Research article

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Indium selenide film: a promising saturable absorber in 3- to 4- μm band for mid-infrared pulsed laser

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Abstract: Indium selenide (InSe) film, an emerging two-dimensional chalcogenide semiconductor, has recently attracted growing interests in optoelectronics. However, its nonlinear characteristics and application potentials in mid-infrared (IR) region remain open, which is a very attractive but undeveloped spectral region currently. In this work, it is demonstrated that InSe film possesses excellent nonlinear absorption properties in 3- to 4- μm band. Saturable absorption measurements of InSe film at 2.8 and 3.5 μm show very low saturation energy fluences and moderate modulation depths. Pump–probe measurements at 3 and 4 μm indicate that InSe film has ultrafast responses in mid-IR region. Furthermore, the application of InSe film in mid-IR pulsed laser is demonstrated, and stable Q-switching operation of fiber laser at 2.8 μm is realized. These results show that InSe film is a promising saturable absorber for mid-IR pulsed laser.

Keywords: InSe film; two-dimensional material; nonlinear absorption; mid-infrared; pulsed laser.

1 Introduction

Pulsed laser in the mid-infrared (mid-IR) region has a wide range of applications such as remote sensing, laser lidar, organic materials processing, and free-space optical communications, and so on [1–4]. Pulsed laser around 3.0 μm is especially attractive for laser surgery [5, 6] as it matches with the water absorption band. It is of great importance to develop pulsed laser in the mid-IR region. Currently, lack of robust saturable absorbers (SAs), just like near-IR semiconductor saturable absorber mirror (SESAM), is the main limitation for developing mid-IR pulsed laser. At present, commercial mature SESAM can only operate significantly lower than 3- μm wavelength limited by InGaAs bandgap and crystal lattice mismatching. The development of high-quality SAs that can operate in 3- to 4- μm mid-IR band is still on the way.

In the past decade, two-dimensional (2D) materials have attracted huge interests due to their unique electronic and optical properties [7–15]. Especially, broadband nonlinear absorption properties of 2D materials make them potential SAs for mid-IR pulsed lasers. Graphene, in principle, possesses saturable absorption in the whole mid-IR region, but the low modulation depth and weak optical absorption limit its performance as SA in mid-IR pulsed lasers [16, 17]. Beyond graphene, topological insulators, such as Bi_2Te_3 , were also investigated as SAs for mid-IR pulse generation [18], but the indirect bulk bandgap and complicated preparation process limit their applications as mid-IR SAs. Black phosphorus (BP), a 2D material composed of group VA element, has been studied as mid-IR SA in recent years [19–21], but it is challenging to prepare large-size and high-quality BP sample because of lack of controllable fabrication process such as chemical

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vapor deposition. Belonging to the same group of BP, antimonene and bismuth nanosheets were also investigated as mid-IR SAs [22, 23]. Besides the aforementioned 2D materials, transition metal dichalcogenides (TMDCs) were also studied as mid-IR SAs [24, 25]. Although their bandgaps between 0.7 and 2.5 eV cover the spectral region only from visible to near-IR, TMDCs can also support mid-IR pulses generation driven by new mechanisms such as intraband optical absorption or inducing defects [26–30]. Moreover, TMDC-based SAs are chemically stable in atmosphere and can be fabricated easily and stably, which can significantly expand their applications as SAs for mid-IR pulses generation. It is worth noting that the above investigations on mid-IR SAs mainly focus on 2- to 3- μm band, and there are seldom reports on mid-IR SAs in 3- to 4- μm spectral region [31, 32].

Similar to TMDCs, a type of compound composing of metals from group IIIA (Ga and In) and the chalcogenide from group VIA (S, Se, and Te) with layered structures has aroused renewed interests due to their excellent electrical and optical properties [33–35]. Among them, indium selenide (InSe) is recently attracting great attention [36–39]. Research shows that InSe has a high electron mobility due to weak electron–phonon scattering and also possesses a high environmental stability [40–42]. In addition, similar to other 2D materials [43], the bandgap of InSe can be tuned in a large range by controlling its layer numbers [44, 45]. Thus, InSe is considered as an ideal material for electronic chips to replace silicon in the future. Recent studies also demonstrate that InSe film possesses nonlinear absorption in the 1- to 2- μm spectral region [46, 47]. However, nonlinear absorption characteristics of InSe film in the 3- to 4- μm mid-IR region are still not clear, and the potential of InSe as mid-IR SAs has not been exploited.

