Nonlinear optical properties of WSe$_2$ and MoSe$_2$ films and their applications in passively Q-switched erbium doped fiber lasers

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Transition metal dichalcogenides (TMDs) are successfully applied in fiber lasers for their photoelectric properties. However, in previous work, how to improve the modulation depth of TMD-based saturable absorbers (SAs) has been a challenging issue. In this paper, WSe$_2$ and MoSe$_2$ SAs are fabricated with the chemical vapor deposition method. Compared with previous experiments, the modulation depths of WSe$_2$ and MoSe$_2$ SAs with sandwiched structures are effectively increased to 31.25% and 25.69%, respectively. The all-fiber passively Q-switched erbium doped fiber lasers based on WSe$_2$ and MoSe$_2$ SAs are demonstrated. The signal-to-noise ratios of those lasers are measured to be 72 and 57 dB, respectively. Results indicate that the proposed WSe$_2$ and MoSe$_2$ SAs are efficient photonic devices to realize stable fiber lasers. © 2018 Chinese Laser Press

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1. INTRODUCTION

In recent years, compact and efficient pulsed lasers have been of great usefulness in applications in the fields of harmonic generation, laser ranging, lidar, and laser processing [1–6]. Generally, active and passive Q-switching techniques are two effective methods in Q-switched fiber lasers. Differently than the passive one, the actively Q-switched technique requires the addition of a modulator (acousto-optic modulator or electro-optic modulator) in the laser cavity [7–9]. Thus, passively Q-switched fiber lasers are preferred in applications for the characteristics of high anti-interference and easy integration [10–21].

A saturable absorber (SA) is the key component of a passively Q-switched fiber laser [22]. Because of relatively mature production techniques, semiconductor saturable absorber mirrors (SESAMs) have almost dominated commercial markets for SA-based pulsed lasers [23]. However, the complex manufacture and limited bandwidth of SESAMs hinder their further development [24,25]. Carbon nanotubes (CNTs), graphene, black phosphorus (BP), antimonene, and bismuthene are attracting much attention due to the merits of the large third nonlinearity, wide absorption wavelength, and ultrafast recovery time [26–29]. Those materials inspired fresh exploration and efforts in 2D materials. Transition metal dichalcogenides (TMDs), as a burgeoning type of 2D material, have aroused wide interest due to the optical property of being thickness dependent [30–32]. There is a transition of TMDs from an indirect bandgap to a direct bandgap when the material changes from the bulk to single layer, which makes it possible to engineer the bandgap of TMDs [33–42]. This novel feature brings about some excellent optical properties, such as high carrier mobility and outstanding nonlinear optical absorption [43,44]. Theoretically, the bandgap and saturable absorption bandwidth are inversely proportional. Compared with WS$_2$ and MoS$_2$, WSe$_2$ and MoSe$_2$ have similar chemical structures while possessing smaller bandgaps. The direct bandgaps of WS$_2$, MoS$_2$, WSe$_2$, and MoSe$_2$ are 2.1, 1.8, 1.65, and 1.57 eV, respectively. We believe that perhaps WSe$_2$ and MoSe$_2$ have more potential in broadband absorption.

In the process of mode-locking and Q-switching, SAs with high nonlinearity, ultrafast recovery time, and large modulation depth will bring better optical performance. Large modulation depth speeds up the process of pulse narrowing. Moreover, it is beneficial to the occurrence of self-starting [45]. As far as the current research situation is concerned, there are few effective measures focused on optimizing the modulation depth of...
TMDs. How to improve the modulation depth of SAs is still the challenging issue.

