Near resonant nanosecond laser-driven nonlinear optical response in As$_{50}$S$_{50}$ thin films

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Abstract
Nanosecond near resonant excitation in As$_{50}$S$_{50}$ thin films leads to strong nonlinear optical response, i.e. nonlinear absorption coefficient up to $4 \times 10^6$ cm GW$^{-1}$ and nonlinear refractive index of 8.5 cm$^2$ GW$^{-1}$, both of which are the strongest ever reported in amorphous semiconductors. We propose a three-level energy band model to explain this effect, which indicates that the nonlinear process is reverse saturable absorption in nature, mediated by excited-state absorption from slow interband transition between the conduction and valence band. On the other hand, observation of negative nonlinear refractive index reveals the occurrence of self-defocusing effect. Finally, benefitting from the strong nonlinear response, we demonstrate a promising application of As$_{50}$S$_{50}$ thin films as an optical limiter for optoelectronic sensors.

Keywords: nonlinear optics, Z-scan, chalcogenide, thin films

(Some figures may appear in colour only in the online journal)

1. Introduction

In recent years, there has been a huge surge in understanding the third-order nonlinearities of optical materials from both fundamental and a plethora of application aspects, including optical switching [1], optical modulation [2], optical limiting [3, 4], etc. Among these, the optical limiter is of particular importance because it helps in protecting the human eye as well as optical sensors in optoelectronic applications from an intense laser source [4]. In principle, an ideal optical limiter must have high transmission in low-intensity beam, but reduced transmission against intense beam, over a wide dynamic working range. Optical limiting is typically associated with the nonlinear optical process, e.g. multiphoton or excited-state absorption (ESA) [5–8]. Therefore, the quest for materials with high optical nonlinearity, i.e. high nonlinear absorption ($\beta$) and high nonlinear refractive index ($n_2$) has remained a central research question over many years. A wide range of amorphous and crystalline materials, for example, porphyrin [9], ZnO nanorods [10], plasmonic materials [11], nanocomposites of transition metal dichalcogenides [12], graphene oxide [4, 13], etc, have shown their applicability to some extent in optical limiting. However, fabricating such structures is a real challenge because it involves complicated synthetic routes that require the utmost precision. In this regard, amorphous chalcogenide glasses (ChGs) and their thin films hold advantages because of their easy synthetic procedure via a thermal evaporation technique [14, 15]. In addition, ChGs possess high linear refractive index, high third-order nonlinear refractive index ($n_2$) and ultrafast response time [16]. ChGs are formed by chalcogen elements (S, Se, Te) in combination with elements such as As, Ge, Ga, Sb, etc [14, 15, 17]. Among the family of ChGs, As-based compositions are preferable due to their high chemical stability. Compared to the conventional As$_{40}$S$_{60}$ (As$_2$S$_3$), which has mean coordination number (MCN) 2.4, in our present study we choose over-constrained As$_{50}$S$_{50}$ (As$_2$S$_2$), with MCN 2.5, because of its intrinsic structural rigidity and thermal stability against pulsed laser.
In this article, we employed the conventional Z-scan technique to demonstrate strong nonlinear optical response in As$_{50}$S$_{50}$ thin films. A comparative study reveals that both $\beta$ and $n_2$ are among the highest reported in the family of amorphous semiconductors. ESA observed in our sample is explained from a three-level energy band model. We also showed that the strong nonlinear effects in As$_{50}$S$_{50}$ hold potential applications in fabricating optical limiting devices.

2. Methods

2.1. Sample preparation

As$_{50}$S$_{50}$ thin films were prepared by using the conventional melt-quenching method starting from 99.999% pure As and S. The cast samples were used as the source material for depositing thin films on microscopic glass substrate by the thermal evaporation technique. To preserve the target stoichiometry from the starting bulk material, we used a low deposition rate of 2–5 Å s$^{-1}$. We later performed energy-dispersive x-ray analysis and confirmed the uniformity of composition is within the experimental error of this technique, i.e. within 2%–3%. We prepared film with thickness of ~420 nm, which was verified by using ellipsometric measurements [18]. X-ray diffraction measurements further indicate that the sample is amorphous in nature.

