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Effect of self assembly on the nonlinear optical characteristics of ZnO thin films

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Abstract

In the present work, we report the third order nonlinear optical properties of ZnO thin films deposited using self assembly, sol gel process as well as pulsed laser ablation by *z* scan technique. ZnO thin films clearly exhibit a negative nonlinear index of refraction at 532 nm and the observed nonlinear refraction is attributed to two photon absorption followed by free carrier absorption. Although the absolute nonlinear values for these films are comparable, there is a change in the sign of the absorptive nonlinearity of the films. The films developed by dip coating and pulsed laser ablation exhibit reverse saturable absorption whereas the self assembled film exhibits saturable absorption. These different nonlinear characteristics in the self assembled films can be mainly attributed to the saturation of linear absorption of the ZnO defect states.

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1. Introduction

The search for new nonlinear optical materials with high optical nonlinearities is gaining interest both from the research as well as industrial point of view. In recent years, wide band gap semiconductors have been subjected to extensive studies because of the increasing interest in the development of new nonlinear optical materials for potential applications in integrated optics [1]. ZnO is an interesting wurtzitic II–VI wide band gap semiconductor that has a room temperature band gap of ~3.3 eV, combined with high excitonic gain and large excitonic binding energy [2]. The optical properties of this material are currently the subject of tremendous investigations, in response to the industrial demand for optoelectronic devices that could operate at short wavelengths. There is a significant demand for thin film nonlinear optical materials, which can be integrated into an optoelectronic device. Recent studies have revealed that ZnO thin films have a strong nonlinear second order susceptibility $\chi^{(2)}$ and hence can be used for efficient second harmonic generation [3]. The third order susceptibility, $\chi^{(3)}$ is of interest because of its importance in applications such as nonlinear propagation in fibers, fast optical switching, self-focusing, damage in optical materials and optical limiting in semiconductors.

In the present investigation, we focus on the third order susceptibility of ZnO thin films deposited on glass substrate by the techniques of self assembly, sol gel process and pulsed laser ablation, employing the technique of single beam *z* scan. ZnO thin films clearly exhibit a negative nonlinear index of refraction, however there is a change in the sign of the absorptive nonlinearity of the films at 532 nm. The films developed by dip coating and pulsed laser

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ablation exhibit reverse saturable absorption whereas the self assembled film exhibits saturable absorption.

2. Experiment

Thin films of ZnO used for the present study are deposited using three different methods. Zinc oxide is a promising candidate for photonic devices. One of the simplest techniques of fabricating photonic crystals involves colloidal self assembly, wherein, monodisperse colloidal spheres will spontaneously assemble into periodic arrays under certain circumstances. Colloids of ZnO are synthesized by a modified polyol precipitation method which involves the hydrolysis of zinc acetate dihydrate in diethylene glycol medium [4]. Self assembled films are then produced from the ZnO colloid by the technique of drop casting onto a preheated glass substrate maintained at a temperature of 120 °C.

In the second method, deposition is carried out by the sol gel technique on commercially available glass substrate by the process of dip coating. A stable hydrolysed solution is prepared using stoichiometric quantities of zinc acetate dissolved in diethanolamine and the cleaned substrate is immersed into this solution for 30 s at a controlled rate of 5 cm/min. The film is then kept for drying in a furnace for nearly 15 min at a temperature of 150 °C and annealed for half an hour at a temperature of 600 °C, to get good quality crystalline homogenous oxide films.

In the third technique, ZnO films are prepared by laser ablation of sintered ZnO target in the presence of an ambient gas at room temperature and a pressure of 500 mbar using the second harmonic of a Q-switched Nd:YAG laser. The second harmonic beam from the Nd:YAG laser provide 300 mJ pluses of 7 ns pulse width at a repetition rate of 10 Hz. The laser beam is focused using a spherical convex lens on to the surface of the sample kept inside a stainless steel vacuum chamber through a glass window. The target is fixed at an angle of 45° with respect to the laser beam and is rotated at a constant rate during laser deposition, so that pitting of the target surface by the laser beam is uniform. The chamber gas environment during pulsed laser deposition (PLD) consisted of oxygen partial pressure of 0.008 mbar and the deposition is carried out for one hour duration at a laser beam power of 50 mW.

