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Femtosecond laser-induced nonlinear absorption in thick polystyrene

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Abstract

The nonlinear absorption behavior of thick polystyrene sample was experimentally investigated and theoretically analyzed. As polystyrene is transparent to the applied laser wavelength, the absorption was mainly through nonlinear absorption by the bulk material. The effective second order nonlinear absorption coefficient (β) was determined with the z scan technique. The nonlinear behavior at different laser powers: 5.2 mW, 10.4 mW, 14.4 mW and 23.5 mW were investigated. The transmittance of laser energy was measured and a significant change was observed with different sample distance from the laser focal plane. By treating the thick polystyrene sample as a stack of thin layers, the effective nonlinear absorption coefficient was determined to be 0.000695 m/W with a standard deviation of 0.000026.

Keywords

Femtosecond laser; Nonlinear absorption; Thick material; Polystyrene; Laser intensity; Z scan technique.

1. Introduction

Photon absorption is an important phenomenon as it is the first step of laser material interaction. For continuous and long pulsed lasers, the energy is absorbed by linear absorption. The photon energy should be larger than the material bandgap to enable the absorption [1]. While for short pulsed lasers and ultrashort pulsed lasers, the energy can be absorbed through multiphoton absorption, i.e. at high laser peak power intensities (typically $> 10^{13}$ W/cm²), an electron can absorb multiple photons to overcome the bandgap. This requires $m h \nu \geq E_g$, where m is the number of photons [2]. Multiphoton absorption is through direct ionization. By going through several metastable quantum states, the absorption process can be achieved. It is an mth order photoionization process. At low laser peak power intensity, the multiphoton absorption cross section is small, and thus the laser peak power intensity should be increased to achieve significant multiphoton absorption. Among the reported research on investigation on nonlinear absorption, z scan technique is a well-established and generally used technique to study the nonlinear behavior induced by ultrashort pulsed laser. This technique was firstly introduced by Sheik-bahae et al in 1989 [3]. Later on it is widely applied at different materials such as polymers [4,5], glasses [6-10], semiconductors [11-14], carbyne [15], liquid crystals [16] and organics [17,18] to determine the nonlinear properties. z scan technique was generally applied on thin films (sample thickness much less than the Rayleigh range of the laser beam). This is because it was assumed that the laser beam maintains a Gaussian distribution and the absorption was calculated based on the surface incident laser intensity, which is not applicable for bulk materials. The analysis of a thick sample is much more complicated compared with a thin sample [19-21]. There are only few works on bulk materials [20,21] and are limited to theoretical analysis.

Polystyrene (PS) is a transparent and rigid polymer [22], with good resistance to alcohols, concentrated

acid, alkaline and polar solvent [23]. It is widely used in industries, chemistries, biotechnologies and life sciences with many applications [24-26]. In this paper, we have investigated the nonlinear absorption behavior of thick polystyrene both theoretically and experimentally. The experimental measurement results were verified to be consistent with the theoretical analysis. Most importantly, to the best of our knowledge, it is the first time that the effective nonlinear absorption coefficient has been measured for the thick polystyrene samples. The result will have reference value and potential applications in the investigation of ultrafast fs laser micromachining and processing of transparent materials.

2. Experimental set-up

A commercial polystyrene sheet with a thickness of 1.2 mm was used in the experiment. A Quantronix integra-C femtosecond laser with a wavelength of 795 nm, a pulse duration of 130 fs and a repetition rate of 1 KHz was employed for the laser beam polymer interaction. The laser beam was focused through the scanner with a f- θ lens. The focus lens has a focal length of 163 mm. The laser raw beam diameter before the scanner is 7 mm. After the scanner, the laser beam focal spot diameter is around 30 μm . A FieldMaxII power meter with PM30 thermal sensor from Coherent was employed for power measurement. The experiment set-up is shown in Fig.1.

