Stoichiometric dependent optical limiting in PLD SiO_x thin films

Partha P. Dey, Alika Khare*

Department of Physics, Indian Institute of Technology Guwahati, Guwahati, Assam 781039, India

*Corresponding author, E-mail: alika@iitg.ernet.in

Received: 26 May 2016, Revised: 20 August 2016 and Accepted: 30 October 2016

DOI: 10.5185/amlett.2017.6931
www.vbripress.com/aml

Abstract

In this letter, optical limiting property of the insufficiently oxidized silicon oxide (SiO_x) thin films is reported. Films were deposited by Pulsed Laser Deposition technique using Q-switched Nd: YAG laser (532 nm) onto fused silica substrate at a substrate temperature of 400 °C by varying the O_2 pressure in the range of 5×10^{-5} to 0.5 mbar. Energy Dispersive X-Ray spectra showed the increase in oxygen content with increasing O_2 pressure. Raman spectra of SiO_x films depicted the presence of micron sized clusters composed of nanocrystalline Silicon embedded in uniform matrix of oxidized amorphous Silicon. The open Z-scan of the thin films, under cw He-Ne laser irradiation, showed strong reverse saturation absorption (RSA) features and non linear absorption (NLA) coefficient, β, was found to be decreasing from 23.5 cm/W to 1.64 cm/W, with increase in O_2 pressure from 5×10^{-5} to 10^{-1} mbar, respectively. Also, the SiO_x films except that with maximum oxygen content showed optical limiting, where limiting threshold increases with increasing transparency controlled by oxygen content. The key feature of the present work is the tunability in linear absorption, nonlinear RSA and optical limiting in the SiO_x films which can be used as novel material for optical switching application. Copyright © 2017 VBRI Press.

Keywords: Thin film, pulsed laser deposition, raman, Z-scan, optical limiting.

Introduction

Nonlinear optical (NLO) properties of materials have been used for various applications such as optical switching, optical waveguide, optical limiting (OL), harmonic generation and information storage [**1**]. The OL properties of colloids and thin films of semiconductors, metals, and carbon nano-tubes have been reported in literature [**2–5**]. OL can be achieved by means of various nonlinear optical mechanisms, including self-focusing, induced scattering, induced-refraction, induced aberration, excited state absorption, two-photon absorption, photo-refraction and free-carrier absorption in nonlinear optical media [**5**, **6**]. These optical limiters are suitable for laser pulse shaping applications, passive mode locking, pulse smoothening, etc. [**6**, **8**]. Linear and nonlinear optical properties of Silicon (Si) based materials have attracted much attention in the recent years since it can be potentially applied in many kinds of optoelectronic devices because of its compatibility with well-established Si-based micro-electronics technology. The bulk crystalline Si and Silicon dioxide (SiO_2) possess weak NLO effect thereby restricting its applications [**9**]. Nonlinear optical properties have been observed in nc-Si films prepared by various techniques such as various chemical vapor deposition (CVD) and sputtering methods. It is found that the observed nonlinear optical properties are strongly dependent on the deposition techniques as well as the film microstructures [**8-10**]. Martínez *et al.* fabricated nc-Si films by three different deposition techniques: e-beam evaporation, plasma-enhanced chemical vapor deposition, and low-pressure chemical vapor deposition (LPCVD), and reported that the nc-Si films prepared by LPCVD show the saturation absorption behavior, while the other two samples displayed the reverse saturation absorption characteristics [**10**]. Spano *et al*. reported the change of nonlinear refraction indices from positive to negative with changing the film composition and measurement conditions [**11**]. However, SiO_x in which nanocrystalline (nc) Si is embedded in SiO_2 matrix, could be a technologically useful material for producing tunable optically nonlinear Si based thin films. The ability to control the size and structure of Si nanoparticles as well as the oxygen content (x) in the surrounding SiO_2 matrix would allow tuning the compositional, structural, morphological, and optical properties of SiO_x which may affect the NLO properties of such films. Keeping this objective in mind, in the present work, SiO_x thin films with varied oxygen content were deposited via Pulsed Laser Deposition (PLD) technique and the effect of oxygen concentration on the linear and nonlinear optical absorption properties of these thin films along with OL properties were studied. The novelty of the present work lies on the simplicity of single step PLD technique used for fabricating SiO_x films in presence of oxygen ambient. The shift in stoichiometry of

the SiO_x films from Si-rich to oxygen rich obtained by increasing the oxygen pressure resulted in modulating the RSA and optical limiting behaviour.

