Determination of Non-linear Refractive Index of Pure SnO₂ and TiO₂ Doped SnO₂ Thin Films Using Z-scan Technique

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Abstract

In this research work the non-linear refractive indices n₂ was determined for the pure SnO₂ and TiO₂ doped SnO₂ thin films by using the Z-scan technique. We have used a continuous wave Ar-ion laser with incident wavelength of 514 nm as the source. n₂ was measured by varying three quantities: the incident laser intensity, thickness of the pure SnO₂ films and doping concentration of TiO₂ in SnO₂ films. From the experimental results, the values of n₂ were found to be increasing with the increase of thickness of the pure SnO₂ films and also with the increase of doping concentration of TiO₂ in SnO₂ thin films.

Keywords: Z-scan; Ar-ion laser; non-linear refractive index; thin films.

I. Introduction

Materials with large optical nonlinearities have changed into the topic of a great scientific interest, because of their inclusive applications in high speed optical switching devices¹. Z-scan method is one of the easiest methods to determine the nonlinear optical properties of materials. It has been developed for boundless applications like optical limiting², Multi-photon polymerization³, as well as optical switching⁴. Many thin films have shown non-linear properties that may use in developing the high speed optical switching devices and other electrical devices.

Among them SnO₂ is one of the important films that have high non-linear properties as well as highly transparent⁵. By doping various metal ions or nanoparticles, one can able to enhance the nonlinearities in SnO₂ thin films⁶.⁷.⁸.⁹.¹⁰.¹¹.¹².¹³.¹⁴.¹⁵.¹⁶.¹⁷. There are many techniques, for example chemical vapor deposition⁸, sputtering⁹, sol-gel¹⁰, reactive evaporation¹¹, pulse laser ablation¹², screen printing technique¹³, and spray pyrolysis¹⁴ by which one can prepare SnO₂ thin films with smooth surface. In this experimental work, SnO₂ was deposited on sodalime glass by spray pyrolysis process. Sodalime glasses have fascinated much research attention due to better glass-forming nature compared with many other traditional systems. This type of glass has excellent optical and mechanical properties, good chemical stability, high UV transparency, strong thermal resistance, low non-linear refractive index, high surface damage threshold and good durability¹⁵.¹⁶. The thickness of the films can be controlled by deposition time, that means with the increase of time, the thickness of the films also increases. In this research work, the SnO₂ thin films were prepared for different time duration via spray pyrolysis process. The doping of TiO₂ with different metal ions has frequently been tried to enhance the absorption of visible light by giving faulty states in the band gap¹⁷.

W. M. Mat Yunus et al.⁶ investigated the non-linear optical properties of phosphate glasses based on ZnO by using Z-scan technique. They used a continuous-wave laser with a wavelength of 405 nm and estimated the values of the non-linear refractive index and the absorption coefficient. They found that the nonlinear refractive index was increasing with the increase of the ZnO concentration in the glass samples. They also calculated the real and imaginary parts of the third-order nonlinear susceptibility. A. M. Yahya et al.¹⁸ observed the optical properties of CuS thin films by Z-scan system. The films were prepared by spray pyrolysis process. They used Q-switched Nd:YAG laser with 1064 nm wavelength to perform the experiment. They observed that n₂ values were decreasing with the increase of incident laser beam intensity and thicknesses of the films. P. Kockaert et al.¹⁹ investigated the values of non-linear refractive index of graphene using Z-scan technique. They varied the input intensity of source and estimated the nonlinear refractive index for varying intensity. From the result it was seen that the nonlinear refractive index n₂ was decreasing with the increase of peak input intensity.

Nonlinearity of films has become more important for developing the high speed switching devices as well as many other electrical devices. This can be played a vital role to enhance the optoelectronics devices. In our present research work, we have investigated the variation of non-linear refractive index for different thickness of Pure SnO₂ thin films and also for different doping concentration of TiO₂ doped SnO₂ thin films. We also have investigated the variation of nonlinear refractive index with respect to the input power of the continuous wave Ar-ion laser source.

II. Experimental Details

In this experiment, pure SnO₂ thin films for different thickness and TiO₂ doped SnO₂ films with different doping concentrations were prepared using spray pyrolysis process. The thickness of the films was varied from 100 to 300 nm. The concentration of TiO₂ was varied from 1 to 10 wt%. The Z-scan technique was used to measure the non-linear refractive index. A continuous wave Ar-ion laser with a wavelength of 514 nm was used as the source. The non-linear refractive index was calculated using the formula n₂ = (2πd)/(λ²A₀), where d is the thickness of the film, λ is the wavelength of the laser, A₀ is the peak laser intensity, and 2π is a constant.

