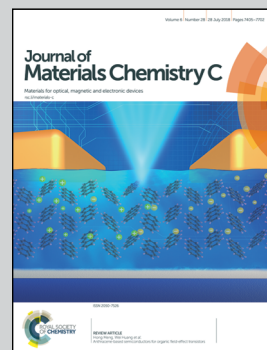


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Technique and model for modifying the saturable absorption (SA) properties of 2D nanofilms by considering interband exciton recombination

By considering interband exciton recombination, two-dimensional nanofilms saturable absorption properties under excitation by laser pulses with various durations in the fs, ps and ns ranges, are investigated theoretically and experimentally.

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# Technique and model for modifying the saturable absorption (SA) properties of 2D nanofilms by considering interband exciton recombination†

Guowen Liang,<sup>‡a</sup> Longhui Zeng,<sup>‡b</sup> Yuen Hong Tsang,<sup>\*b</sup> Lili Tao,<sup>b</sup> Chun Yin Tang,<sup>b</sup> Ping Kwong Cheng,<sup>b</sup> Hui Long,<sup>b</sup> Xin Liu,<sup>a</sup> Ji Li,<sup>a</sup> Junle Qu<sup>id a</sup> and Qiao Wen<sup>id \*a</sup>

In this study, we have successfully demonstrated a method of greatly modifying the nonlinear saturable absorption (SA) properties of WS<sub>2</sub> nanofilms by controlling their thickness and morphology via magnetron sputtering deposition times. The nonlinear SA properties of these nanofilms were also investigated systematically under excitation by laser pulses with various durations in the fs, ps and ns ranges, and prominent ultrafast SA parameters were demonstrated for different pulse durations in the fs, ps and ns ranges. A pulse width-dependent theoretical model of SA that considers the effects of interband exciton recombination has now been proposed for the first time. Two analytical expressions for calculating the variation of key SA parameters (the onset fluence  $F_{on}$  and the modulation depth  $\Delta T$ ) with the excitation laser pulse width have been derived and experimentally verified. The theoretical model and analytical expressions have great value for understanding and interpreting the variation of the SA behaviors of 2D nanofilms in the fs, ps and ns regions, and for the developments of ultrafast lasers and nanosecond lasers based on 2D materials. These studies open up exciting avenues for engineering the SA properties of 2D nanofilms for a wide range of laser photonic devices and applications.

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## 1 Introduction

Two-dimensional (2D) layered materials are currently attracting great research interest and attention from the optics, laser, photonics and optoelectronics research communities for their potential to bring revolutionary changes to these fields. 2D materials exhibit exceptional electrical and optical properties compared to their bulk forms due to the quantum confinement perpendicular to the 2D plane.<sup>1</sup> Soon after the discovery of graphene in 2004,<sup>2,3</sup> scientists demonstrated advanced electric and photonic applications such as photodetectors,<sup>4–8</sup> light-emitting diodes,<sup>9</sup> phototransistors,<sup>10,11</sup> solar cells,<sup>12</sup> optical waveguides,<sup>13</sup> and ultrafast lasers<sup>14</sup> by using graphene. However, the zero-bandgap nature and low layer optical absorption of graphene limits its application in the field of photonics and nonlinear optics. Therefore, the research focus has been extended