To improve the modulation depth of 2D materials, the surface-to-volume ratio is a significant aspect to break through. It has been reported that high uniformity will lead to high surface-to-volume ratio [46]. Moreover, the nonlinear optical absorption characteristics of 2D materials are related to the thicknesses of the materials. 2D materials with controllable thicknesses exhibit desired nonlinear absorption characteristics. In this paper, few-layer MoSe₂ and WSe₂ SAs with large modulation depth are prepared by the chemical vapor deposition (CVD) method. CVD, as a powerful candidate for the fabrication of layered TMDs, is able to produce films with high crystalline and uniform thickness. Furthermore, the film thickness is easy to control because it is proportional to the deposition time. A sample without polyvinyl acetate (PVA) or polymethyl methacrylate (PMMA) is transferred onto the end face of fiber connectors, and then is assembled into SAs. The surface of the SAs is characterized by atomic force microscopy (AFM) and transmission electron microscopy (TEM). We have successfully fabricated layered WSe₂ and MoSe₂ SAs with thicknesses of 1.5 and 3 nm, respectively. Because of the high quality and good transfer technology, the modulation depths of WSe₂ and MoSe₂ SAs are significantly increased to 31.25% and 25.69%. Stable Q-switched fiber lasers based on WSe₂ and MoSe₂ SAs have been implemented separately. Results indicate that WSe₂ and MoSe₂ SAs with large modulation depth have broad application prospects in fiber lasers.

2. EXPERIMENT

A. Preparation and Characterization of WSe₂ and MoSe₂ SAs

The CVD method, which can synthesize films with controllable thickness and high purity and quality, is promising in the preparation of various 2D materials. Before heating, the MoO₃/WO₃ (0.1 g) and Se (0.5 g) powders are placed in the reaction chamber individually. For MoSe₂, the temperature in the reaction zone is heated to 800°C at a constant rate of 15°C/min and held for 25 min. For WSe₂, the WO₃ powder is heated to 920°C at a constant rate of 25°C/min and held for 15 min. During heating, gasified MoO₃/WO₃ and Se vapors mix and react with the assistance of Ar/H₂ mixture gas [Ar of 65 sccm (sccm denotes cubic centimeters per minute at standard temperature and pressure), H₂ of 10 sccm for MoSe₂; Ar of 100 sccm and H₂ of 10 sccm for WSe₂]. When temperature falls to room temperature, the layered WSe₂ and MoSe₂ films are obtained. With the attachment of the PMMA, WSe₂ and MoSe₂ films are prone to detach from the substrate and transfer to the end face of fiber connectors. Acetone is finally used to melt and remove the residue of the PMMA.

AFM is commonly used to measure the thickness of films [47]. The different thicknesses of films with different colors are clearly observed in Figs. 1(a) and 1(d). The function curves of height and lateral distance are measured in Figs. 1(b) and 1(e). The thicknesses of WSe₂ and MoSe₂ films are about 1.5 and 3 nm, respectively. From previous work [48,49], the film thickness of 1.5 nm corresponds to 2 or 3 layers, and 3 nm corresponds to 4 or 5 layers. TEM is utilized to minutely investigate the surface microstructure and morphologies of films. As presented in Figs. 1(c) and 1(f), at the length of scale bar of 10 nm, WSe₂ and MoSe₂ particles are evenly distributed and neatly arranged.

From the absorption spectra in Fig. 2, the absorption efficiencies of WSe₂ and MoSe₂ SAs are 16.15% and 58.66% at the corresponding bandwidth. To verify whether the light passed the effective area of the films, we observed the distribution of materials with the aid of the microscope. The deep yellow region in Fig. 3(a) is the overlay area of the material, and the light yellow region is the area where the light passes in Fig. 3(b). We can see that the light passes through the center of the films,

![Image](image-url)
which indicates that MoSe₂ and WSe₂ films have been completely covered on the effective area of the end face of optical fiber ferrules.

The Raman spectrum of WSe₂ is displayed in Fig. 4(a), in which a pronounced spike at 247 cm⁻¹ and a weak peak at 260 cm⁻¹ can be observed. The peak at 247 cm⁻¹ corresponds to the A₁g Raman mode, and the weak peak at 260 cm⁻¹ is the second-order peak 2LA(M) because of the appearance of longitudinal acoustic phonons at the M-point in the Brillouin zone. Those results well correspond with previous Raman characteristics of WSe₂ [50].