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Concentrations were prepared by spray pyrolysis process, using a homemade spray pyrolysis system. At first 10 mL ethanol was mixed with 90 mL distilled water and made 100 mL solution. Then 2.0 gm of SnCl$_2$.2H$_2$O was dissolved in the previous 100 mL solution to acquire the precursor solution of strength 0.1 M. After that we added 1 mL HCl in the solution to make it more transparent. The solution was stirred for 2.5 hours in a magnetic stirrer.

The ultrasonically cleaned soda-lime glass was used as a substrate. We prepared different thickness of the SnO$_2$ films by changing the time duration of the Spray. Films were made for 5 min, 10 min, 15 min & 20 min and as for higher spray time, the thickness was also developed. We also used different percentage of TiO$_2$ with this pure SnO$_2$ solution for producing SnO$_2$ films of different doping concentrations.

The optical Thin-Film measurement instrument (Model TF-166) was used to measure the thickness of the films.

Fig. 1. Schematic diagram of homemade Spray Pyrolysis System

In this Z-scan technique, a Gaussian laser beam was focused by a convex lens to scan third order nonlinear materials. The samples were moved through the focal point of the lens. In general, non-linearity comes from the non-centrosymmetric structure of the sample. For centrosymmetric media, the properties of the medium are not change by the transformation $\vec{r} = -\vec{r}$, so the second-order nonlinear susceptibility is zero means $\chi^{(2)} = 0$. Therefore the third-order term becomes more important. An interesting and important effect that can be seen in the third order nonlinear medium is known as self-focusing.

The variation of transmittance depends on the non-linear phase shift and the phase shift $\Delta \phi_0$ is related to the non-linear refractive index $n_2$. The total refractive index $n$ for cubic non-linearity can be expressed as:

$$n = n_0 + n_2 I$$

where $n_0$ is the linear refractive index.

We used a continuous wave Ar-ion laser as the source to measure the $n_2$ of thin films. A convex lens of 100 mm focal length was used for focusing the laser beam.

We also used LabVIEW programming (2015 version) to control the translation motor and tracking the positions of the sample and corresponding power simultaneously.

Fig. 2. Schematic diagram of the set up of the Z-scan experiment

III. Results and Discussion

From the peak-valley differences of close aperture z-scan curve, the nonlinear refractive index for different peak intensities was estimated and verified.

Fig. 3. Close aperture curve with theoretical fitting for SnO$_2$ thin films with input power $P = 24$ mW at fixed wavelength 514 nm

Fig. 4. Non-linear refractive index vs peak intensity at focus for SnO$_2$ thin films at 514 nm wavelength
So from the graph (in Fig. 4), it can be said that the non-linear refractive index decreases with the increment of the peak intensity for a certain wavelength. This above variation for \( n_2 \) vs \( I_0 \) has been in well agreement with the result of P. Kockaert et al.\(^{19} \).

For a TEM\(_{00}\) Gaussian laser beam with waist radius \( \omega_0 \) propagating in the +z direction, the electric field can be written as\(^{22,23} \),

\[
E(r,z) = E_0 \frac{\omega_0}{\omega(z)} \exp \left[ -i \left( k z + \tan^{-1} \left( \frac{2z}{z_0} \right) \right) \right]
\]

\( \text{(2)} \)

The parameters are \( \omega(z) = \omega_0 \left( 1 + \left( \frac{z}{z_0} \right)^2 \right)^{\frac{1}{2}} \), \( \omega_0 \) is the beam waist at \( z = 0 \), \( z_0 = \frac{k \omega_0^2}{2} \) is the Rayleigh length, \( k = \frac{2\pi}{\lambda} \) is the wave number, \( \lambda \) is the wavelength of laser source and \( r(x, y) \) is the transverse radial distance\(^{22,24} \).

The normalized transmittance for open aperture calculations is given\(^{22,23} \),

\[
T(z) = -\frac{4q_0}{2\sqrt{2}} \frac{1}{\left( 1 + \frac{z^2}{z_0^2} \right)^{\frac{1}{2}}} + 1
\]

\( \text{(3)} \)

The far field condition a geometry-independent normalized transmittance for a thin sample is found to be\(^{22,23} \),

\[
T(z, \Delta \phi_0) = 1 + \frac{4\Delta \phi_0}{\left( 1 + \left( \frac{z}{z_0} \right)^2 \right)^{\frac{1}{2}} + \left( \frac{z}{z_0} \right)}
\]

\( \text{(4)} \)

where at the laser focus, the on-axis phase change can be given as\(^{24} \),

\[
| \Delta \phi_0 | = \frac{2\pi}{\lambda} n_2 I_0 L_{\text{eff}}
\]

and

\[
\Delta T_{\text{p-\nu}} = 0.406 (1 - S)^{0.25} | \Delta \phi_0 |
\]

The non-linear index \( n_2 \), can be determined from the phase shift using,

\[
n_2 = \frac{\Delta \phi_0}{\Delta T_{\text{p-\nu}}} L_{\text{eff}}
\]

\( \text{(5)} \)

where, \( L_{\text{eff}} = \frac{1-e^{-\alpha L}}{\alpha} \), \( L_{\text{eff}} \) is the effective sample thickness, \( L \) is the thickness of the samples and \( \alpha \) is the linear absorption coefficient.