The films deposited by the above methods are characterized by optical absorption studies. In the present investigation, we have employed the single beam z scan technique with nanosecond laser pulses to measure nonlinear optical absorption and refraction properties of ZnO thin films [5]. A Q-switched Nd:YAG laser (Spectra Physics LAB-1760, 532 nm, 7 ns, 10 Hz) is used as the light source. The sample is moved in the direction of light incidence near the focal spot of the lens with a focal length of 200 mm. The transmitted beam energy, reference beam energy and their ratio are measured simultaneously by an energy ratiometer (Rj7620, Laser Probe Corp.) having two identical pyroelectric detector heads (Rjp735). The linear transmittance of the far-field aperture S, defined as the ratio of the pulse energy passing the aperture to the total energy is measured to be approximately 0.21. The z scan system is calibrated using CS_2 as the standard. The data are analyzed by using the procedure described by Sheik Bahae et al. and the nonlinear coefficients are obtained by fitting the experimental z scan plot with the theoretical plots.

3. Results and discussion

Fig. 1 gives the room temperature absorption spectra of the ZnO thin films. The breadth of the absorption edge of the self assembly film indicates that there exists defect-related transitions. Defects usually create discrete electronic states in the band gap, and therefore influence both optical absorption and emission processes. The two most common defects in ZnO are likely to be oxygen and zinc vacancies and the visible band in the absorption spectrum can be related to the presence of these defect states in the self assembled film. The excitonic peak of the other two films is found to be blue shifted from that of bulk ZnO which could be attributed to the confinement effects [6].

The direct bandgap of ZnO colloids are estimated from the graph of $h\nu$ vs $(\alpha h\nu)^2$ for the absorption coefficient α that is related to the bandgap E_g as $(\alpha h\nu)^2 = k(h\nu - E_g)$, where $h\nu$ is the incident light energy and k is a constant. Extrapolation of the linear part until it intersects the $h\nu$ axis gives E_g. The optical band gap (E_g) is found to be shifted from that of the bulk as shown in Fig. 2. The total change in the band gap of the material is simultaneously contributed by shifts of the valence and the conduction band edges away from each other [7]. In general, the shift of the top of the valence band (TVB) is not the same as that of the bottom of the conduction band (BCB). A larger shift for the BCB is indeed expected in view of the fact that the band-edge shifts are related inversely to the corresponding effective masses and the effective mass of the electron is always much smaller than that of the hole in these II–VI semiconductors [8]. From Fig. 2, it is clear that the band gap of self assembled film is reduced to 3.1 eV from that of bulk (3.3 eV) whereas the band gap energies of the other two films are higher than that of bulk.

Typical results of the open aperture z scan measurements of the films which correspond to the far-field normalized transmittance as a function of the distance from the lens focus at an intensity of 220 MW/cm^2 are shown in Fig. 3. The open aperture curve exhibits a normalized transmittance valley, indicating the presence of reverse saturable absorption in the films which are developed by dip coating and pulsed laser ablation and a transmittance peak, indicating the presence of saturable absorption, in the self assembled film.

In the presence of RSA, transmittance T of the films can be described by a two photon absorption (TPA) process given by