Fig. 1 Experimental set-up for nonlinear absorption coefficient measurement, the symbol “z” is defined as the distance from the focal plane to the sample top surface.

3. Theoretical analysis

For a thin sample, the nonlinear absorption may be described as [11-14,3]:

$$\frac{dI}{dz'} = (\alpha + \beta I)I \quad (1)$$

where I is the laser intensity, α is the linear absorption coefficient and β is the effective nonlinear absorption coefficient. By solving equation 1, the irradiance distribution at the exit surface of a sample can be calculated as [27]:

$$I_e(z, r, t) = \frac{I(z, r, t)e^{-\alpha L}}{1 + q(z, r, t)} \quad (2)$$

where $I_e(z, r, t)$ is the laser intensity at the exit surface of the sample. $I(z, r, t)$ is the incident laser power intensity without energy absorption, and [27]

$$q(z, r, t) = \beta I(z, r, t)L_{eff} \quad (3)$$

Without any nonlinear absorption ($\beta = 0$), equation 2 becomes:

$$I_e(z, r, t) = I(z, r, t)e^{-\alpha L} \quad (4)$$

Equation 4 is the standard Beer-Lambert law for linear absorption. As shown in Fig. 2, the linear absorption coefficient α measured over a range of wavelength is close to zero by employing a UV-VIS-NIR scanning spectrophotometer (UV-3101PC, SHIMADZU). In particular, at 795 ± 10 nm, which is the wavelength of the femtosecond laser employed, the laser beam absorbance is close to 0 %, transmission 90.5 % and reflection 9.2 %. This means that the linear absorption of laser beam during femtosecond laser PS interaction is negligible and may be neglected; the dominant absorption mechanism is through nonlinear absorption.

Fig. 2 Measured photon absorption of PS as a function of wavelength.

With negligible linear absorption ($\alpha = 0$), $L_{eff} = L$ where L is the sample thickness, equation 2 becomes [27]:

$$I_e(z, r, t) = \frac{I(z, r, t)}{1 + q(z, r, t)} \quad (5)$$

The instantaneous transmitted power can be obtained by spatially integrating equation 2 [27]:

$$P(z, t) = P_i(t) e^{-\alpha L} \frac{\ln[1 + q_0(z, t)]}{q_0(z, t)} \quad (6)$$

Where $P(z, t)$ is the instantaneous transmitted power and $P_i(t)$ is the instantaneous incident power.

This analysis is only applicable for a sample with thickness less than the laser Rayleigh range z_0 . The

Rayleigh range is defined as [27]:

$$z_0 = \frac{\pi \omega_0^2}{\lambda} \quad (7)$$

where ω_0 is the focal spot radius (15 μm) and λ is the laser wavelength (795 nm). For this investigation, the Rayleigh range is calculated to be around 0.889 mm.

The PS sample thickness is 1.2 mm which is larger than the Rayleigh range. Thus, the sample cannot be considered as a thin sample. Zang and his group [21] have provided an analytic solution to characterize a thick media with nonlinear absorption. For a thin medium, equation 6 may be re-written for the instantaneous normalized transmittance T as:

$$T(z, t) = \frac{\ln[1 + q_0(z, t)]}{q_0(z, t)} \quad (8)$$

A thick sample may be treated as a stack of many thin samples. The normalized transmittance of a thick sample can be written as a summation of these many layers of thin samples as [21]:

$$\begin{aligned}
T(z, t) = \prod_{i=1}^n \left\{ \frac{1}{q_{0i}(z_i, t)} \ln[1 + q_{0i}(z_i, t)] \right\} \cong 1 - \frac{1}{2} \sum_{i=1}^n q_{0i}(z, t) + \left[\frac{1}{2} \sum_{i=1}^n q_{0i}(z, t) \right]^2 \\
+ O \left\{ \left[\frac{1}{2} \sum_{i=1}^n q_{0i}(z, t) \right]^3 \right\}
\end{aligned} \tag{9}$$

To transform the summation to an integral for ease of calculation, equation 9 can be approximated as [21]:

$$T(x, t) = \frac{1}{1 + \frac{1}{2} \sum_{i=1}^n q_{0i}(x, t)} = \frac{1}{1 + \frac{1}{2} \int_x^{x+l} q_0(x, t) dx} \tag{10}$$

Where $x = z / z_0$ and $l = L / z_0$. The truncation error from equation 9 to equation 10 is second order.