For MoSe₂, the peaks at 241 and 286 cm⁻¹ in Fig. 4(b) correspond to the A₁g and E₁g Raman modes, respectively [51]. According to preceding characterization results, the WSe₂ and MoSe₂ films fabricated by the CVD method are of high purity and quality. To further explore the saturable absorption properties of WSe₂ and MoSe₂ SAs, the balanced twin detector measurement technology is applied. Detailed experimental procedures and schematic diagrams have been presented in previous work [40]. A fiber laser with pulse duration of 600 fs, central wavelength of 1541 nm, and repetition rate of 131 MHz is used as the light source. The data can be well fitted by

\[ \alpha(I) = \frac{\alpha_s}{1 + I/I_{sat}} + \alpha_n, \]  

where \( \alpha_s, \alpha_n, \) and \( I_{sat} \) are the saturable absorption, nonsaturable absorption, and saturation intensity, respectively. The saturation intensity, modulation depth, and corresponding nonsaturable loss of the WSe₂ SA are measured to be 0.734 MW/cm², 31.25%, and 54.77%, respectively. For MoSe₂, the corresponding saturation intensity, modulation depth, and nonsaturable loss parameters are 9.352 MW/cm², 25.69%, and 50.09%, respectively. Large modulation depths are obtained in Figs. 4(c) and 4(d), which show that the WSe₂ and MoSe₂ SAs have outstanding saturable absorption properties.

X-ray photoelectron spectroscopy (XPS) is an effective technology to determine the elemental composition of WSe₂ and MoSe₂ samples. As shown in Fig. 5(a), the double peaks located at 32.5 and 34.8 eV correspond to the 4f⁷/₂ and 4f⁵/₂ binding energies of W, respectively, which indicates the existence of W⁶⁺. The peaks at 35.5 and 37.7 eV indicate the presence of W⁴⁺, which may come from WO₃. Similarly, the binding energy of Se is shown in Fig. 5(b). Two peaks representing 3d⁵/₂ and 3d₃/₂ of Se are located at 54.9 and 55.9 eV, respectively. The component characterization of W⁶⁺ and Se indicates the successful synthesis of WSe₂ films on substrates. The presence of W⁴⁺ indicates there may exist a small amount of WO₃, which is probably due to the oxidation of the edge of the sample. For MoSe₂, the double peaks located at 229 and 232 eV correspond to the 3d⁵/₂ and 3d₃/₂ of Mo, respectively, in Fig. 5(c), which confirms the existence of Mo⁶⁺. There are no peaks that correspond to Mo⁴⁺ at 235 eV, which proves that there is no residue of MoO₃ in the sample. The peaks located at 54.5 and 55.6 eV in Fig. 5(d) are generally attributed to Se 3d₃/₂ and Se 3d₅/₂, respectively. The presence of Mo⁴⁺ and Se indicates the successful synthesis of MoSe₂ films. Moreover, the purity of the sample is high—there is no material residue or oxidation.

B. Experimental Process

The schematic diagram of our experimental installation is shown in Fig. 6. A ring cavity structure is adopted in the passively Q-switched pulse fiber lasers based on WSe₂ and MoSe₂ SAs. The ring cavity consists of the polarization independent isolator (PI-ISO), erbium doped fiber (EDF), polarization controller (PC), pump, optical coupler (OC), WSe₂/MoSe₂ SA, and wavelength division multiplexer (WDM). The 40 cm long EDF and other optical devices with 1.17 m long single-mode fiber (SMF) are included in the laser cavity. A pump source with center frequency of 976 nm and maximum output power of 680 mW is used in the experiment. The pump light is injected into the cavity through the WDM, 20% of which is extracted by the OC and used for the measurements of experimental results. The PC is able to change the polarization states of the transmitted light, and can be applied to adjust the birefringence in the cavity. The PI-ISO is used to ensure unidirectional transmission of light. The WSe₂ and MoSe₂.