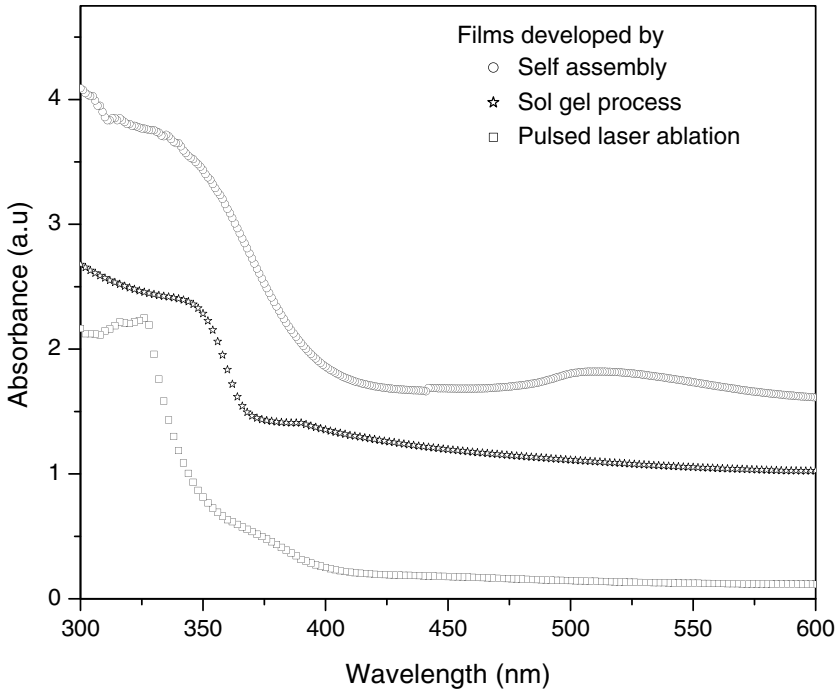

Fig. 1. Absorption spectra of ZnO thin films.

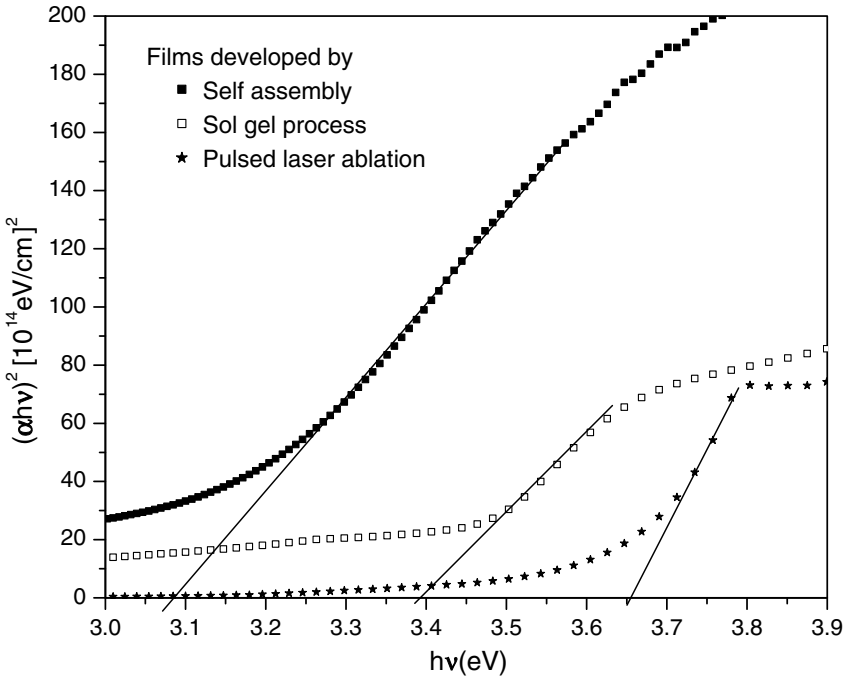

Fig. 2. Optical band gap of ZnO thin films.

$$T(z) = \frac{C}{q_0\sqrt{\pi}} \int_{-\infty}^{\infty} \ln\left(1 + q_0 \mathrm{e}^{-t^2}\right) \mathrm{d}t \quad \text{and}$$
$$q_0(z,r,t) = \beta I_0 L_{\text{eff}} \tag{1}$$

Here, $L_{\text{eff}} = \frac{1-\mathrm{e}^{-\alpha_0 L}}{\alpha_0}$ is the effective thickness of the film with linear absorption coefficient α_0 and I_0 is the irradiance at focus. From the value of β, we can calculate the imaginary part of susceptibility through the relation $\mathrm{Im}(\chi^{(3)}) = \frac{\lambda \varepsilon_0 n_0^2 c \beta}{4\pi}$ where λ is the excitation wavelength, $n_0 = 2.008$ is the linear refractive index of ZnO, ε_o is the permittivity of free space and c the velocity of light in vacuum.