![Fig. 5. Close aperture curves with theoretical fit for (a) thickness 209.9 nm (b) thickness 216.6 nm (c) thickness 217.2 nm](image-url)
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From the close aperture Z-scan curves (in Fig.5), the nonlinear refractive index $n_2$ is calculated from the peak-valley differences of the curves and is tabulated in Table 1. It shows that the nonlinearity increases with the increase of the thickness of SnO$_2$ thin films for a certain peak intensity or input power.

Also from the Open aperture curves (in Fig.6), the Rayleigh length $z_0$ was found almost same for all SnO$_2$ samples and so the average value of $z_0$ was calculated 2.13 mm & beam waist $w_0$ was found 18.68 μm.

### Table 1. The following table describes the results of non-linear refractive index for SnO$_2$ thin films of different thickness.

<table>
<thead>
<tr>
<th>Thickness of the SnO$_2$ thin film samples (L) nm</th>
<th>Non-linear refractive index with std. $(n_2 \pm \sigma) \times 10^{-3} \text{mm}^2/\text{mW}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>209.9</td>
<td>0.9771 ± 0.0239</td>
</tr>
<tr>
<td>216.6</td>
<td>2.186 ± 0.1320</td>
</tr>
<tr>
<td>217.2</td>
<td>1.821 ± 0.0973</td>
</tr>
<tr>
<td>218.0</td>
<td>2.308 ± 0.0416</td>
</tr>
<tr>
<td>219.4</td>
<td>2.457 ± 0.0510</td>
</tr>
</tbody>
</table>
Fig. 7. Nonlinear refractive index vs thickness of the SnO$_2$ thin films.

From the close aperture curves (in Fig.8), the important parameter $\Delta T_{p-v}$ values are calculated to determine the values of non-linear refractive index of the films for different doping concentrations and are tabulated in table 2.

Fig. 8. Close aperture curve with theoretical fitting for (a) 12.5% doping (b) 25% doping

Fig. 9. Non-linear refractive index vs different doping concentrations of TiO$_2$ in SnO$_2$ thin films

From the close aperture curves (Fig.8), it is determined that with the increase of the doping concentration of the films the peak-valley difference $\Delta T_{p-v}$ increases and effective thickness $L_{eff}$ reduces. The more doping concentration makes the films more absorptive. With the increase of Ti$^{4+}$ in SnO$_2$ films the electronic polarizability highly enhances.
Table 2. The following table describes the results of non-linear refractive index for different doping concentration of TiO$_2$ in SnO$_2$ thin films.

<table>
<thead>
<tr>
<th>Doping concentrations of TiO$_2$, %</th>
<th>Thickness of films, L (nm)</th>
<th>Effective thickness of films, L$_{\text{eff}}$ (nm)</th>
<th>Non-linear refractive index with std, $(\bar{n}_2 \pm \sigma) \times 10^{-5} \text{mm}^2/\text{mW}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.5</td>
<td>209.6</td>
<td>187.00</td>
<td>3.4525±0.0269</td>
</tr>
<tr>
<td>25.0</td>
<td>209.6</td>
<td>170.05</td>
<td>3.8100±0.0181</td>
</tr>
<tr>
<td>50.0</td>
<td>211.6</td>
<td>161.66</td>
<td>3.9875±0.0179</td>
</tr>
<tr>
<td>75.0</td>
<td>212.5</td>
<td>158.33</td>
<td>4.415±0.0371</td>
</tr>
</tbody>
</table>

So on the whole, the increase of numerator $\Delta T_{\text{p-w}}$ and decrease of denominator $L_{\text{eff}}$ in equation (5), magnifies the values of $n_2$. So the refractive index increases with the increment of doping concentrations of TiO$_2$ in SnO$_2$ thin films. This result indicates that the light energy is absorbed as much as the number of TiO$_2$ molecules increases. This same result for varying doping concentration was found similar with that of W.M. Mat Yunus et al. $^6$, L. Irimpan et al. $^7$, H. M. Shanshool et al. $^8$.

IV. Conclusions

We have found that the non-linear refractive index $n_2$ decreases with the increase of input intensity and the values of $n_2$ saturate when the input intensity is very high ($I_0 > 30000 \text{ mW/mm}^2$). We also determined that the non-linear refractive index increases with the increment of the thickness of the SnO$_2$ thin films as well as the doping concentrations of TiO$_2$ in SnO$_2$ thin films due to the electronic polarizability. The values of $n_2$ show that these materials have enough non-linearity for its applications in the photonics.

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References