Fig. 4. (a) Raman spectrum of the WSe₂ SA. (b) Raman spectrum of the MoSe₂ SA. (c) Non-linear saturable absorption of the WSe₂ SA. (d) Non-linear saturable absorption of the MoSe₂ SA.

Fig. 5. (a) and (b) are the XPS profiles of WSe₂. (c) and (d) are the XPS profiles of MoSe₂.
films fabricated by the CVD method are transferred onto the end faces of fiber connectors to assemble into WSe\textsubscript{2} and MoSe\textsubscript{2} SAs for Q-switched operation. The output pulse trains from the OC are measured by a 500 MHz oscilloscope, an optical spectrum analyzer, and a radio frequency spectrum analyzer.

3. RESULTS AND DISCUSSION

A. WSe\textsubscript{2} SA

By adjusting the PC to optimize the polarization states and properly controlling pump power, stable Q-switched output pulses are observed on the oscilloscope. The starting operation threshold of the Q-switched fiber laser is 110 mW. As we continue to increase pump power, stable Q-switched pulse trains at different power levels are obtained, as presented in Fig. 7(a).

From Fig. 7(b), we obtain a pulse envelope with a symmetrical Gauss shape at the maximum pump power of 680 mW, which indicates that the shortest pulse duration is 1.14 \mu s. As presented in Fig. 7(c), the optical spectrum of the fiber laser indicates that the central wavelength of the laser is 1562 nm.

The signal-to-noise ratio (SNR) is measured to be 72 dB at 300 Hz resolution bandwidth (RBW) in Fig. 7(d). The laser is stable over 12 h under laboratory conditions, with no significant degradation in performance.

Through modulating the pump power, the variation tendencies in relevant parameters of the Q-switched fiber laser are summarized in Fig. 8. In Fig. 8(a), the repetition rate of the fiber laser is increasing as the pump power is boosted, but the trend of the pulse duration is opposite to that of the pump power, which is consistent with the inherent characteristics of the Q-switched fiber laser. That is to say, the Q-switched fiber laser is able to achieve stable output pulses at different repetition rates. The adjustable range is 77 to 242 kHz. With the pump power boosting from 110 to 680 mW, the output power of the fiber laser simultaneously increases from 2.3 to 26.7 mW, as shown in Fig. 8(b), and the single pulse energy varies in the range of 30 to 110 nJ.

B. MoSe\textsubscript{2} SA

Similar to WSe\textsubscript{2}, a stable Q-switched fiber laser is established with the MoSe\textsubscript{2} SA. In Fig. 9(a), Q-switched pulse trains at different power levels are shown. The shortest pulse duration is 1.53 \mu s, as shown in Fig. 9(b). A typical Q-switched output spectrum with central wavelength of 1558 nm is presented in Fig. 9(c). From Fig. 9(d), the SNR of 57 dB indicates the high stability of the Q-switched fiber laser.
The repetition rates of the fiber laser can be tuned over a range of 64 to 122 kHz when the pump power increases from 160 to 680 mW, as shown in Fig. 10(a). When the pump power is at a lower level, the pulse duration changes more intensely. As the pump power continues to increase, the pulse duration trend is relatively flat, which indicates that the SA tends to be saturated. The single pulse energy and average output power at different power levels are exhibited in Fig. 10(b).

When the pump power increases to 680 mW, the maximum output power and single pulse energy are 17.2 mW and 140.6 nJ, respectively.

A comparison of the passively Q-switched fiber laser based on WSe$_2$ and MoSe$_2$ SAs among previous and current works is presented in Tables 1 and 2. It is found that the modulation depths of WSe$_2$ and MoSe$_2$ SAs in this paper are much larger compared to previous experimental materials. We attribute the success of better performance to the potentially promising CVD approach. The ability to manufacture thin films with high uniformity is a major superiority of the CVD approach.

