Research article

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Physical vapor deposition of large-scale PbSe films and its applications in pulsed fiber lasers

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Abstract: Lead selenide (PbSe) is a new emerging semiconductor with layer-dependent bandgap that has attracted much interest due to its high infrared response and good environmental stability. We have prepared large-scale PbSe films with the area of 7 cm² and thickness of 25 nm based on physical vapor deposition approach at 160°C. The PbSe films exhibit saturable absorption property at 1.55 μm and a polarization-sensitive saturable absorber is obtained by growing PbSe on D-shaped fiber. Single-pulse with the duration of 490 fs is generated at the pump of 12 mW and the mode-locking operation is maintained at the pump of 1500 mW, indicating the high damage threshold of the D-shaped fiber based saturable absorber. Two polarization-insensitive saturable absorbers are achieved by depositing PbSe on fiber facet and polyvinyl alcohol film, respectively. For fiber facet (polyvinyl alcohol film) based saturable absorber, the repetition rate of Q-switched pulses increases from 8.6 (16.3) kHz to 45.4 (59.2) kHz while the duration decreases from 7.92 (12) μs to 2.06 (3.12) μs by tuning the pump from 15 mW to 90 (60) mW. Such large-scale PbSe films possess features of low cost and high modulation ability, and can find important applications in infrared optical modulators and detectors.

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1 Introduction

Two-dimensional (2D) materials are attracting rising research attentions due to their remarkable physical and chemical properties, as well as the unique dimensionality effect [1–4]. In these 2D materials, the atoms in layer are linked by strong covalent bonds while layers are adhered by weak van der Waals interactions to form the bulk-state crystal [5]. The layered structure of materials ensures them to be exfoliated into few-layer nanosheets or single-layer nanosheets for preparing high-performance optoelectronic devices, such as photodetectors [6], optical thresholders [7], all-optical modulators [8, 9], and nonlinear saturable absorbers [10, 11]. Graphene, as the most famous 2D material, possesses the high third-order nonlinear susceptibility, ultrafast carrier dynamics, and zero-bandgap structure [12–15], allowing it to be applied in saturable absorbers (SAs) [16, 17], frequency converters [18], and optical modulators [19]. However, the light modulation ability of monolayer graphene is limited due to the small absorption coefficient of 2.3%.

Different from the zero-bandgap graphene, transition metal dichalcogenides (TMDs) are a new host of layered semi-conductive 2D materials with a bandgap of 0.8–2.1 eV [5, 20]. A unique feature of TMDs is that the physical property depends on the number of layers. For example, the bulk-state WS₂ crystal is an indirect semiconductor with a bandgap of 1.34 eV [21], while monolayer WS₂ is a direct semiconductor with a bandgap of 2 eV [22]. By introducing atom defects into few-layer WS₂, the bandgap can be decreased to 0.65 eV and they show broadband saturable absorption property from 1 to 2 μm [23–25]. However, the absorption coefficient at the infrared wavelength is quite small as the defects are minority in such materials [26]. Black phosphorus is a new-emerging direct bandgap 2D material with a bandgap from 1.5 eV (monolayer) to

0.3 eV (bulk), which can cover the gap between TMDs and graphene for the infrared photonics and optoelectronics [27–31]. Nanoscale black phosphorus has been prepared by various methods to achieve Q-switched and mode-locked operations in fiber lasers [32–34]. However, few-layer black phosphorus tends to be oxidized in atmosphere, and the antioxidation treatment [35] or protection system [36] is indispensable for practical applications.

Lead selenide (PbSe) is an IV–VI semiconductor with a cubic crystal structure, possessing inherent features of high stability, broadband optical response, and high electron mobility [37]. Bulk-state PbSe has a bandgap of 0.28 eV at room temperature [38], which is between the bandgap of graphene and TMDs. The grain size of PbSe varies with the thickness of the film, thereby tuning the optical bandgap of the material [39, 40]. The bandgap of PbSe is comparable with that of black phosphorus, while PbSe has better environmental stability than black phosphorus [38]. Attributing to these intrinsic features, PbSe films have found important applications in infrared detections [41], field-effect modulations [42], and solar conversions [43]. However, the nonlinear optical property of PbSe films is rarely reported and its application in infrared pulsed lasers should be further explored.