In this article, we demonstrate that InSe film has excellent nonlinear absorption characteristics in the 3- to 4- μm mid-IR region. Using mechanical exfoliation (ME) method, high-quality InSe film was prepared. The saturable absorption properties of InSe film at 2.8 and 3.5 μm show a very low saturation energy fluence and moderate modulation depth. Furthermore, pump–probe measurements demonstrate that InSe has an ultrafast absorption recovery time at 3- and 4- μm wavelengths. To verify the potential of InSe as mid-IR SAs, Q-switching experiment of Er:ZBLAN fiber laser was performed, and long-term stable Q-switching operation at 2.8 μm was realized by using InSe film as SA. These results demonstrate that InSe film possesses an excellent nonlinear absorption property in mid-IR region and will be a promising SA for mid-IR pulsed laser.

2 Preparation and morphological characterization

Indium selenide has a rhombohedral unit cell ($a=b=4.05 \text{ \AA}$, $c=25.32 \text{ \AA}$), and each Se (In) atom connects with three In (Se) atoms by covalent bonds. The layer structures of InSe at top (a - b plane) and side (b - c plane) views are shown in Figure 1A. The adjacent layers with a distance of $\sim 0.83 \text{ nm}$ interact by weak van der Waals forces (Figure 1A). Therefore, InSe film can be easily stripped from bulk Bridgman-grown InSe crystal. Mechanical exfoliation method is a general method for preparing high-quality 2D film. In our experiment, InSe films were prepared using ME method by tearing the bulk InSe (purity of 99.995%; Shanghai Juna Technology, Shanghai, China) with Scotch tapes and then were transferred onto substrates with tweezers.

To identify the morphology and chemical composition of the prepared InSe films, various characterizations were performed. The morphology of the prepared InSe film was characterized by scanning electron microscopy, presenting a large ($\sim 50 \mu\text{m}$ in width) sheet structure and a quite smooth surface (Figure 1B). Energy-dispersive X-ray spectroscopy was used to analyze the elements in InSe film [48]. The corresponding element map shows a homogeneous distribution of In and Se elements (Figure 1B), and the atomic number ratio of In and Se elements was 0.83:1 (Figure 1C). Raman spectra of InSe film and bulk InSe were measured, as shown in Figure 1D. Compared with bulk InSe, resonant Raman modes of A_1' (Γ_1^2) at 115 cm^{-1} , E' (Γ_3^1)-TO, and E'' (Γ_3^3) at 178 cm^{-1} and A_1' (Γ_1^3) at 227 cm^{-1} of InSe film are stronger, and another mode of A_2'' (Γ_1^1)-LO at 187 cm^{-1} is observed. The crystallographic phase of the prepared InSe film was also measured by X-ray diffraction. The diffraction peaks given in Figure 1E are in accordance with the Bragg position of InSe (JCPDS-34-1431) [49]. In addition, for obtaining the linear absorption property of the prepared InSe film, the absorption spectrum was measured by a Fourier transform spectrometer. As shown in Figure 1F, the absorption covers the spectral range of 2 to 6 μm , which makes it possible for the InSe film to act as a wavelength-versatile optical switching device in mid-IR region.

3 Mid-IR nonlinear characterization

To reveal the nonlinear absorption property of the InSe film in mid-IR region, power-dependent reflectivity measurements were performed at 2.8- and 3.5- μm wavelengths.

Figure 1: Characterization and optical properties of InSe film.

(A) Structures of InSe at top and side views; d , layer distance: 0.83 nm. (B) Scanning electron microscopy mapping of InSe film. (C) Energy-dispersive X-ray spectroscopy image and the corresponding element content of InSe film. (D) Raman spectra of the prepared InSe film and bulk InSe. (E) X-ray diffraction spectrum of the prepared InSe film. (F) Absorption spectrum of the prepared InSe film.