High SNR of 72 dB/57 dB corresponding to our Q-switched fiber lasers indicates that the proposed WSe$_2$ and MoSe$_2$ SAs are efficient photonic devices to realize highly stable fiber lasers. Performance comparisons with MoS$_2$-based Q-switched pulse fiber lasers are also provided in Table 3. We find that the Q-switched fiber laser based on the WSe$_2$ and MoSe$_2$ SAs has a prominent performance in terms of high output power compared with previous Q-switched fiber lasers based on MoS$_2$ SAs. Results indicate that higher output power may be obtained.

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**Table 1. Performance Comparison of the Passively Q-Switched Fiber Laser Based on the WSe$_2$ SA**

<table>
<thead>
<tr>
<th>Materials</th>
<th>Preparation Method</th>
<th>Modulation Depth (%)</th>
<th>Repetition Rate (kHz)</th>
<th>Pulse Duration (μs)</th>
<th>SNR (dB)</th>
<th>Q-Switching Threshold (mW)</th>
<th>$P$ (mW)</th>
<th>Maximum Pulse Energy (nJ)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>WSe$_2$-PVA</td>
<td>LPE</td>
<td>3.5</td>
<td>4.5–49.6</td>
<td>3.1–7.9</td>
<td>46.7</td>
<td>140</td>
<td>1.23</td>
<td>33.2</td>
<td>[52]</td>
</tr>
<tr>
<td>WSe$_2$-PVA</td>
<td>LPE</td>
<td>4.31</td>
<td>92.5–138</td>
<td>0.75–1.48</td>
<td>50</td>
<td>170</td>
<td>3.54</td>
<td>29</td>
<td>[53]</td>
</tr>
<tr>
<td>WSe$_2$-PVA</td>
<td>LPE</td>
<td>3.02</td>
<td>46.3–85.4</td>
<td>4.0–9.2</td>
<td>41.9</td>
<td>280</td>
<td>3.16</td>
<td>484.8</td>
<td>[54]</td>
</tr>
<tr>
<td>WSe$_2$</td>
<td>CVD</td>
<td>31</td>
<td>77–242</td>
<td>1.2–4.3</td>
<td>72</td>
<td>118</td>
<td>26.7</td>
<td>110</td>
<td>This Work</td>
</tr>
</tbody>
</table>

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**Table 2. Performance Comparison of the Passively Q-Switched Fiber Laser Based on the MoSe$_2$ SA**

<table>
<thead>
<tr>
<th>Materials</th>
<th>Preparation Method</th>
<th>Modulation Depth (%)</th>
<th>Repetition Rate (kHz)</th>
<th>Pulse Duration (μs)</th>
<th>SNR (dB)</th>
<th>Q-Switching Threshold (mW)</th>
<th>$P$ (mW)</th>
<th>Maximum Pulse Energy (nJ)</th>
<th>Ref.</th>
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<tr>
<td>MoSe$_2$-PVA</td>
<td>LPE</td>
<td>6.73</td>
<td>60.724–66.847</td>
<td>4.04–6.506</td>
<td>31.3</td>
<td>570</td>
<td>2.45</td>
<td>369.5</td>
<td>[54]</td>
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<tr>
<td>MoSe$_2$-PVA</td>
<td>ME</td>
<td>4.7</td>
<td>26.5–35.4</td>
<td>4.8–7.9</td>
<td>—</td>
<td>18.9</td>
<td>—</td>
<td>825</td>
<td>[55]</td>
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<tr>
<td>MoSe$_2$-PVA</td>
<td>LPE</td>
<td>1.2</td>
<td>34.5–90</td>
<td>1</td>
<td>35.97</td>
<td>110</td>
<td>2</td>
<td>2.3</td>
<td>[56]</td>
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<tr>
<td>MoSe$_2$-PVA</td>
<td>LPE</td>
<td>0.63</td>
<td>9.9</td>
<td>13.6</td>
<td>—</td>
<td>10</td>
<td>—</td>
<td>—</td>
<td>[57]</td>
</tr>
<tr>
<td>MoSe$_2$</td>
<td>CVD</td>
<td>25.69</td>
<td>64–122</td>
<td>1.53–5.75</td>
<td>57</td>
<td>160</td>
<td>17.16</td>
<td>140.7</td>
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</table>