In this work, we have prepared large-scale PbSe films with the thickness of 25 nm based on the physical vapor deposition approach at 160°C. PbSe films are found to exhibit typical saturable absorption property at 1.55 μm , and a polarization-sensitive SA is prepared by depositing the PbSe on a D-shaped fiber (DSF). Such SA can operate at the mode-locked state in the fiber laser at the pump of 1500 mW. Two polarization-insensitive SAs are achieved by depositing PbSe on fiber facets (FFs) and polyvinyl alcohol (PVA) films, respectively, and both of them can be used to produce microsecond Q-switched pulses.

2 Preparation and characterization of PbSe SAs

The preparation of PbSe films can be mainly classified as physical methods including physical vapor deposition [44] and molecular beam epitaxy [45], and chemical methods including chemical bath deposition [46] and electrochemical deposition [47]. In our experiment, the PbSe films are prepared by the thermal evaporation deposition method that belongs to physical vapor deposition approach, which has advantages of low cost, good repeatability, and suitability for large-area deposition [48]. The preparation process is described as follows. Firstly, in

the vacuum chamber, the high-purity PbSe pellets (JHD, 99.999%) worked as the target, and a glass slide is used as the substrate. Secondly, the vacuum degree is decreased to 5×10^{-3} Pa by a vacuum pump and the temperature of target is raised by increasing the heating current. Thirdly, the evaporation of PbSe starts from 100°C, and the deposition temperature is set to 160°C to ensure the growth speed and the flatness of the film. The deposition rate is 0.2 Å/s and the total time of the deposition process is ~20 min.

The deposition parameters are identical for four substrates (glass slide, DSF, FF, and PVA film), and we have characterized the PbSe films deposited on the glass slide for convenience. Figure 1A shows the photograph of the as-prepared PbSe film with an evaporation area of ~7 cm². The scale of the film can be easily controlled by the size of the substrate. Figure 1B shows the surface topography of the PbSe film measured by a scanning electron microscope (SEM). The PbSe arrangement is relatively dense, and each particle has a size in the range of 30–60 nm. Figure 1C shows the atomic force microscope (AFM) image of the PbSe film, which gives the thickness of 25 nm and the flatness of 6 nm. Figure 1D shows transmission spectra of the glass slide before and after depositing the PbSe film measured by a spectrometer (Hitachi UV4100). The transmission coefficient decreases from the near-infrared to visible wavelength, which is consistent with the earlier report [49].

In our experiment, three types of SAs were prepared by depositing the PbSe on the DSF, FF, and PVA film, respectively. The first SA is based on the nonlinear interaction of the PbSe film with the evanescent field of light on a DSF, while the other SAs are based on the direct absorption of PbSe films with light. The fabrication processes are as follow. Firstly, the DSF is fabricated by side-polishing a section of single mode fiber (SMF) and the insertion loss of SMF is monitored using an optical power meter simultaneously. The D-shaped fiber without depositing PbSe is insensitive to the input polarization state of laser, similar with the previous report [50]. The insertion loss of the as-prepared DSF is 2.2 dB, and the evanescent field is strong enough for the application. The PVA film is prepared by a simple cast drying method [51], and the insertion loss is given as 0.2 dB. Secondly, the PbSe films are directly deposited on the DSF, FF, and PVA film using the same method and experimental parameters as those are on the glass slide. After depositing the PbSe film, the insertion losses of the DSF, FF, and PVA film reached 5.85 dB, 2.17 dB, and 4.21 dB, respectively.

We first investigated the polarization response of the DSF deposited with PbSe film. Figure 2A illustrates that the transmitted power varies periodically with the polarization

Figure 1: Surface morphology and transmission characterization of PbSe films.