to other 2D materials<sup>15–18</sup> with natural bandgaps. In the past few years, the emergence of 2D transition metal dichalcogenides (TMDs), *e.g.*, MX<sub>2</sub> (M = Mo, W; X = S, Se), has attracted increasing attention because of their wide bandgap range from near-infrared to the visible region<sup>19</sup> and their unique and favorable electrical, optical, thermal and mechanical properties.<sup>20</sup> Layered TMDs are a new class of functional materials and have been used extensively in various applications such as nanoelectronics,<sup>21</sup> solar cells,<sup>22</sup> photodetectors,<sup>23</sup> nonlinear optics<sup>24–26</sup> photocatalysis<sup>27</sup> and energy storage.<sup>28</sup> Molybdenum disulfide (MoS<sub>2</sub>) is the most studied member of the TMD family for nonlinear optical applications,<sup>29–31</sup> and very recently, the novel tungsten disulfide (WS<sub>2</sub>) began to receive significant attention because of its tunable bandgap arising from indirect-to-direct bandgap transition with a decreasing number of layers, high carrier mobility and strong spin-orbit coupling due to its asymmetric structure and favorable photonic properties.<sup>32,33</sup> WS<sub>2</sub> exhibits strong nonlinear optical limiting properties and is tunable by adjustment of the size and thickness.<sup>24</sup> Therefore, the saturable absorption (SA) properties of these novel 2D materials are an important research topic, as the mainstream saturable absorbers used for Q-switching and mode locking, *e.g.*, doped crystals and SESAMs, still have some limitations such as narrow operation wavebands, limited response times, high cost, and complex fabrication processes.<sup>34,35</sup> A previous study confirmed that WS<sub>2</sub> exhibits strong SA properties and an

<sup>a</sup> Key Laboratory of Optoelectronic Devices and Systems of Ministry of Education and Guangdong Province, College of Optoelectronic Engineering, Shenzhen University, Shenzhen 518060, China. E-mail: wengqiao@szu.edu.cn

<sup>b</sup> Department of Applied Physics and Materials Research Center, The Hong Kong Polytechnic University, Kowloon, Hong Kong, China. E-mail: yuen.tsang@polyu.edu.hk

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‡ These authors contributed equally to this work. Both institutes contributed equally to this work.



ultrahigh optical damage threshold with a broad operational wavelength range from the visible range<sup>36–38</sup> up to the mid infrared range;<sup>39,40</sup> therefore, Q-switching<sup>32,34,36–38,40–45</sup> and mode locking<sup>32,35,39,46–48</sup> laser pulses can be generated by utilizing WS<sub>2</sub> as a saturable absorber in various laser systems. The fabrication of WS<sub>2</sub> film is relatively simple and low cost compared with that of the mainstream saturable absorbers used in commercial pulsed laser products.

Additionally, WS<sub>2</sub> and other new TMDs, can be widely used in other photonic device applications, *e.g.*, optical communications and optical computing.<sup>49</sup> The performance of such devices is largely dependent upon the nonlinear optical parameters of the 2D SA materials, and therefore, tuning and characterizing the parameters of 2D SA properties has become a highly important research topic for various nonlinear optical applications.<sup>50–53</sup> For the above reasons, this research aims to examine the SA properties of TMDs with different film thicknesses and structures for different pulse durations and lifetimes.

In this study, polycrystalline WS<sub>2</sub> film samples with various thicknesses were fabricated by the magnetron sputtering deposition method because of its high production speed and scalability compared with the CVD method. The WS<sub>2</sub> film thickness and structure depend on the sputtering time. The SA properties of the WS<sub>2</sub> films were then investigated under excitation by an 800 nm laser pulse with various pulse widths (100 fs, 10 ps, 200 ps, 10 ns) but the same pulse energy by using an open aperture (OA) Z-scan method. A theoretical model showing the relationship between the key SA parameters and the excitation pulse width, considering the effects of interband exciton recombination, was developed for the first time, and analytical expressions for the variation of these key SA parameters with the pulse width were deduced. The expressions were experimentally verified by Z-scan experiments. These analytical expressions provide a new way to estimate the SA parameters of any TMD film for various ultrafast pulse duration ranges. These studies will allow us to gain deeper understanding for engineering the nonlinear SA properties of the 2D materials and will significantly benefit the development of 2D materials for a wide range of nonlinear optical applications, including passive mode-lockers, passive Q-switchers, optical switches, ultrafast pulse shaping devices, and optical signal processing devices used in optical communication systems and optical computing.