2.2. Raman spectroscopy

The Raman spectra are obtained in a Horiba JY LabRam HR Evolution Spectrometer mounted with a grating of 1800 grooves/mm using a 50X objective with NA = 0.5 lens in back-scattering configuration. We excite the sample by a diode laser with a wavelength of 532 nm and spot diameter of ~0.5 μm. The detection is performed by an air-cooled charge-coupled device detector. To avoid local heating by the laser, measurements are performed at very nominal power of ~1 mW.

2.3. Z-scan measurements

To unveil the third-order nonlinear optical response of As$_{50}$S$_{50}$ thin films, we employed the Z-scan technique, which is a precise method based on self-focusing. A schematic diagram of the Z-scan setup is shown in figure 1. In a typical Z-scan setup, transmission is measured in the far field as a function of sample position $Z$, along the laser propagation of a focused laser beam. In our present study, we measured transmission in two different configurations. In the first case, known as ‘open-aperture’ Z-scan, all the transmitted laser beam is collected and measured after the sample. In the second case, laser light is transmitted through a small aperture placed in the far field, which is defined as ‘closed-aperture’ Z-scan. By performing open- and closed-aperture Z-scan measurements, we can determine the nonlinear absorption coefficient and non-linear refractive index of the films, respectively. We excite the sample with the second harmonics (532 nm) of Nd:YAG laser with a pulse width of 7 ns. To exclude the possibility of heating and photo damage, we used a fixed repetition rate of 10 Hz [19]. We expect that for 10 Hz repetition rate, the temporal separation between two pulses in 100 ms, which is reasonably long, will dissipate the heat and avoid progressive heating before the arrival of the next pulse to the sample. Explicitly, although the cumulative thermal effects are absent, it can possibly contribute to the overall nonlinearity of the sample within the regime of single pulse. The beam is focused on the axis of a lens with a focal length of 20 cm where the film is moving by computer controlled translational stage. The Rayleigh length and beam waist are measured to be 3.7 mm and 25 μm, respectively. The linear transmission of the film on glass is $\approx60\%$ measured in the far-field region.

2.4. Nanosecond pump-probe measurements

For pump-probe transient absorption (TA) measurements, we used second harmonics of the Nd:YAG laser (7 ns pulses centred at 532 nm with an average fluence of 26 mJ cm$^{-2}$ and having a repetition rate of 10 Hz) as the pump in single-shot mode. The probe beam was selected from a Xenon Arc lamp (120 W) using a holographic grating with 1200 grooves/mm and delayed with respect to the pump beam using a digital delay generator. The pump and probe beams were overlapped at the sample. The change in absorbance of the probe beam, $\Delta A = -\log(I_{gs}/I_{es})$ at different delays was recorded using a photomultiplier tube and a digital oscilloscope. Here, $I_{gs}$ and $I_{es}$ are the transmitted intensities of the probe beam after delay time $t$ following the pump-beam excitation and in the ground state, respectively.

3. Results and discussions

To analyze the structural composition of our As$_{50}$S$_{50}$ thin films, first, we recorded Raman spectra, as shown in figure 2. We clearly observe two intense broad peaks centred at 348 and 235 cm$^{-1}$ followed by two residual peaks at 275 and 187 cm$^{-1}$. The Raman band centred at 348 cm$^{-1}$ is assigned to the vibrations of AsS$_3$ pyramids with minor contributions from $\alpha$-As$_3$S$_4$, $\beta$-As$_4$S$_5$, $\chi$-As$_4$S$_4$, $\alpha$-As$_3$S$_4$ and $\beta$-As$_4$S$_5$ [20].

From this, it is clear that the assignment of Raman modes to individual structural units is quite complicated due to the high number of possible Raman active vibrational modes and their strong overlapping. Another strong Raman band around 235 cm$^{-1}$ is attributed to the As-As vibrations in As$_4$S$_4$ molecules. The weak peak at 275 cm$^{-1}$ is assigned to pararealgar ($\gamma$-As$_4$S$_5$) and $\chi$-As$_4$S$_4$. The other weak peak at 187 cm$^{-1}$ belongs to $\beta$-As$_4$S$_5$.

To select the excitation wavelength for performing Z-scan measurements, first we measured the band gap of the sample. In this context, figure 3(a) shows the optical absorption spectra of the film. Since As$_{50}$S$_{50}$ is an indirect bandgap material, we use the following Tauc equation to calculate the band gap of the sample as:

$$ (\alpha h\nu) = B(h\nu - E_g)^2 $$

where $\alpha$, $h$, $\nu$, $E_g$ and $B$ are the absorption coefficient, Plank’s constant, frequency, optical band gap and a band tail (Tauc)
parameter, respectively. The intercept of the straight line at the photon energy axis will provide $E_g$, as shown in figure 3(b). The best fit of the experimental data indicates that the band gap of the sample is $2.05 \pm 0.01$ eV.

