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Enhancement of the efficiency of the third harmonic generation process in ZnO:F thin films probed by photoluminescence and Raman spectroscopy

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ABSTRACT

ZnO:F nanostructures at varying fluorine doping concentrations were prepared by spray pyrolysis technique. Effect of fluorine on structure, surface morphology, optical absorption and linear and nonlinear optical properties of the nanostructures were investigated by photoluminescence (PL), raman spectroscopy, THG (third harmonic generation) and Z-Scan analysis. The gaussian fitting on the PL spectra shows different luminescent centers and increase in the intensity. An increase in the PL emission intensity was observed due to the incorporation of fluorine in ZnO lattice which correlates to the formation of various defect states. Prominent emission in the blue, green and violet region along with a weak UV-violet near band edge (NBE) emission was noted in the nanostructures resulted by the Zn and O vacancy defect. ZnO related phonon modes were observed in the raman spectroscopy along with E2 high mode around 439 cm^{-1} as the signature peak of wurtzite ZnO nanostructures. Z-scan measurements were performed to determine the absorptive and refractive nonlinearity of ZnO:F thin films. The nonlinear optical properties of the ZnO:F thin films found to be enhanced on fluorine incorporation into ZnO lattice. The third order optical susceptibility $\chi(3)$ increased from 3.5×10^{-4} esu to 6.17×10^{-3} esu due to the enhancement of electronic transition to different defect levels formed in the films. The third harmonic generation studies on ZnO:F thin films were investigated using Nd:YAG laser at a wavelength of 1064 nm and 8 ns pulse width. The THG signal intensity has shown an increment upon fluorine incorporation. The highest value of THG signal was obtained for the 1% ZnO:F thin films. The enhancement of third harmonic response shows that ZnO:F nanostructures finds immense applications in photonic device applications.

1. Introduction

Nanostructured semiconductor thin films have been under continuous scientific interest due to their unique optical, electrical and large nonlinear optical properties [1]. The technological expansions in the field of photonics and integrated optics has led to a renewed interest in the development of new nonlinear optical (NLO) materials [2–7]. Among the various NLO materials investigated Zinc oxide (ZnO) have been under continual scientific interest because of their attractive properties such as a direct band gap of 3.3 eV, exciton binding energy of 60 meV, cohesive energy of 1.89 eV, nontoxic and abundance in nature etc. [2–5]. The combination of excellent physical and chemical properties has made ZnO a potential candidate for various nonlinear optical applications such as optical limiting, frequency tripling, optical switching and pulse shaping etc. [8–17]. In spite of the wide investigations, the effect of halogen elements (Fluorine, Chlorine) doping on the linear and nonlinear optical properties of ZnO thin films is limited [18]. The halogen elements such as fluorine has advantages over the other dopants such as low cost, abundance and size compatibility between fluorine and oxygen atoms which results in trivial perturbation in the lattice [19].

In the recent years many efforts have been made in the field of thin film deposition techniques to invent a method that is simple, low cost and attuned with current device fabrication technologies. Ease of handling, low cost, large area deposition, safe and simple deposition methodology makes spray pyrolysis technique more dependable compared to other deposition techniques [20]. Furthermore material with high nonlinear optical susceptibility is required to meet the present demand of nonlinear device applications. ZnO thin films has always been regarded as an ideal material for optoelectronics device applications due to its outstanding physical and chemical properties. The majority of reports on ZnO nanostructures are concentrated on optical

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and electrical applications [2–7]. Although ZnO is investigated for optical nonlinearity, but lacks investigations in nonlinear mechanisms and the affecting parameters which is essential for nonlinear optical devices. Therefore exploring ZnO as NLO material is of great significance to understand the basic physical mechanisms of optical nonlinearity arising in it and to design and intend the versatile nonlinear optical devices with cost effective and enhanced performance. The studies related to cubic nonlinear optical properties of ZnO:F nanostructures based on optical limiting and frequency tripling applications are comparatively less to date. In this context the current work aims at understanding the basic physical mechanisms of optical nonlinearity in ZnO:F thin films and the parameters which affects the nonlinearity has been investigated using the UV–Visible spectroscopy, X-ray diffraction, atomic force microscopy, photoluminescence and raman spectroscopy analysis.

2. Experimental details

2.1. Sample preparation

The fluorine doped ZnO (ZnO:F) thin films were grown by spray pyrolysis technique [19,21,22]. The precursor solution used for deposition was Zinc chloride ($ZnCl_2$) and ammonium fluoride (NH_4F) dissolved in double distilled water and stirred for 30 min separately [22]. The fluorine doping was done by adding ammonium fluoride at a doping concentration of 1%, 3% and 5%. The concentration of $ZnCl_2$ and NH_4F solutions were fixed to 0.05 M. The final solution was stirred again for 30 min before the deposition process. The glass substrates used for thin film deposition were ultrasonically cleaned using double distilled water, acetone and isopropyl alcohol, and dried under nitrogen flow. The substrates was placed on a hot plate fixed at 400 °C. Flow rate of the solution was fixed at 2 ml/min. The deposition time was fixed to attain the constant film thickness of ~ 310 nm for all the concentrations.

