targets with various Mn concentration (0, 5, 10 and 15 wt.%) were prepared using solid state reaction technique in which ZnO (99.99%, from Sigma) and MnO_2 (99.99%, from Sigma) were mixed thoroughly in a planetary ball mill for 10 h. This homogeneous mixture was calcinated at 400 °C for 6 h. The calcinated powders were cold pressed using hydraulic press at a pressure of 25 MPa to get 50 mm diameter pellets. The pressed pellets were sintered at 950 °C for 6 h to get dense pellets. These pellets were used as targets and they are mounted on the water magnetron cooled cathode. The targets with different Mn concentration were sputtered to get thin films on pre-cleaned glass substrates. Before each sputter process the chamber was pumped down to a pressure less than 5×10^{-6} mbar. The sputtering was performed in the growth ambient with mixture of high purity Ar (99.999%) and O_2 (99.8%) at a constant working pressure of 0.02 mbar. The oxygen to argon ratio was adjusted to three and kept constant for all our experiments. Before each sputtering process, the targets were pre-sputtered in pure Ar for 30 min to remove any contamination on the target surface and to make the system stable. The RF power, sputter duration and the target to substrates distance were kept constant at 200 W, 60 min and 50 mm respectively in all experiments.

The thickness of deposited film is measured by using Filmetrics film thickness measurement system (Model-F 20) and found to be 125 ± 20 nm for Mn doped ZnO films and it is 350 ± 20 nm for undoped ZnO film. Topography of the deposited films was characterized using commercially available AFM system (Veeco, Innova) in contact mode. Nanoscope software was used to examine the three dimensional features of AFM image. The linear refractive index was measured using spectroscopic ellipsometry. The optical transmittance measurements were done using Ocean Optics USB4000 UV–VIS spectrophotometer in the spectral range 300–800 nm.

2.2. z-Scan technique

The nonlinear index of refraction n_2, the nonlinear absorption coefficient β_{eff}, the magnitude of the real and imaginary parts of third-order nonlinear susceptibility $\chi^{(3)}$ of Mn doped and undoped ZnO thin films was characterized using z-scan technique developed by Sheik Bahae et al. [27,28]. z-Scan is a single-beam technique based on spatial beam distortion principle, offers simplicity as well as high sensitivity for measuring the sign and magnitude of refractive nonlinearities. In this technique, a polarized Gaussian laser beam is focused to a narrow waist. The samples were mounted on a translation stage and moved along *z*-direction through the beam focus ($z = 0$), self-focusing or self-defocusing modifies the wave front phase, there by modifying the detected beam intensity. The schematic experimental setup used for z-scan technique is shown in Fig. 1.

The optical power limiting responses of the films was studied by placing the samples at the focus. The input power of the laser beam was varied by using neutral density filter and the resultant output power through the samples was recorded using a photodetector fed to the power meter. For the present studies a cw He–Ne laser at 633 nm wavelength was used as excitation source. The laser beam with power input 21.8 mW was focused using a 5 cm focal length lens. The measured laser beam waist ω_0 and the Rayleigh length Z_R are 36.78 μm and 6.71 mm respectively.

3. Results and discussions

3.1. Structure and surface morphology

Fig. 2 shows XRD patterns of undoped and Mn doped ZnO thin films having thickness of about 350 nm for undoped film and 125 nm for Mn doped films. The undoped thin films show a preferred orientation along *c*-axis which is confirmed by the presence of a strong peak along (002) planes at 2θ value 34.337°. This value is slightly less than the actual value 34.43° (JCPDS-01-089-0511) which is due to stresses in the films during the deposition. The preferred orientation disappears for doped films as indicated by XRD

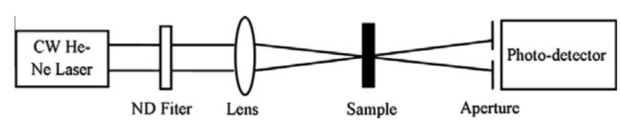

Fig. 1. The schematic z-scan experimental setup.

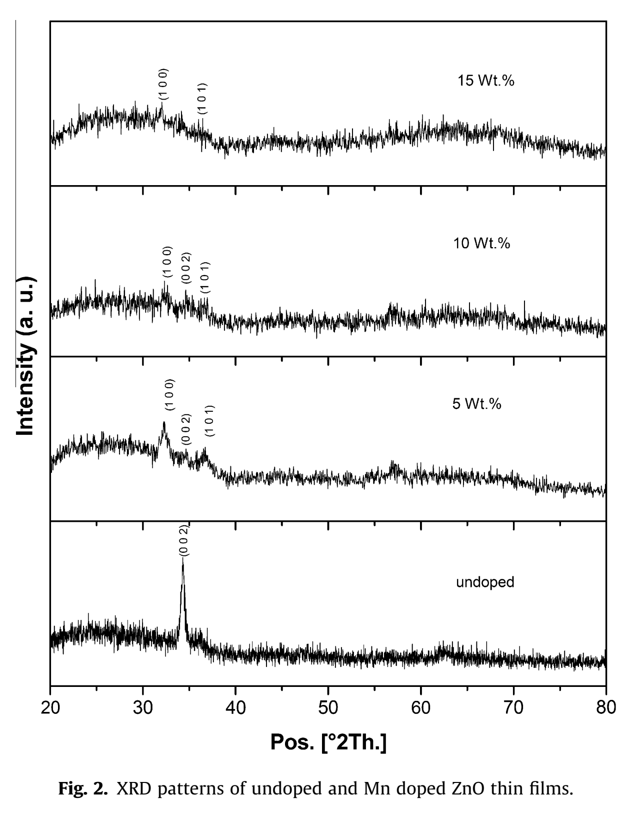

Fig. 2. XRD patterns of undoped and Mn doped ZnO thin films.