Experimental

Materials

For PLD of SiO_x films, crystalline Si (100) wafer (Alfa Aesar, CZ grade, USA) was used as the target while oxygen gas (Janex, 99.99 % pure, Assam-India) was used as ambient.

Materials and method

Fabrication method

SiO_x thin films with varying oxygen content were fabricated by PLD technique onto glass substrates at a substrate temperature (T_s) of 400 °C. The second harmonic of a high power Q-switched Nd:YAG laser (λ=532 nm, 10 ns pulse duration, rep. rate - 10 Hz) was focused to provide a laser fluence of 2.5 J/cm^2, onto the Si (100) wafer in oxygen (O_2) ambient pressure of 5×10^{-5}, 10^{-4}, 10^{-3}, 10^{-2}, 10^{-1} and 0.5 mbar. With the focusing of the laser beam onto the Si target, formation of laser produced plasma of the target material and the oxygen ambient in the focal region takes place, which contains electrons, Si ion and oxygen ions. The plasma plume expands adiabatically with high kinetic energy toward the substrate forming mixture of SiO_2 and Si followed by the deposition onto the substrate surface placed parallel to and 3 cm away from the target. The films were deposited for duration of 30 minutes.

Characterizations

The Energy Dispersive X-Ray (EDX) **(**LEO, Model: *1430 v**p***) spectra of SiO_x thin films were recorded (under 10 kV EHT) for elemental analysis of the films and to estimate the respective atomic percentages. For analysis of bonding structures, the Raman spectra of SiO_x thin films were recorded at room temperature (RT) by micro-Raman setup (Horiba Jobin Vyon, Model: *Lab-Ram HR 800*) in back scattering geometry. The 488 nm emission from Ar ion laser was used as the excitation source. The transmission spectra of SiO_x thin films were recorded at RT by the UV-vis-NIR spectrometer (SHIMADZU, Model: *UV-3101 PC*) within the wavelength range of 200 nm to 3000 nm which is used for linear absorption coefficient (α) estimation. Nonlinear absorption coefficient (β) was estimated by recording Z-scan spectrum using charge-coupled device (CCD) at RT [**12**]. For this, a cw He-Ne laser (λ=632.8 nm, 32mW, model: *05-LHP-927*, MELLES GRIOT) was focused by a convex lens of focal length 5 cm on the SiO_x film. The transmitted beam was recorded on CCD (PCO, Model: *PixelFly*) by scanning the film to 15 mm on either side of the focus of the lens. To test the optical limiting (OL) capability, a 32 mW cw He-Ne laser beam (MELLES GRIOT, Model: *05-LHP-927*) was allowed to transmit through the SiO_x films and was detected by CCD. The power of the laser illuminating the sample was controlled by neutral density (ND) filters.

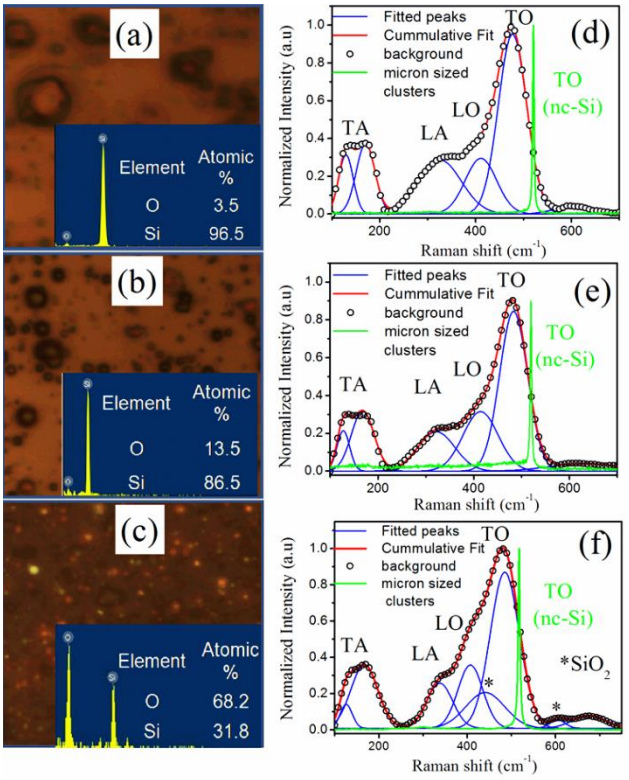

Fig. 1. Optical micrograph images (30μm × 30μm) and respective EDX in inset (a-c) and corresponding Raman spectra of micron sized clusters and background (d-f) of SiO_x PLD thin films deposited at O_2 pressure of 10^{-4}, 10^{-2} and 0.5 mbar, respectively.