Indium selenide film was transferred onto a gold-coated mirror for measurement. In the experiment, the used laser source is an optical parametric amplifier (OPA) source that emits mid-IR femtosecond pulses with a repetition rate of 1 MHz and a pulse duration of 213 fs. By controlling the laser power incident on the InSe–gold coating mirror using various attenuation plates, power-dependent reflectivity of the InSe–gold coating mirror was then obtained. As shown in Figure 2, the InSe film exhibits saturable absorption at both 2.8 and 3.5 μm . The saturable energy fluence and modulation depth can

be obtained by fitting the measurement data using the following function:

$$R(F) = 1 - \Delta R \cdot \exp(-F/F_{\text{sat}}) - R_n \quad (1)$$

where $R(F)$ is the reflectivity, F is the pulse energy fluence, F_{sat} is the saturable energy fluence, ΔR is the modulation depth, and R_n is the nonsaturable loss. At 2.8 μm , the InSe film possesses a saturable absorption with a modulation depth of 12%, a saturable energy fluence of 18 nJ/cm^2 , and a nonsaturable loss of 23.4%. At 3.5 μm , it presents a similar saturable absorption with a modulation depth of

Figure 2: Saturable absorption measurement results of the InSe film. Reflectivity of the InSe film versus incident fluence at (A) 2.8 μm and (B) 3.5 μm .

12%, a saturable energy fluence of 16 nJ/cm^2 , and a non-saturable loss of 24%. Compared with other 2D materials [19, 23–25, 50], InSe film possesses a much lower saturable energy fluence, which means that low power can initiate pulse operation.

In order to reveal the ultrafast nonlinear optical response of the InSe film in 3- to $4\text{-}\mu\text{m}$ spectral region, pump–probe measurement was also performed. The pump laser is an 800-nm Ti:sapphire femtosecond laser and the probe laser is an OPA that emits femtosecond mid-IR pulses. Indium selenide film was transferred onto a CaF_2 mirror for the measurement. The pump laser and probe laser were incident to the same position on the InSe film, and the time delay between the pump laser and the probe laser was controlled via a delay line settled in the pump path. A chopper rotating with a specific reference frequency was settled in the pump path, and the variation of the probe beam transmittance with the time delay was recorded via a lock-in amplifier [51]. In the experiment, two probe wavelengths were chosen at 3 and $4\text{ }\mu\text{m}$, respectively, and the results are shown in Figure 3. The transmittances

exhibit sharp increasing at zero time delay, indicating that the InSe film possesses saturable absorption at 3- and $4\text{-}\mu\text{m}$ wavelengths. As nondegenerate pump–probe measurement was performed in the experiment, the decay traces at positive time delays are fitted by single-exponential kernel functions [52]. The measured absorption recovery time is 12.3 ps for $3\text{-}\mu\text{m}$ wavelength and 6.8 ps for $4\text{-}\mu\text{m}$ wavelength, which are associated with carrier-phonon coupling [51, 52]. The difference of recovery times at 3 and $4\text{ }\mu\text{m}$ suggests different cooling rates of electrons, which were also observed in graphite [7] and BP [53]. Note that there exists a photoinduced absorption process at $4\text{ }\mu\text{m}$, which may be caused by surface-related defects and trap states [54]. The pump–probe experimental results reveal the ultrafast nonlinear optical response of the InSe film in mid-IR region, showing the potential of the InSe film as SAs for mid-IR pulses generation. It is worth mentioning that the bandgap of pure InSe is 1.26 (bulk) to 2.11 eV (monolayer) [45], which do not cover mid-IR region. Here nonlinear absorption in 3- to $4\text{-}\mu\text{m}$ band should be attributed to defect bandgap, as observed in MoS_2 [24] and ReS_2 [25].

Figure 3: Pump–probe measurement results of the InSe film. Transient transmittance versus time delays at (A) $3\text{ }\mu\text{m}$ and (B) $4\text{ }\mu\text{m}$.

Figure 4: Schematic of Q-switched Er:ZBLAN fiber laser using InSe film as SA. LD, laser diode; L1, L2, L3, and L4, lenses; M1 and M2, dichroic mirrors.

Figure 5: Q-switching results of 2.8 μm Er:ZBLAN fiber laser using InSe film as SA.