Next, we performed both open- and closed-aperture Z-scan measurements with near bandgap 532 nm excitation laser. In this regard, figure 4(a) shows the open-aperture Z-scan traces of $\text{As}_50\text{S}_{50}$ thin films at peak intensities of 10 and 30 MW cm$^{-2}$, which are measured at the focal point ($z = 0$). To obtain reference signal, first we recorded the Z-scan measurements of bare glass substrate without any coating of $\text{As}_50\text{S}_{50}$ thin films, represented by solid blue circles in figure 4(a). For bare substrates, we kept the intensity at 50 MW cm$^{-2}$, which is higher than the intensity used for our nonlinear measurements on thin films to discard any contribution from the substrate. Clearly a horizontal line is

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**Figure 1.** Schematic diagram of Z-scan measurement.

**Figure 2.** Raman spectrum of $\text{As}_50\text{S}_{50}$ thin films.
Figure 3. (a) Optical absorption spectrum of As$_{50}$S$_{50}$ thin film. (b) Tauc plot used for calculating the band gap.

Figure 4. (a) Intensity-dependent open-aperture Z-scan of As$_{50}$S$_{50}$ thin film. Horizontal blue line represents the absence of nonlinear response from the glass plate. (b) Energy-level diagram for the ESA. (c) Nanosecond transient absorption kinetics for selected wavelengths. (d) Variation of ESA coefficient as a function of input intensity.

observed before and after the focal point, which indicates that the bare substrate does not contribute to the nonlinear optical response of As$_{50}$S$_{50}$. For As$_{50}$S$_{50}$ thin films, it can be seen from the figure that at both intensities, normalized transmittance exhibits a gradual decrease while the sample moves towards the focal point, and reaches minimum at $z = 0$. This nonlinear response indicates that As$_{50}$S$_{50}$ undergoes reverse saturable absorption (RSA) similar to the observation by Elim et al [21]. It is important to note that Z-scan curves do not exhibit any asymmetry before and after the focal point, i.e. the transmission value remains the same, which indicates that the sample does not undergo any thermal or photo damage upon nanosecond laser illumination.
In semiconductors, RSA can be classified into two types; the first is two-photon absorption (TPA) and the second is ESA) [22]. Recently, Poornesh and co-workers explained the RSA observed in organic molecules by assuming a five-level model [23]. However, in solid-state As$_{50}$S$_{50}$ thin films, the RSA can be explained from the energy-level diagram, as shown in figure 4(b). In general, nonlinear optical response can be explained in terms of two physical processes, intraband (within the band) and interband (between two bands) transitions. Let us assume that time constants related to intraband and interband transitions are $\tau_1$ and $\tau_2$. In the present case, the band gap ($E_g$) of As$_{50}$S$_{50}$ thin film is found to be 2.05 eV, which is less than the excitation photon energy 2.33 eV (532 nm). Therefore, both intraband and interband transitions can contribute to the overall RSA observed in As$_{50}$S$_{50}$. However, as we used nanosecond laser pulses to excite the sample, the pulse width (7 ns) is much longer than the intraband relaxation time $\tau_1$, which is approximately of the order of femtosecond to sub-picosecond time frame. So, we can discard the possibility of intraband transition in our sample. Likewise, the only plausible mechanism remains interband transition between the valence band (ground state) and conduction band (excited state). In general, when the values of $\tau_2$ are smaller, the excited carriers can quickly revert to the ground state. Consequently, strong ground-state absorption gives rise to saturable absorption (SA). On the other hand, for larger $\tau_2$ values, i.e., when the excited carriers slowly return to the ground state, ESA dominates and the sample exhibits RSA. As$_{50}$S$_{50}$, being a ChG, possesses many deep and shallow trap states, between the bands. In such cases, excited carriers may not return to the ground state directly; rather they are trapped in a metastable state via non-radiative decay. To find the interband relaxation time, we performed the nanosecond TA measurements in As$_{50}$S$_{50}$ thin films. In this regard, temporal evolution of TA at selected wavelengths is shown in figure 4(c). Quite clearly, for some wavelengths, TA is reversible, indicating that excited carriers return to the ground state whereas for some other wavelengths TA is irreversible, which indicates that the carriers get trapped in the metastable state. In this regard, table 1 reveals the interband relaxation time for the selected wavelengths following TA measurements. From the $\tau_2$ values, we found that excited carriers non-radiatively decay to the metastable trapped state or ground state slowly within few microseconds, which is much longer than the pulse duration of nanosecond laser. The obtained results are similar to our recent work in As-based ChG films, i.e. As$_{5}$Se$_{65}$ [24], As$_{40}$S$_{60}$ [17] and Ge$_{5}$As$_{85}$Se$_{65}$ [25] thin films. Consequently, excited-state cross-section remains higher than ground-state cross-section and the sample exhibits RSA.