(A) Photograph, (B) SEM image, and (C) AFM image of the PbSe films deposited on glass slide. (D) Linear transmission spectrum of the glass slide before and after depositing PbSe films.

angle, indicating that the DSF-PbSe can work as an in-line polarizer. The parallel and perpendicular modes relative to the PbSe plane correspond to the minimum and maximum transmitted powers, respectively. This phenomenon can be understood by noting that the light polarized parallel to the surface of PbSe film is absorbed, while the perpendicular polarized light is unaffected during the propagation. The polarization extinction ratio is calculated as 14 dB from the fitting curve. We repeated the measurement for several times and obtained the similar results, confirming the good repeatability of the experiment. Then, based on the typical balanced twin-detector scheme [52], we studied nonlinear optical responses of three SAs. The illumination pulses were delivered from a homemade mode-locked fiber laser with central wavelength of 1.56 μm , pulse duration of 568 fs, and repetition rate of 30 MHz. The power-dependent transmittance T can be fitted by $T = A \exp[-\Delta T / (1 + P/P_{\text{sat}})]$, where A is a normalization constant, ΔT is the modulation depth, P is the incident optical power, and P_{sat} is the saturation optical power [53]. As illustrated in Figure 2B–D, the DSF-PbSe, FF-PbSe, and PVA-PbSe exhibit typical saturable absorption characteristics, and modulation depths are given as 0.66%, 1.59%, and 1.25%, respectively. Actually, the modulation depth of DSF-PbSe SA varies with the input

polarization state, and Figure 2B shows a common case that the polarization state is not orthogonal or parallel to the surface of the DSF. However, saturable absorption property is not observed by replacing the mode-locked pulses with the continuous wave at the same wavelength. During the experiment, we have not observed the saturable absorption property from components without PbSe, confirming that the saturable absorption is purely caused by the PbSe films.

3 Mode-locked and Q-switched fiber lasers based on PbSe SAs

3.1 Configuration of the fiber laser

Fiber lasers possess inherent advantages such as excellent heat dissipation, high gain coefficient, as well as strong mode confinement, and provide a cost-effective research platform to study the evolution of optical solitons [54, 55] and the nonlinear absorption of nano-materials [56–59]. During the experiment, the DSF-PbSe SA, FF-PbSe SA, and PVA-PbSe SA are inserted into the laser cavity, respectively. Figure 3 demonstrates the configuration of

Figure 2: Polarization dependence and nonlinear optical response of PbSe SAs.

(A) Transmitted power of DSF-PbSe vs. the angle of the linearly polarized light. The Y-axis has been normalized by dividing by the maximum transmitted power. Nonlinear transmission of (B) DSF-PbSe SA, (C) FF-PbSe SA, and (D) PVA-PbSe SA.

Figure 3: Pulsed fiber laser based on PbSe SAs.

Laser diode: LD; wavelength division multiplexer: WDM; erbium-doped fiber: EDF; optical coupler: OC; single-mode fiber: SMF; polarization controller: PC; polarization-independent isolator: PI-ISO; DSF-PbSe: SA₁; FF-PbSe: SA₂; PVA-PbSe: SA₃.

the erbium-doped fiber (EDF) laser, which consists of a 980/1550 nm wavelength-division multiplexer, 3.5 m EDF (Nufen: EDFL-980-HP) with an absorption coefficient of 13.5 dB/m at 980 nm, 10.5 m SMF, a 30:70 fused-fiber optical coupler, a polarization controller, a polarization-independent optical isolator and a PbSe SA. A 980 nm

laser diode with the maximum power of 1500 mW works as the pump source for the fiber laser. The dispersion parameters D for SMF and EDF are 17 ps/(nm · km) and -18.5 ps/(nm · km) respectively, and the net cavity dispersion β_2 is estimated at -0.14 ps².