In the presence of SA, the intensity dependent absorption coefficient, α_i is given by

$$\alpha_i(I) = \frac{\alpha_0}{1 + \left(\frac{I}{I_S}\right)} \tag{2}$$

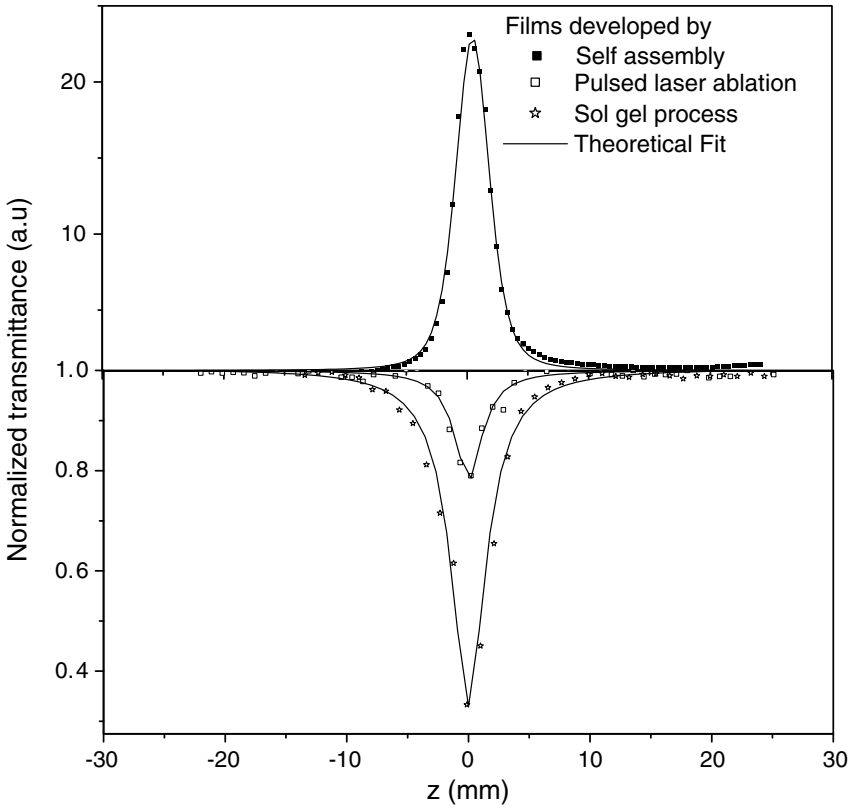

Fig. 3. Open aperture z scan traces of ZnO thin films at an intensity of 220 MW/cm^2 for an irradiation wavelength of 532 nm.

where I_S is the saturation intensity. If excitation intensity I is less than I_S, we can consider SA as a third order process and in such cases $-\alpha_0/I_S$ is equivalent to nonlinear absorption coefficient β which will then give $\mathrm{Im}(\chi^{(3)})$.

In general, induced absorption can occur due to a variety of processes. The theory of two photon absorption 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 the possibility of higher order nonlinear processes such as free carrier absorption (FCA) contributing to induced absorption. The free carrier lifetime of ZnO is reported to be 2.8 ns [9]. Hence there is a strong possibility that the 7 ns pulses used in the present study is exciting the accumulated free carriers generated by TPA by the rising edge of the pulse. Considering all these factors and also that we used nanosecond excitation pulses, it is reasonable to assume that TPA and FCA are the important mechanisms contributing to induced absorption in our dip coated and laser ablated samples.

The self assembled film exhibits saturation of absorption and bleaching and possesses a larger absorption coefficient than the other films and thereby, may have been even more susceptible to thermal effects. For semiconductor materials, heat tends to reduce the fermi energy level and thereby, increase the number of carriers in the conduction band. This, in turn, depletes the ground level and induces bleaching in the ground state absorption, which results in SA process. The origin of optical nonlinearity is not only dependent on polarization response of bound electrons leading to dielectric contributions but also from conduction electrons in semiconductors to which ZnO can be categorized. From Fig. 2, it is clear that the band gap of self assembled film is reduced to 3.1 eV from that of bulk (3.3 eV) and the laser intensity induces bleaching in the ground state absorption, which results in SA process. But the band gap energies of the other two films are higher than the bulk which leads to induced absorption. These different nonlinear characteristics in the self assembled films can be attributed to the electronic transitions involving defect states.