Results and discussion

Fig. 1 (a-c) show optical micrograph (30μm × 30μm) while its inset shows the EDX of respective films deposited at O_2 pressure of 10^{-4}, 10^{-2} and 0.5 mbar, respectively. EDX was performed at different regions of the thin film but hardly any change in the composition was observed. This shows that the atomic composition of the film was nearly uniform throughout. Each spectrum shows the presence of silicon and oxygen in the thin film indicating the SiO_2 matrix formation. During the laser ablation of Si target under oxygen ambient, the ions of Si and oxygen present in laser produced plasma forms Si and SiO_2 during adiabatic cooling of plasma followed by the nucleation and growth onto the substrate surface. The atomic percentage of oxygen is found to be 3.5(±1) %, 13.5 (±2) % and 68.2 (±2) % corresponding to x=0.03, 0.15 and 2.1, in SiO_x thin films deposited at O_2 pressure of 10^{-4}, 10^{-2} and 0.5 mbar, respectively. Thus the increase in O_2 concentration in the SiO_x thin films with increasing O_2 pressure is due to the increase in oxygen in laser produced plasma (LPP) at higher O_2 pressure, facilitating the formation of more and more Si-O bonds before deposition. The microscopic images depict micron sized spherical clusters embedded in uniform background**.** **Fig. 1 (d-f)** shows corresponding Raman spectra of both these regions of SiO_x thin films. The Raman spectrum of

embedded cluster is shown as green coloured line in the figure. It exhibits an intense sharp peak around 520.7, 519.5 and 517.4 cm^{-1} for the films deposited at O_2 pressure of 10^{-4}, 10^{-2} and 0.5 mbar, respectively. The peaks are asymmetric on lower wavenumber side and is red shifted w.r.t that of bulk c-Si (521 cm^{-1}). This pattern of Raman spectra is a feature of nc-Si. It arises from the first-order Raman scattering of the longitudinal optical (LO) and the transverse optical (TO) phonon modes which are degenerate at the Brillouin zone centre in crystalline Si [**13**]. The Raman spectra of background region of the films, **Fig**. **1** (**d-f**), represented as open circle (○), were deconvulated with Gaussian lineshape to unveil different constituent peaks (blue colour). They display one prominent broad band (400-550 cm^{-1}) with a high intense peak around 480 cm^{-1} and a shoulder toward the low energy tail (350-400 cm^{-1}). Another broad band (100-280 cm^{-1}) with relatively less intense peak near 160 cm^{-1} has also been observed. These broad peaks corresponds to Raman TO, LO, longitudinal acoustic (LA) and transverse acoustic (TA) phonon modes of a-Si (marked in **Fig. 1[d-f]**) [**14**]. An additional broad peak is observed at 441 cm^{-1} which is marked as '*' in the **Fig. 1(f)** only. This additional peak is attributed to the six-membered rings of Si_2O_4 and the presence of five-, seven- and higher member rings is responsible for broadening of this band [**15**]. The signature of this peak was absent in **Fig. 1 (d)** and **(e)** due to lower oxygen content in these samples. The EDX of film fabricated at O_2 pressure of 0.5 mbar showed presence of 68 % (x=2.1) of elemental oxygen, therefore Raman mode corresponding to SiO_2 is distinguishable. Hence from the Raman studies it can be inferred that the thin films were composed of clusters of nc-Si embedded in background composed of a-Si and a-SiO_2, where the concentration of later increases with the increase in O_2 pressure.

Fig. 2 shows the linear absorption coefficient (α) as a function of wavelength, for the SiO_x thin films at different O_2 pressure. This figure shows decrease in values of α and a gradual shift of absorption edge of the thin films toward lower wavelength with increase in O_2 pressure indicating a gradual blue shift in optical band gap with increase in oxygen content. This is due to the shift in stoichiometry from Si-rich to SiO_2 rich SiO_x films with increasing O_2 pressure during deposition.