3.2 Mode-locked fiber lasers based on DSF-PbSe SA

A continuous wave is observed in the EDF laser at the pump of 10 mW using the DSF-PbSe SA. By enlarging the pump power and adjusting the PC, mode-locking operation is established in the EDF laser. Multiple pulses are achieved when the pump increases to 35 mW while single-pulse state disappears until the pump reduces to 10 mW. Figure 4 shows a typical single-pulse mode-locked state at the pump of 12.1 mW. As solitons experience periodical perturbations including amplification, output loss, and insertion loss in the resonator, they modulate themselves by shading a part of energy in the form of dispersive waves [60]. As demonstrated in Figure 4A, the pulse spectrum is centered at 1563.6 nm with a 3-dB bandwidth of 5.8 nm.

Figure 4: Performances of the DSF-PbSe mode-locked fiber laser.

(A) Spectrum. (B) Auto-correlation trace. (C) RF spectrum, inset: pulse trains. (D) Output power vs. pump power.

The unsymmetrical spectral sidebands arise from the non-uniform gain spectrum of the EDF. The auto-correlation trace of the mode-locked pulses is plotted in Figure 4B, which has the full width at the half maximum of 0.76 ps. By using the sech^2 fitting, the pulse duration is given as 0.49 ps, and the corresponding time bandwidth product is calculated to be 0.35, which indicates that the soliton is slightly chirped. Figure 4C shows the radio frequency spectrum recorded at a resolution of 9.1 Hz and a span of 800 Hz. The fundamental repetition rate of the pulses is 14.06 MHz, which matches with the pulse interval of 70.8 ns in the inset. The signal-to-noise ratio is 65 dB, suggesting the good stability of the mode-locked pulses. Moreover, the laser operation can be simply controlled by the PC, for example, the status can be switched between continuous-wave and mode-locked state, and the central wavelength can be adjusted from 1532 nm to 1563 nm, which can be attributed to polarization-sensitive absorption of the DSF-PbSe SA.

A notable advantage of the DSF-PbSe SA is the extra-high optical damage threshold. In the experiment, the mode-locked operation is maintained at the maximum available power from 12 to 1500 mW, as shown in Figure 4D. One can observe that the average output power nearly grows linearly with the incident pump power, and the highest output power reaches 50 mW. We deliberately replaced the DSF-PbSe SA with a clear DSF to confirm

whether the mode-locking operation results from PbSe films. In this situation, mode-locking cannot be obtained, although the pump power and PC are tuned for many times over a full range. The mode-locking operation can be obtained again by inserting the DSF-PbSe SA to the fiber laser. Therefore, we conclude that the DSF-PbSe SA exhibits polarization-sensitive saturable absorption characteristic and can serve as a high-power mode locker to realize passive mode-locking operation in EDF lasers.

3.3 Q-switched fiber lasers based on FF-PbSe and PVA-PbSe SAs

By replacing the DSF-PbSe SA with FF-PbSe and PVA-PbSe SAs, the mode-locking operation can be transformed into the Q-switched operation in the EDF laser. Figure 5A and B show the typical spectra and pulse trains of the Q-switched laser at the pump of 57.6 mW (34.1 mW) for FF-PbSe SA (PVA-PbSe SA). The spectrum is centered at 1561 nm (1564 nm) with a 3-dB spectral bandwidth of 1.72 nm (1.64 nm). The corresponding pulse interval is 36.1 μs (43.5 μs) and the pulse width is 2.24 μs (3.44 μs).

We further studied the evolution of the Q-switched pulses vs. the pump power for a fixed polarization state. For FF-PbSe SA, as illustrated in Figure 5C and D, the repetition rate increases from 8.6 to 45.4 kHz, while the

Figure 5: Performances of the FF-PbSe/PVA-PbSe Q-switched fiber laser.