### Table 1. Interband relaxation time obtained for selected wavelengths following nanosecond TA measurements.

| Wavelength (nm) | $\tau_2$ (µs) |
|-----------------|---------------|
| 450             | 1.01 ± 0.01   |
| 500             | 1.38 ± 0.02   |
| 550             | 1.40 ± 0.07   |
| 600             | 1.92 ± 0.18   |

### Table 2. Nonlinear parameters obtained from the fitting of the experimental data shown in figure 4(a).

| Intensity (MW cm$^{-2}$) | $\beta \times 10^6$ (cm GW$^{-1}$) | $I_0 \times 10^4$ (GW cm$^{-2}$) |
|--------------------------|----------------------------------|----------------------------------|
| 10                       | 4.3 ± 0.7                        | 37.7 ± 0.5                       |
| 20                       | 3.2 ± 0.3                        | 38.5 ± 0.3                       |
| 30                       | 2.71 ± 0.05                      | 45 ± 0.2                         |

In this context, we calculated the absorption cross-sections for the excited and ground state from the following equations:

\[
\sigma_{es} = -\frac{\log T_{max}}{NL}, \tag{2}
\]

\[
\sigma_{gs} = -\frac{\log T_0}{NL}, \tag{3}
\]

where $T_0$, $T_{max}$, $N$ and $L$ are the linear transmittance of the material, transmittance peak of the SA, carrier density of the material at the ground state and the thickness of the sample, respectively. In As$_{50}$S$_{50}$, calculated values of $\sigma_{es}$ and $\sigma_{gs}$ are found to be $2.25 \times 10^{-12}$ cm$^2$ and $1.28 \times 10^{-12}$ cm$^2$, respectively. Consequently, we found that the ratio $\sigma_{es}/\sigma_{gs}$ (= 1.76) is greater than unity, which indicates that the nonlinear optical process is RSA from ESA.

To quantify the observed ESA, we used the following propagation equation in the dispersion as a function of the position as:

\[
\frac{dl}{dz} = -\alpha(I)I, \tag{4}
\]

where $l$ and $z$ are the intensity of the laser beam and propagation distance inside the sample. $\alpha(I)$ is the intensity-dependent absorption coefficient, which is defined by:

\[
\alpha(I) = \frac{\alpha_0}{1 + \frac{I}{I_0}} + \beta_{ESA}I, \tag{5}
\]

where $\alpha_0$, $I_0$ and $\beta_{ESA}$ are the linear absorption coefficient, saturable intensity and ESA coefficient, respectively. To obtain a more quantitative picture, we exploit Z-scan theory by expressing normalized transmittance as a function of position $z$ as:

\[
T_N = \frac{1}{q_0\sqrt{\pi}} \int_{-\infty}^{+\infty} \ln(1 + q_0e^{-\tau^2})dt, \tag{6}
\]

where $q_0 = \frac{\beta_{ESA}I_0}{1 + \frac{I_0}{I_0^{eff}}}$. The best fit to the normalized transmittance provides us with $\beta_{ESA}$. In this regard, figure 4(d) shows the variation of $\beta_{ESA}$ with input peak intensity ($I_0$). If the nonlinear process is associated with simple TPA alone, $\beta_{ESA}$ should not exhibit any variation with $I_0$. But in stark contrast, $\beta_{ESA}$ decreases with the increase in $I_0$, which is attributed to sequential TPA via ESA (RSA) similar to the
observation of Couris [26] and Bindhu [27]. Our results indicate that $\beta_{\text{ESA}}$ is found to be $(4.3 \pm 0.7) \times 10^3$ cm GW$^{-1}$ at the peak intensity of 10 MW cm$^{-2}$. In this regard, all nonlinear parameters are tabulated in table 2. Such enhanced ESA in our sample intrigues us, and thus we compare the present result with the previous reports, and the results are summarized in table 3 [13, 28–32]. Quite clearly, the amplitude of $\beta_{\text{ESA}}$ is ~6 orders $(10^6)$ higher than previously obtained results and also surpasses the nonlinearity obtained in our last measurement on the As-Sh-Se system by a factor of 10 [19]. Such an extremely high value of nonlinear absorption coefficient of $\text{As}_2\text{S}_6/\text{GO}$ also motivates us to explore the potential of our sample in device making when the input laser intensity ($I$).