2.2. Characterization techniques

The Optical Profilometer (Veeco Dektak) was used to determine thickness of the deposited films. Structural analysis of the films were carried out using Rigaku X-ray diffractometer (Cu $K\alpha_1$ $\lambda = 1.54A^{\circ}$) with 2Θ range from 20° to 90° and grazing angle of 0.6°. Bruker Icon atomic force microscope (AFM) was used to determine the average surface roughness and to study the surface morphology of films. Bruker nano scope software was used to analyze the AFM images. Linear optical properties of the films were studied using UV–Visble spectrophotometer (Shimadzu-1800), where a glass substrate was set in a reference path light to counterbalance the substrate's absorption. The photoluminescence analysis of the films were carried out at an excitation wavelength of 325 nm using Horiba fluromax-4 spectroflurometer. The vibrational modes of the ZnO:F thin films were studied by recording the raman spectra using Horiba JOBINYVON LabRAM HR spectrometer with 532 nm diode pump solid state(DPSS) laser as the excitation source.

2.3. Z-scan measurement

Z-scan measurement technique was used to determine the nonlinear absorption and refraction properties of ZnO:F thin films. The excitation signals for nonlinear measurements were generated by (Thorlabs HRP350-EC-1) He-Ne continuous wave (CW) laser with 632.8 nm wavelength at an input power of 20 mW. Fig. 1 shows the schematic diagram of Z-Scan system used to determine the nonlinearity of ZnO:F thin films. It is based on the principle of spatial beam distortion was originally proposed by Sheik-Bahae et al. [23,24] and has been implemented to the study of third-order optical nonlinearity. In Z-scan measurement, the sample is translated horizontally around the focal plane of a focused gaussian beam. Due to optical nonlinearity the incident intensity distribution induces a change in the refractive index and the absorption coefficient of the material which affects beam propagation. The change in the beam profile is monitored by performing two scans, with and without aperture in front of the detector from which nonlinear refraction and absorption were determined.

2.4. Third harmonic generation (THG) studies

Third harmonic signals generated by ZnO:F thin films were studied using the experimental set up presented in Fig. 2. THG measurements were carried out before and after laser treatment using a coherent continuous wave (CW) laser light of wavelength 532 nm and power about 200 mW with respect to third harmonic generation at 355 nm [25]. As a source of fundamental radiation a 8 nanosecond pulse from Nd: YAG laser with a wavelength of 1064 nm and frequency repetition rate of 10 Hz was used. The power of the incident laser light was tuned by glan's polarizer. The laser beam profile diameter was equal to about 8 mm. The value of fundamental laser energy signal was detected by the germanium photodetector and it's THG by a Hamamatsu photomultiplier with an installed interferometer filter at 355 nm with spectral width about 5 nm. Levels of obtained fundamental and third harmonic signals were measured using a Tektronix MSO 3054 oscilloscope with a sampling rate of 2.5 GS/s. To eliminate possible parasitic background the studies have been done at wavelengths 320 nm and 380 nm and they have shown a magnitude of THG at least half order less. Additionally the maximum of the THG was evaluated from angle dependences by a first THG maximum

3. Results and discussions

3.1. Linear optical properties

Absorbance vs wavelength spectra of the ZnO: F thin films were recorded in the wavelength range of 350–1000 nm and shown in Fig. 3. It is observed from the spectra that the investigated films exhibits a transmittance of more than 85%. The interference fringe pattern observed in undoped films become less pronounced upon doping as the films probably becomes more irregular and scatters more light leading to change in absorbance. From the shift observed in absorbance edge it is expected a variation in optical energy band gap. By adopting tauc plot, energy band gap of deposited films were determined from absorbance spectra [26]. It is observed from the Fig. 4 that fluorine incorporation into ZnO lattice doesn't change the band gap of the films considerably (band gap was in the range 3.26–3.29 eV). Size compatibility between fluorine and oxygen atoms can be a possible reason for the observed results [27].

3.2. Structural and morphological studies

The grazing angle X-ray diffraction pattern of the ZnO:F nanostructures are shown in Fig. 5. The obtained structure for all the deposited films are polycrystalline in nature and can be indexed to hexagonal wurtzite structure of ZnO (JCPDS card No: 036-1451). The presence of strong X-ray diffraction peak upon doping indicates that the fluorine incorporation doesn't alter the basic structure of the ZnO:F films. The XRD pattern of undoped ZnO are similar to that of fluorine doped ZnO films indicates that impurity phases corresponds to fluorine doping were not observed. This concludes that fluorine has uniformly doped into the ZnO lattice sites [28]. In case of undoped ZnO thin film (101) is the dominant peak. The preferred growth orientation will depend upon factors such as growth parameters, thickness of the films, substrate temperature, deposition method etc. For instance, Zhong et al. [29] reported the effect of films thickness on preferential growth orientation where they observed (101) as the dominant peak instead of (0 0 2) upon varying the film thickness, similarly Singh et al. [30] also