The sensitivity of ZnO to impurities as well as native defects with respect to electronic properties is well known [10]. The breadth of the absorption edge of the self assembly film indicates that there are defect-related transitions in this case. The negative β value in ZnO thin films were reported to be due to the saturated absorption of the defect states [10]. A similar explanation can hold for our self assembled films also. Thus we propose the mechanism behind the saturable absorption in self assembled films can be attributed to saturation of linear absorption of the ZnO defect states.

Generally ZnO exhibits reverse saturable absorption. The saturable absorption behaviour in self assembled ZnO films is an interesting effect and can be used for opti-

cal pulse compression, optical switching and laser pulse narrowing [11]. The z scan data shows that, along with moving the self assembled film towards the focus, the increase in the laser intensity induces bleaching in the ground state absorption, which results in SA process. In the self assembled film, the strong SA and the absence of RSA implies that the absorption cross section of ground state is much larger than the absorption cross section of excited state. All RSA materials possess a higher absorption cross section of excited states compared to that of the ground state at the excitation radiation wavelength. Interestingly they will also give a positive value for the imaginary part of susceptibility $\mathrm{Im}(\chi^{(3)})$ which is actually a measure of the induced absorption. On the other hand, a saturable absorber has a negative value for $\mathrm{Im}(\chi^{(3)})$. The most important application of these materials is in optical limiting and to be used as a saturable absorber.

Fig. 4 gives the closed aperture z scan traces of ZnO films at an intensity of 220 MW/cm^2. The closed aperture curve exhibited a peak to valley shape, indicating a negative value of the nonlinear refractive index n_2. There is no change in the sign of nonlinear refractive index whereas the absorptive nonlinearity for the self assembled film exhibits a trend which is reverse to that of the bulk. The value of $\Delta T_{\mathrm{p-v}}$ *i.e.*, the difference between the peak and valley transmittance could be obtained by the best theoretical fit from the results of z scan curve. The nonlinear refractive index n_2 and the real part of nonlinear susceptibility $\mathrm{Re}\,\chi^{(3)}$are given respectively by

$$n_2(\mathrm{esu}) = \frac{Cn_0}{40\pi^2}\frac{\lambda\Delta T_{\mathrm{p-v}}}{0.812(1-S)^{0.25}L_{\mathrm{eff}}I_0} \quad \text{and}$$

$$\mathrm{Re}(\chi^{(3)})(\mathrm{esu}) = \frac{n_0 n_2(\mathrm{esu})}{3\pi} \tag{3}$$

The major mechanism behind nonlinear refraction is two photon absorption and ZnO exhibits negative nonlinear refractive indices at 532 nm since the band gap of bulk ZnO is 3.3 eV. It is reported that all materials exhibit a sign change of the nonlinear refraction at about 2/3 of the band gap [12]. There is no change in the sign of nonlinear refractive index as the band gap is widely similar between the samples and so one therefore gets a negative contribution to nonlinear refraction and the sign change can be expected near 600 nm. The SA in self assembled films can be attributed to bleaching of defect states and this does not affect the nonlinear refraction and hence there is no change in the sign of nonlinear refractive index whereas the absorptive nonlinearity for the self assembled film exhibits a trend which is reverse to that of the bulk. TPA always exists, even when saturable absorption appears to overlie this mechanism in self assembled films.

The nonlinear absorption coefficient, refractive index and third order susceptibility of ZnO films at an intensity of 220 MW/cm^2 for a wavelength of 532 nm are tabulated in Table 1. When it is a saturable absorber, a more useful parameter to extract from the transmission measurements is the saturation intensity I_S, which is also given in the table. These values are within an error of 7% contributed