(A) Q-switching pulse train; inset: RF spectrum. (B) Optical spectrum of the Q-switched laser. (C) Average output power and pulse energy versus the incident pump power. (D) Repetition rate and pulse width versus the incident pump power. (E) Output power stability in 24 h. (F) Pulse trains recorded at 0 h, 12th h, and 24th h.

4 Mid-IR pulsed laser experiment

Motivated by the nonlinear absorption property of the InSe film in mid-IR region, the InSe film was then applied as SAs for mid-IR pulsed laser generation. In the experiment, a 2.8-μm Q-switched Er:ZBLAN fiber laser was built by using InSe–gold coating mirror as an end mirror of cavity. As shown in Figure 4, the pump source is a commercial 976-nm laser diode coupled with a pigtail silica fiber that has a numerical aperture (NA) of 0.22 and a core diameter of 105 μm. A 3.2-m-long 6 mol.% Er-doping double-clad

ZBLAN fiber with a core diameter of 16.5 μm and an NA of 0.12 are used as the gain fiber. For efficiently coupling the pump beam into the cladding of the gain fiber, the pump beam is collimated by L1 ($f=50$ mm) and focused by L2 ($f=70$ mm) and then is incident to the front-end face of the Er:ZBLAN fiber. The front end of the fiber is perpendicular-cleaved, serving as an output coupler with Fresnel reflection (4%) as feedback. A 45° placed dichroic mirror M1 is used to separate the output laser beam from the pump light. At the rear end of the fiber, a pair of off-axis parabolic mirrors L3 and L4 ($f=12.7$ mm) are used to collimate and

then focus the laser beam onto the reflection-type InSe SAM. The laser mode size on the InSe SAM is $\sim 16.5\ \mu\text{m}$ in diameter. Between L3 and L4, another 45° placed dichroic mirror M2 is used for filtering out residual pump light.

By using InSe film as SA, stable Q-switching operation is achieved, and the results are shown in Figure 5. Figure 5A shows stable Q-switching pulse train. The radio frequency (RF) spectrum (inset of Figure 5A) shows a signal-to-noise ratio of 42.4 dB. The spectrum of the Q-switching laser (Figure 5B) shows a central wavelength of 2765 nm. Detailed characterization of the Q-switching laser performance was conducted by changing the pump power. The maximum average output power of the Q-switching laser is 70 mW, and the corresponding pulse energy is 1.3 μJ (Figure 5C). The low output power is mainly attributed to the relatively large nonsaturable loss of InSe film. The variations of repetition rate and pulse width with the pump power are shown in Figure 5D. The shortest pulse width of 1.2 μs is obtained at the maximum pump power of 2.5 W. For characterizing the stability of Q-switching operation, the output power was recorded for 24 h (Figure 5E). The fluctuation of the output power was $\pm 3.5\%$ in 24 h. The pulse trains were also monitored as shown in Figure 5F, and the fluctuations of pulse width and pulse repetition rate were $\pm 3\%$ and $\pm 1.4\%$, respectively. The results in Figure 5E–F indicate the long-term stability of Q-switching operation by using InSe film as SA. Overall, the Q-switching results show that InSe film is a promising SA for 2.8- μm pulsed laser. Moreover, according to the demonstrated nonlinear absorption property, InSe film even can serve as a wavelength-versatile SA in a wide mid-IR region.

5 Conclusions

High-quality InSe film was prepared via ME method, and its nonlinear absorption property was studied in 3- to 4- μm mid-IR region. By power-dependent reflectivity measurement, InSe film exhibits saturable absorption at 2.8 and 3.5 μm . Furthermore, pump–probe measurements at 3 and 4 μm were also performed to demonstrate ultrafast absorption recovery time of InSe film. To verify the potential as mid-IR SA, the InSe film was applied in a 2.8- μm Er:ZBLAN fiber laser, and long-term stable Q-switching operation was realized. The successful demonstration of long-term stable 2.8- μm pulsed laser shows the potential of InSe film as a robust SA in mid-IR region. Moreover, the demonstrated broadband nonlinear absorption of InSe film will also expand its application in mid-IR optoelectronic devices.

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