As the experimental results are based on the Z-scan setup, the reliability of the optical limiter is a selective nonlinear device that attenuates intense laser beam while allowing low-intensity beams. It also plays a crucial role in protecting optoelectronic devices, e.g., photomultiplier tube, photodiode and human eye from intense laser. To demonstrate the device potential, we have plotted in figure 5(a) the variation of transmitted output intensity ($I_{\text{out}}$) as a function of input intensity ($I_{\text{in}}$). Quite clearly, at lower intensities, $I_{\text{out}}$ scales linearly with $I_{\text{in}}$, following Beer–Lambert law; thus the device remains inactive. However, as $I_{\text{in}}$ increases, $I_{\text{out}}$ exhibits deviation from linearity, as shown by the dashed line in figure 5(a), which shows that $\text{As}_2\text{S}_6/\text{GO}$ thin film limits $I_{\text{out}}$ for all higher $I_{\text{in}}$ above a certain threshold of 5 MW cm$^{-2}$. This particular value of $I_{\text{in}}$ is very important to determine the performance of an optical limiter. As the experimental results are based on the Z-scan setup, the reliability of the optical limiter is also checked by plotting the normalized transmittance as a function of the input intensity, as shown in figure 5(b). It can be seen that the transmission starts decreasing when the input laser intensity ($F_{\text{in}}$) exceeds 5 MW cm$^{-2}$, as in figure 5(a), which is a necessary criterion for the working principle of an optical limiter.

After demonstrating large nonlinear absorption coefficient by open-aperture Z-scan measurements, we performed closed-aperture Z-scans to determine the sign and magnitude of the nonlinear refractive index $n_2$ of $\text{As}_2\text{S}_6/\text{GO}$ thin films. We adjusted the size of the aperture in front of the detector in such a way that the transmission reduced to one third of the incident value. Typical normalized closed-aperture Z-Scan traces are shown in figure 6 at peak intensity of 30 MW cm$^{-2}$. Our sample exhibits pre-focal transmittance maximum (peak) followed by a post-focal transmittance minimum (valley), i.e. peak–valley (P–V) behaviour, which is associated with self-defocussing effect and characterized by negative $n_2$. The nonlinear refractive index $n_2$ is calculated using the equation:

$$n_2 = \frac{\lambda}{2\pi I_0 L_{\text{eff}}},$$

where $I_0$ is the peak intensity at the focus and $L_{\text{eff}}$ is the effective thickness of the sample, expressed as $L_{\text{eff}} = \frac{1}{\alpha}$. In order to extract the contribution purely from nonlinear refraction, we used the division method described by Sheik-Bahae et al [33] and fitted the experimental data with the equation:

$$|\Delta\phi_0| = \frac{\Delta T_{p\rightarrow v}}{0.406(1 - s)^{0.25}},$$

where $\Delta T_{p\rightarrow v}$ is the difference in magnitude between the normalized transmittance at peak ($T_p$) and at the valley ($T_v$). $S$ is the transmittance of the aperture without any sample and is represented as $S = 1 - \exp(-\frac{2\pi r^2}{\lambda^2})$, where $r_a$ is the aperture radius and $w_a$ is the beam radius at the aperture. From our calculation, the axial peak valley difference is 2.65 Zr, which is greater than 1.7 Zr, which gives a clear indication that the observed nonlinear process has thermal contribution and can be assigned as a third-order process as proposed by Nagraja and co-workers [22]. In order to extract the contribution purely from nonlinear refraction, we used the division method described by Sheik-Bahae et al [33] and fitted the experimental data in figure 6 with the equation:

$$T(x) = 1 + \frac{4x\Delta\phi_0}{(1 + x^2)(9 + x^2)} + \frac{4(3x^2 - 5)\Delta\phi_0^2}{(1 + x^2)(9 + x^2)(25 + x^2)},$$