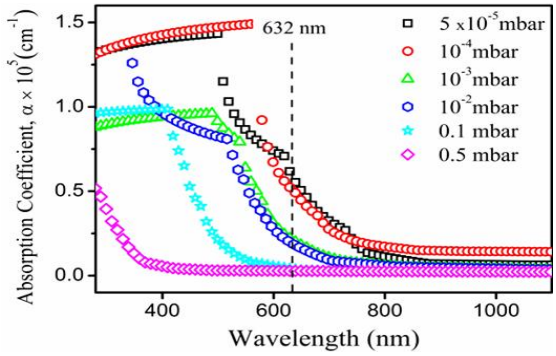

Fig. 2. Linear absorption coefficient (α) of the SiO_x PLD thin films deposited at different O_2 pressure from 5×10^{-5} to 0.5 m bar.

Fig. 3 (a) shows the normalized transmittance plot for open aperture Z-scan as a function of the sample position (z) w.r.t focus of the lens for SiO_x thin films deposited at various O_2 pressures. All the normalized transmittance curves except that for the film fabricated at 0.5 mbar O_2 pressure, in **Fig. 3 (a),** exhibit minimum transmission at focus which indicates the presence of strong reverse saturation absorption (RSA). As the cw-laser was used in Z-scan experiment, the origin of optical nonlinearity is attributed mainly to the thermal effects. In the focal region, the laser intensity is maximum and hence laser induced heating is also maximum in the sample. While away from the focal region, on either side, due to the gradual fall of laser intensity, laser induced heating is also curtailed. Therefore, the generated phonon density within the material is larger at focus compared to other scanning positions [**4**]. Hence the probability of phonon mediated optical absorption in this indirect band gap SiO_x thin film was maximum (minimum transmission) at focus while the absorption decreased as the sample moved away from focus on either side. The experimental data points for all the open Z-scan spectra were fitted to the transmission profile, T_{op}, for determining non-linear absorption coefficient (β), given by [**16**], $T_{op} = 1 - \frac{c}{(1+bz^2)}$, where $c = \beta I L_{eff} / 2^{3/2}$ and $b = 1/z_o^2$. Here, I is the intensity of the laser beam at focus within the thin film, β is the nonlinear absorption coefficient, z_o is rayleigh length of focussed beam while $L_{eff} = \frac{1-exp(-\alpha L)}{\alpha}$ is the effective thickness of the nc-SiO_x thin film with α and L being linear absorbtion coefficient and thickness of the film, respectively. From this fitting β was calculated. **Fig. 3 (b)** shows the variation of β for the SiO_x thin films as a function of O_2 pressures. The β for the SiO_x films was observed to be decreasing from 25.1 cm/W to 2.07 cm/W, with increase in O_2 pressure from 5×10^{-5} to 10^{-1} mbar. With increase in oxygen content, values of α of the films at 632 nm decrease from 5.89 × 10^4 cm^{-1} to 0.28 × 10^4 cm^{-1}, as observed in **Fig. 2,** making the film optically thin. The decrease in α reduces the laser absorption induced heating in the films resulting in reduced production of phonons. This gradual decline in phonon density reduces the probability of optical absorption in these indirect band gap SiO_x thin films resulting in the decrease in RSA and hence β [**4**].

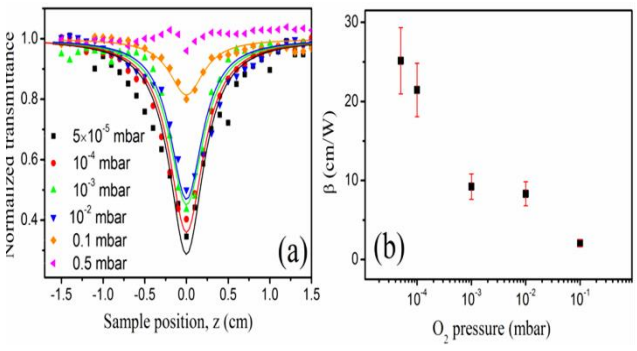

Fig. 3. (a) Open Z-scan Normalized Transmission intensity and (b) values of non-linear absorption coefficient (β) for SiO_x PLD films deposited at O_2 pressure from 5×10^{-5} to 0.5 mbar.