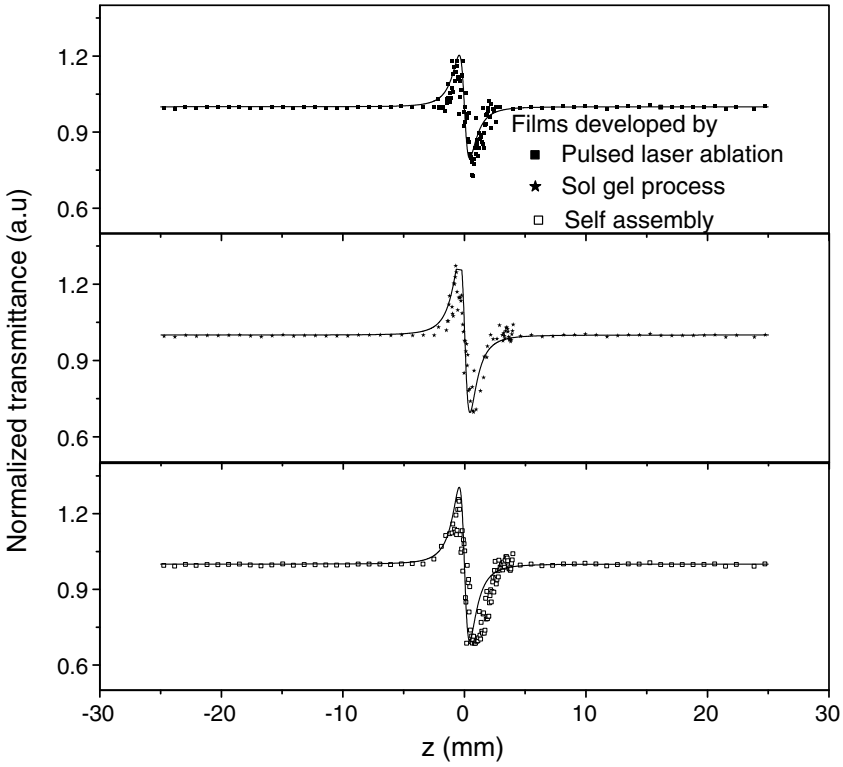

Fig. 4. Closed aperture z scan traces of ZnO thin films at an intensity of 220 MW/cm^2 for an irradiation wavelength of 532 nm.

Table 1
Measured values of nonlinear absorption coefficient, saturation intensity, refractive index and third order susceptibility of ZnO thin films at an intensity of 220 MW/cm^2 for an irradiation wavelength of 532 nm

Films developed by	β (10^{-5} m/W)	I_S (GW/cm^2)	n_2 (10^{-5} esu)	Im($\chi^{(3)}$) (10^{-6} esu)	Re $\chi^{(3)}$ (10^{-6} esu)	$\lvert\chi^{(3)}\rvert$ (10^{-6} esu)
Self assembly	–	0.4	−2.77	−0.57	−5.91	5.93
Sol gel process	4.59	–	−2.59	1.99	−5.51	5.86
Pulsed laser ablation	0.73	–	−1.85	0.31	−3.94	3.95

mainly by the uncertainty in intensity measurements on the sample and the fitting error. Based on these measurements we found that the imaginary part of the susceptibility is an order of magnitude smaller than the value for the real part of the susceptibility function. This means that the refraction effect is stronger than the absorption. The values of $\chi^{(3)}$ measured at room temperature by femtosecond degenerate four wave mixing technique on ZnO microcrystalline thin films range from 10^{-4} to 10^{-7} esu [13]. The β values obtained are quite high, and are of the same order of magnitude as those obtained for ZnO–Cu and ZnO–Mg nanocomposite films [10,14]. Thus, the real and imaginary parts of third order nonlinear optical susceptibility measured by the z scan technique revealed that the ZnO films investigated here have good nonlinear optical response and could be chosen as ideal candidates with potential applications in nonlinear optics.

4. Conclusion

We have investigated the nonlinear optical properties of ZnO thin films developed by self assembly, dip coating and pulsed laser ablation. ZnO thin films clearly exhibit a negative nonlinear index of refraction at 532 nm and the observed nonlinear refraction is attributed to two photon absorption followed by free carrier absorption. Although the absolute nonlinear values for these films are comparable, there is a change in absorptive nonlinearity of the films. The films developed by dip coating and pulsed laser ablation exhibit reverse saturable absorption whereas the self assembled film exhibits saturable absorption. This behaviour can be attributed to the saturation of linear absorption of the ZnO defect states.

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