where $T(x)$ is the transmittance of the sample and $x = \frac{r_a}{w_a}$ is the fraction of axial distance with Rayleigh length. Our calculation shows that $n_2$ is ~ $(8.49 \pm 0.81)$ cm$^2$ GW$^{-1}$, which is seven orders of magnitude higher compared to the reported value of

| Sample          | Intensity | Band gap/excitation type | Pulse duration | $\beta$ (cm GW$^{-1}$) | $n_2$ (cm$^2$ GW$^{-1}$) | Ref    |
|-----------------|-----------|--------------------------|----------------|------------------------|--------------------------|-------|
| Ge$_{25}$Sb$_{30}$Te$_{50}$ | 200 MW cm$^{-2}$ | 2.9 eV/OR | 7 ns | 400 | [-28] |
| Ge$_{25}$Sb$_{30}$Te$_{50}$ | 178 MW cm$^{-2}$ | 2.19 eV/NR | 7 ns | 17.92 | [-29] |
| ZnO            | 360 MW cm$^{-2}$ | 3.01 eV/OR | 5 ns | 7.6 | [-30] |
| $\alpha$-NiMo$_6$O$_4$ | 210 MW cm$^{-2}$ | 3 eV/OR | 7 ns | 71 | [-31] |
| Neutral red dye | 50 MW cm$^{-2}$ | 2.64 eV/NR | 30 ns | 1100 | $1.5 \times 10^{-3}$ | [-32] |
| GO             | 160 MW cm$^{-2}$ | 4.1 eV/OR | 5 ns | 20 | [-13] |
| MoSe$_2$/GO    | 160 MW cm$^{-2}$ | broadband | 5 ns | 580 | [-13] |
| As$_{25}$S$_{60}$ | 10 MW cm$^{-2}$ | 2.05 eV/NR | 7 ns | $4.3 \times 10^4$ | Present Work |

Table 3. Comparison of nonlinear absorption coefficient ($\beta$) and refractive index ($n_2$) with previously reported samples when excited with 532 nm (2.33 eV) laser. OR and NR refer to off-resonant and near-resonant excitation, respectively.
Figure 5. (a) Output intensity as a function of input intensity. Output intensity deviates from the input intensity after a threshold of 5 MW cm$^{-2}$. (b) Normalized transmittance as a function of input intensity.

Figure 6. Closed-aperture Z-scan traces of As$_{50}$S$_{50}$ thin films at 30 MW cm$^{-2}$. Hollow circles and solid line represent experimental data and theoretical fit, respectively.

fused silica (3.0 ± 0.4) $\times$ 10$^{-7}$ cm$^2$ GW$^{-1}$. At this point, for practical application, we calculated the figure of merit (FOM) in our sample, which is defined by $n_2/\beta \lambda$, where $n_2$ and $\beta$ are the nonlinear refractive index and nonlinear absorption coefficient defined before. Using the $n_2$ value from above and $\beta$ from table 2, we found that FOM ~0.06 is at 30 MW cm$^{-2}$.

The ChGs exhibit stronger nonlinear response than their counterparts because of their low vibrational bond energy induced by heavy chalcogen atoms. Consequently, ChGs become optically transparent up to mid-IR wavelength range [34]. Apart from that, the glass density of the ChGs is also higher, which when combined with strong polarizability, gives rise to high linear refractive index $n$ ~$2$–$3$ [34, 35]. Likewise, higher linear refractive index following empirical Miller’s rule [36] exhibits high nonlinear refractive index, as well as strong nonlinear optical response [35]. Nevertheless, such high nonlinear optical constants observed in our sample intrigue us; thus we desire to understand the underlying physical mechanisms behind such effects in detail for future studies.

In summary, we demonstrated that nonlinear response in As$_{50}$S$_{50}$ thin films can be successfully exploited in fabricating the optical limiting device. Intensity-dependent open-aperture Z-scan curves indicate that the nonlinear process is consistent with RSA. A three-level energy band model explains that RSA originated from the ESA via slow interband transition. On the other hand, closed-aperture Z-scan measurements indicate that As$_{50}$S$_{50}$ thin films have negative $n_2$, which is associated with self-defocussing effect. Finally, experimental results obtained in terms of $\beta$ and $n_2$ are found to be significantly higher by up to a few orders of magnitude than any previously reported results.

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