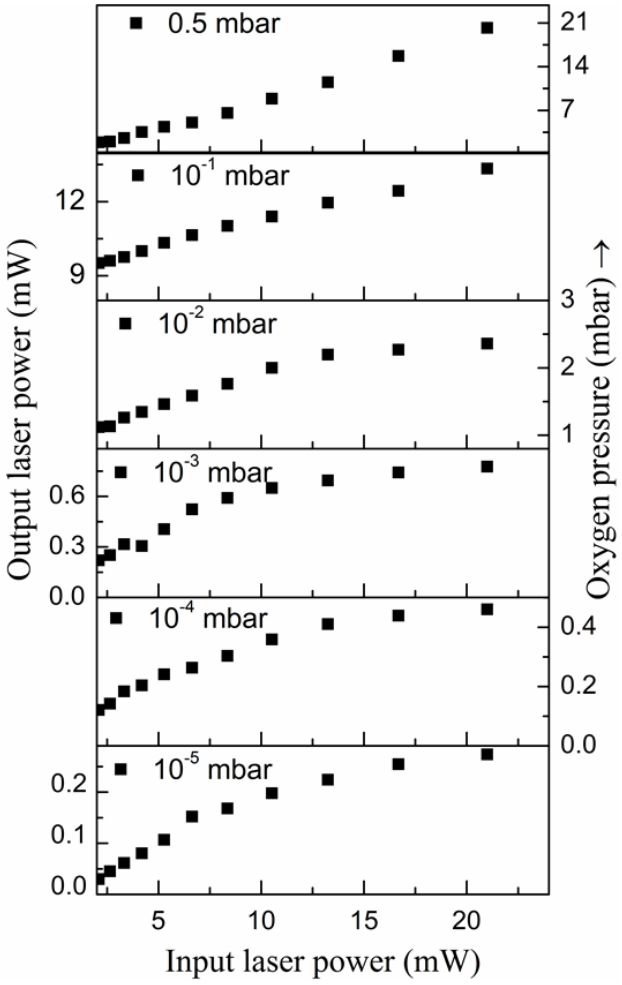

Fig. 4. Optical limiting property for SiO_x PLD films fabricated at different O_2 pressure.

Reverse saturable absorbers exhibit a decrease in transmittance with increase in incident intensity. Hence materials with large RSA can be used in optical limiting applications. An ideal optical power limiter has a linear transmission below a particular threshold and above which the output becomes constant. This property could be used for providing safety to optical sensors and eye. **Fig. 4** shows the characteristic OL curves for the SiO_x films. It is shown clearly in **Fig. 4** that at low incident laser power, the output varies linearly with input power and deviates from linearity displaying a sign of saturation at higher laser powers in SiO_x films. The point of onset of deviation from linearity of the plot of output laser power versus input laser power is termed as optical limiting threshold. The deviations from linearity began at around 7 mW for the films deposited at 5×10^{-5} mbar while that for 10^{-4} and 10^{-3} mbar films, it starts at comparatively higher power around 10 mW and finally at 14 mW, for film deposited at 10^{-2} mbar. The optical limiting threshold for film fabricated at 5×10^{-5} mbar was observed at comparatively lower power as its nonlinear absorption was higher compared to that fabricated at higher O_2 pressures. As the ß for the films reduces with increasing oxygen content the limiting threshold also shifts to higher laser power. For film fabricated at 0.5 mbar, no clear signature of OL was observed, as SiO_x films fabricated at this pressure shows the absence of nonlinear absorption. The increase in β of SiO_x films with shift in stoichiometry from oxygen rich (x=2.1) to Si-rich (x~0.03) result in decrease in OL threshold with decrease in oxygen content.

Conclusion

In conclusion, SiO_x thin films were deposited via PLD at different O_2 pressure, from 5×10^{-5} to 0.5 mbar in order to obtain nanostructured films. With increase in ambient O_2 pressure, a shift in stoichiometry in SiO_x films from Si rich (x=0.03) to oxygen rich (x=2.1) was observed as confirmed by EDX. Linear absorption coefficient (at λ = 632.8 nm) decreases from 8.5×10^4 cm^{-1} to 0.67×10^4 cm^{-1} with the increase in O_2 pressure from 5×10^{-5} to 0.5 mbar, respectively. Accordingly, there was a decrease in β from 23.5 cm/W to 1.64 cm/W, with increase in O_2 pressure from 5×10^{-5} to 10^{-1} mbar, respectively. The origin of this nonlinearity is overwhelming due to thermal effects, induced by cw laser irradiation. The OL effect in these films is due to RSA and optical limiting threshold was found to increase with increasing oxygen content. Hence these results indicate that a tunable NLO and OL films can be fabricated by controlling the stoichiometry of SiO_x films.