With the integration of equation 10, the normalized transmittance becomes [21]:

$$T = \frac{1}{1 + \frac{1}{2} * Q_R [\tan^{-1}(x+l) - \tan^{-1}(x)]} \tag{11}$$

Where $Q_R = \beta I_0 z_0$. I_0 is the peak laser intensity at the irradiation center.

4. Results and discussion

The theoretical and experimental normalized transmittances at different laser power of 5.2 mW, 10.4 mW, 14.4 mW and 23.5 mW are shown in Fig. 3a), 3b), 3c) and 3d) respectively. Least square fitting the experiment data with equation 11, the effective nonlinear absorption coefficient β is determined to be 0.00066 m/W, 0.00071m/W, 0.00072 m/W and 0.00069 m/W with R^2 values of 0.92, 0.94, 0.95, and 0.91 respectively. The average β is 0.000695 m/W with a standard deviation of 0.000026.

Fig. 3 Normalized transmittance z scan curve for 1.2 mm thick PS sample at a wavelength of 795 nm with laser power at a) 5.2 mW, b) 10.4 mW, c) 14.4 mW and d) 23.5 mW. z is defined as the distance from the focal plane to the sample top surface. The black dots are the experiment data while the red line is the fitting curve using equation 11.

As shown in Fig. 3, the transmittance was observed to increase as the sample moved away from the focal plane either in the positive or negative direction. For instance, for laser power of 5.2 mW as shown in Fig. 3a), the normalized transmittance at $z = 0$ mm is 0.12, while it increased to 0.44 at $z = 1$ mm and 0.5 at $z = -3$ mm. This increase in transmittance was due to the decreased laser power intensity at the sample. As the sample moved away from the laser focal position, the laser power intensity at the sample decreased. As such, the fs laser induced nonlinear absorption decreased, which corresponded to an increased transmittance.

It was also found that the valley shown in Fig. 3d) for a laser power of 23.5 mW is much wider than that in Fig. 3a) for a laser power of 5.2 mW. This indicates that for the higher laser peak power intensity of $5.12 \times 10^{13} \text{ W/cm}^2$ at 23.5 mW, even though the sample was a bit further away from the

focus plane, the laser intensity within the sample was still high enough to induce high nonlinear absorption. As a result, the valley became wider at higher laser power intensity.

The laser induced nonlinear absorption phenomenon has various applications in various areas. For instance, it can be used as an autocorrelator. In a photodiode, when bandgap energy is larger than photon energy the nonlinear absorption can be exploited and used for pulse characterization. It also can be applied on multiphoton imaging; the induced nonlinear absorption is only occurring at the focal spot, which improves the image accuracy with better image quality [28]. In addition, the two-photon spectroscopy can be exploited to characterize the material properties. The nonlinear absorption is laser intensity dependent, by controlling of the laser intensity and thus the absorption of material, the light propagation characteristic can be modified by the laser beam itself [29].

5. Conclusion

The fs laser induced nonlinear absorption behavior of thick PS sample has been investigated. Z scan technique was applied for the analysis. The thick sample was treated as a stack of thin samples and the effective nonlinear absorption coefficient of PS was determined to be 0.000695 m/W. The nonlinear behavior at different powers, namely 5.2 mW, 10.4 mW, 14.4 mW and 23.5 mW were investigated. As the laser power intensity increased, the nonlinear absorption was found to increase while the transmittance decreased. The experiment results are consistent with the theoretical analysis.

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