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**Table 3. Performance Comparison with MoS$_2$-Based Q-Switched Fiber Lasers**

<table>
<thead>
<tr>
<th>Materials</th>
<th>Preparation Method</th>
<th>Modulation Depth (%)</th>
<th>Repetition Rate (kHz)</th>
<th>Pulse Duration (μs)</th>
<th>SNR (dB)</th>
<th>Q-Switching Threshold (mW)</th>
<th>$P$ (mW)</th>
<th>Maximum Pulse Energy (nJ)</th>
<th>Ref.</th>
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<tr>
<td>MoS$_2$-PVA</td>
<td>LPE</td>
<td>2</td>
<td>8.77–43.47</td>
<td>3.3</td>
<td>50</td>
<td>18.9</td>
<td>5.91</td>
<td>160</td>
<td>[58]</td>
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<tr>
<td>MoS$_2$-PVA</td>
<td>LPE</td>
<td>2.15</td>
<td>7.758–41.452</td>
<td>9.92</td>
<td>48.5</td>
<td>50</td>
<td>0.77</td>
<td>184.7</td>
<td>[54]</td>
</tr>
<tr>
<td>MoS$_2$-PVA</td>
<td>LPE</td>
<td>1.6</td>
<td>6.5–27.0</td>
<td>5.4</td>
<td>54.6</td>
<td>17.4</td>
<td>1.7</td>
<td>63.2</td>
<td>[17]</td>
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<tr>
<td>MoS$_2$-PVA</td>
<td>LPE</td>
<td>4</td>
<td>72.74–86.39</td>
<td>3.53</td>
<td>51.6</td>
<td>258</td>
<td>6.47</td>
<td>74.93</td>
<td>[59]</td>
</tr>
<tr>
<td>MoS$_2$</td>
<td>CVD</td>
<td>33.2</td>
<td>10.6–173.1</td>
<td>1.66</td>
<td>42.5</td>
<td>20.4</td>
<td>4.71</td>
<td>27.2</td>
<td>[31]</td>
</tr>
<tr>
<td>MoS$_2$</td>
<td>CVD</td>
<td>28.5%</td>
<td>28.6–114.8</td>
<td>2.18</td>
<td>41.1</td>
<td>42</td>
<td>&lt;1</td>
<td>8.2</td>
<td>[32]</td>
</tr>
<tr>
<td>WSe$_2$</td>
<td>CVD</td>
<td>31%</td>
<td>77–242</td>
<td>1.2</td>
<td>72</td>
<td>118</td>
<td>26.7</td>
<td>110</td>
<td>This Work</td>
</tr>
<tr>
<td>MoSe$_2$</td>
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<td>1.53</td>
<td>57</td>
<td>160</td>
<td>17.16</td>
<td>140.7</td>
<td>This Work</td>
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</table>
if the cavity loss is further reduced, and the pump power increases.

4. CONCLUSIONS
In this paper, layered CVD-grown WSe2 and MoSe2 films without PVA or PMMA have been proved to have the modulation functions in Q-switched fiber lasers. The CVD method has been used to optimize the film uniformity and regulate the film thickness. Therefore, the crystallinity and uniformity as significant influencing factors of the modulation depth have been improved. The modulation depths of WSe2 and MoSe2 SAs with sandwiched structures have been effectively upgraded to 31.25% and 25.69%, respectively. The fabricated WSe2 and MoSe2 SAs have achieved stable pulse generation in passively Q-switched fiber lasers with SNRs of 72 and 57 dB, respectively, which are the highest among the same type fiber lasers. The superiorities in nonlinearity and uniformity of the fabricated SAs make WSe2 and MoSe2 promising materials for preparing photonic devices.

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