Acknowledgements

The authors acknowledge CIF, IIT Guwahati, for providing Raman spectrometer and EDX spectrometer. The work was partially supported by DRDO, India (Grant no. ERIP/ER/07003/30/M/01/1138).

References

1. Cotter, D.; Manning, R.J.; Blow, K.J.; Ellis, A.D.; Kelly, A.E.; Nesset, D.; Philips, I.D.; Poustie, A.J.; Rogers, D.C.; *Science*, **1999**, 286, 1523. **DOI:** 10.1126/science.286.5444.1523
2. Souza, R. F.; Alencar, M. A.; da Silva, E. C.; Meneghetti, M. R.; Hickmann, J. M.; *Appl. Phys. Lett.*, **2008**, 92, 201902. **DOI:** 10.1063/1.2929385
3. Nagaraja, K. K.; Pramodini, S.; Poornesh, P.; Nagaraja, H. S; *J. Phys. D: Appl. Phys*., **2013**, 46, 055106. **DOI:** 10.1088/0022-3727/46/5/055106
4. Tiwari, A.; Mishra, A.P.; Dhakate, SR.; Khan, R.; Shukla, S.K.; *Materials Letters*, **2007**, 61, 23, 4587. **DOI:** http://dx.doi.org/10.1016/j.matlet.2007.02.076
5. Tutt, L.W.; Boggess, T. F; *Prog. Quant. Electron*.; **1993**, 17, 299. **DOI:** 10.1016/0079-6727(93)90004-S
6. Ganeev, R.A.; Nonlinear Optical Properties of Materials; Springer: New York, **2013**. **DOI:** 10.1007/978-94-007-6022-6
7. Band, Y. B.; Harter, D.J.; Bavli, R; *Chem. Phys. Lett.*; **1986**, 126, 280.
8. Harter, D. J.; Shand, M. L.; Band, Y. B; *J. Appl. Phys.*, **1984**, 56, 865.
9. Tiwari, A.; Dhakate, S. R.; *International Journal of Biological Macromolecules*, **2009**, 44, 408. DOI: http://dx.doi.org/10.1016/j.ijbiomac.2009.03.002
10. Martínez, A.; Hernández, S.; Pellegrino, P.; Jambois, O.; Miska, P.; Grün, M.; Rinnert, H.; Vergnat, M.; Izquierdo-Roca, V.; Fedel,i J. M.; Garrido, B; *Phys. Status Solidi C*, **2011**, 8, 969. **DOI:** 10.1002/pssc.201000420
11. Spano, R.; Daldosso, N.; Cazzanelli, M.; Ferraiol,i L.; Tartara, L.; Yu, J.; Degiorgio, V.; Jordana, E.; Fedeli, J. M.; Pavesi, L; *Opt. Express*, **2009**, 17, 3941.

DOI: 10.1364/OE.17.003941
12. Kumar, I.; Khare, A; *Opt. Laser Technol*., **2015**, 77, 51. **DOI:** 10.1016/j.optlastec.2015.08.018
13. Smit, C.; van Swaaij, R. A. C. M. M.; Donker, H.; Petit, A. M. H. N.; Kessels, W. M. M.; van de Sanden, M. C. M; *J. Appl. Phys.*, **2003**, 94, 3582. **DOI:** 10.1063/1.1596364
14. Won, D.; Ramirez, M. O.; Kang, H.; Gopalan, V.; Baril, N. F.; Calkins, J.; Badding, J. V.; Sazio, P. J. A; *Appl. Phys. Lett*., **2007**, 91, 1. **DOI:** 10.1063/1.2790079
15. Borodko, Y.; Ager III, J. W.; Marti, G. E.; Song, H.; Niesz, K.; Somorjai, G. A; *J. Phys. Chem. B*, **2005**, 109, 17386. **DOI:** 10.1021/jp051801x
16. Sheik-Bahae, M.;. Said, A. A; Wei, T. H; Hagan, D. J.; Stryland, E. W. V; *IEEE J. Quantum Electron*., **1990**, 26, 760.