(A) Optical spectrum and (B) pulse trains of the Q-switched fiber laser based on FF-PbSe and PVA-PbSe SAs. (C) Pulse width and repetition rate, (D) output power and single pulse energy vs. pump power for FF-PbSe SA. (E) Pulse width and repetition rate, (F) output power and single pulse energy vs. pump power for PVA-PbSe SA.

pulse duration reduces from 792 to 2.06 μs by increasing the pump power from 15 to 90 mW. The average output power grows nearly linearly with the pump power, and the maximum pulse energy is 63.7 nJ. For PVA-PbSe SA, the evolution processes are similar to those of the FF-PbSe SA, as illustrated in Figure 5E and F. The evolution behavior of the pulses can be understood as follows. When the pump power increases, the SAs saturate due to higher pulse intensity, and thus the repetition rate increases and the pulse duration becomes shorter in the Q-switched fiber lasers. The FF-PbSe and PVA-PbSe are destroyed when the pump powers reach 210 m and 113 mW, respectively. Compared with the Q-switched laser based on PVA-PbSe SA, the laser based on FF-PbSe SA has a wider spectral bandwidth, shorter pulse duration, and higher damage threshold.

4 Discussions

The properties of three PbSe SAs and output pulses are summarized in Table 1. Among the three SAs, the absorption of DSF-PbSe SA is sensitive to the polarization state, because the light polarized is parallel to the polished surface is absorbed while the other is unaffected during propagation [61]. The DSF-PbSe SA could initiate mode-locked operation in the fiber laser, which can be mainly attributed to nonlinear polarization rotation technique induced by polarization-sensitive response of the DSF-PbSe device. Attributing to the long interaction length and weak evanescent field, the laser-induced heating can be rapidly dispersed from the DSF. Therefore, the DSF-PbSe SA has the highest damage threshold.

Table 1: Summarizations of three PbSe SAs and corresponding laser performances.

Performances of SAs and pulses		DSF-PbSe	FF-PbSe	PVA-PbSe
Saturable absorption performance	Polarization sensitivity	Sensitive	Insensitive	Insensitive
	Modulation depth	0.66%	1.59%	1.25%
	Saturation power	2.29 mW	8.51 mW	5.71 mW
Laser performance	Operation	Mode-locked	Q-switched	Q-switched
	Center wavelength	1563.6 nm	1561 nm	1564 nm
	Pulse duration	0.49 ps	2.24 μ s	3.44 μ s
	Pulse interval	70.8 ns	36.1 μ s	43.5 μ s
	Pump power	12–1500 mW	15–90 mW	15–60 mW
Evolution properties	Output power	0.1–50 mW	0.22–2.79 mW	0.25–1.72 mW
	Repetition rate	14.06 MHz	8.6–45.4 kHz	16.3–59.2 kHz
	Pulse duration	0.49 ps	7.92–2.06 μ s	12–3.12 μ s
	Maximum pulse energy	12.5 pJ	63.7 nJ	43 nJ

The FF-PbSe and PVA-PbSe are polarization-insensitive SAs, because the PbSe grain is randomly distributed in the film. The PVA-PbSe SA can be prepared over a larger area and is more flexible for practical applications. However, the PVA film is more easily destroyed than fiber facet by the laser-induced heat accumulation, so the Q-switched pulses based on PVA-PbSe SA disappear at a lower pump power. Compared with the PVA-PbSe SA, the FF-PbSe SA has a larger modulation depth and higher damage threshold. Both the two SAs can only achieve Q-switched operation in the fiber laser, which may be attributed to the nanosecond response time of the PbSe [62].

5 Conclusions

We have prepared PbSe films with the thickness of 25 nm based on physical vapor deposition approach. The polarization-sensitive SA was fabricated by directly depositing the PbSe films on the DSF, while polarization-insensitive SAs were prepared by growing the PbSe films on FFs or PVA films. The modulation depths of DSF-PbSe, FF-PbSe, and PVA-PbSe at 1.55 μ m were given as 0.66%, 1.59%, and 1.25%, respectively. Based on DSF-PbSe SA, single pulse with the duration of 0.49 ps was obtained at the pump of 12 mW, and mode-locking operation was maintained at the pump of 1500 mW, indicating the high damage threshold of the SA. Two Q-switched fiber lasers were achieved by using FF-PbSe SA and PVA-PbSe SA, respectively. The PVA-PbSe SA can be prepared over a larger area and was more flexible for applications, while the FF-PbSe SA had better saturable absorption properties and lower insertion loss. Such PbSe SAs possess features of low cost and high stability, and can find important applications in infrared optical modulators and detectors.

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