## 2 Sample preparation and characteristics

The WS<sub>2</sub> samples used for this experiment were fabricated by the magnetron sputtering of WS<sub>2</sub> onto a clean quartz substrate for various periods of time (1 min, 3 min and 5 min) to control its film thickness followed by post-annealing. WS<sub>2</sub> precursor films were first produced through sputtering by using a sintered WS<sub>2</sub> disk as the target. The post annealing process was then conducted to enhance the crystallinity of the WS<sub>2</sub> film and replenish the S contents in the WS<sub>2</sub>. Fig. 1(a) displays photographs of post-annealed polycrystalline WS<sub>2</sub> film on a quartz substrate,

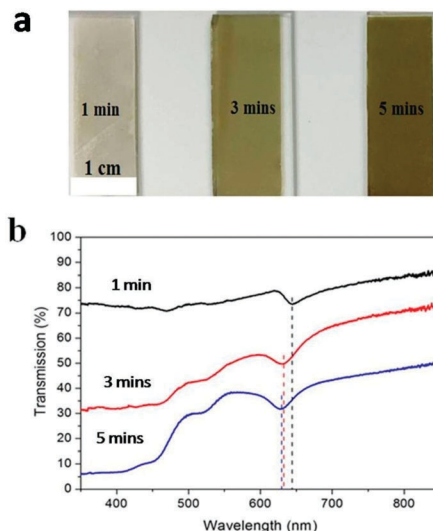


Fig. 1 (a) Photographs and (b) transmission spectra of WS<sub>2</sub> films fabricated with different magnetron sputtering times.

showing a characteristic change from dark gray to yellow and yellowish green. The transmittance spectra of WS<sub>2</sub> films with different thicknesses are presented in Fig. 1(b), which clearly shows absorption characteristic peaks located between 600 and 650 nm. The characteristic absorption peaks of WS<sub>2</sub> films fabricated with different sputtering times (1 min, 3 min, and 5 min) were located at 644.5 nm, 632 nm and 629 nm, respectively. The differences in peak position between samples indicate that polycrystalline WS<sub>2</sub> films with different thicknesses and morphologies can be fabricated by controlling the magnetron sputtering time. The transmittance spectra showed that the peak position of the WS<sub>2</sub> film shifts to shorter wavelengths as the sputtering time increases.<sup>54</sup>

The surface topography of the WS<sub>2</sub> films was investigated by atomic force microscopy (AFM) measurement as shown in Fig. 2(a–c), which revealed that all the WS<sub>2</sub> films were continuous. The corresponding section height profiles of the WS<sub>2</sub> samples were measured and are shown in Fig. 2(d–f). The measured film thicknesses were 8.85 nm, 15.7 nm, and 27.7 nm for the 1 min, 3 min and 5 min WS<sub>2</sub> films, respectively.

Raman spectroscopy is a powerful tool for the investigation of the crystal structures and layer numbers of the WS<sub>2</sub> films. Therefore, Raman mappings of all the WS<sub>2</sub> films samples were recorded and are shown in Fig. 3. As expected, the WS<sub>2</sub> samples show two strong signals due to the in-plane vibration E<sub>2g</sub><sup>1</sup> of the tungsten and sulfur atoms and the out-of-plane vibration A<sub>1g</sub> of the sulfur atoms. Both dominant Raman modes with wave numbers of approximately 350 cm<sup>−1</sup> and 420 cm<sup>−1</sup>, respectively, can be identified in Fig. 3, which is in good agreement with the results found in previous reports.<sup>55</sup> According to previous reports, the frequency difference between the E<sub>2g</sub><sup>1</sup> and A<sub>1g</sub> modes of TMDs, Δω, is dependent on the average layer number.<sup>56</sup> In general, Δω decreases as the average layer number decreases.<sup>57</sup> The measured Δω values of the 1 min, 3 min and 5 min WS<sub>2</sub> samples were 65.7 cm<sup>−1</sup>, 65 cm<sup>−1</sup> and 64.2 cm<sup>−1</sup> respectively. These results





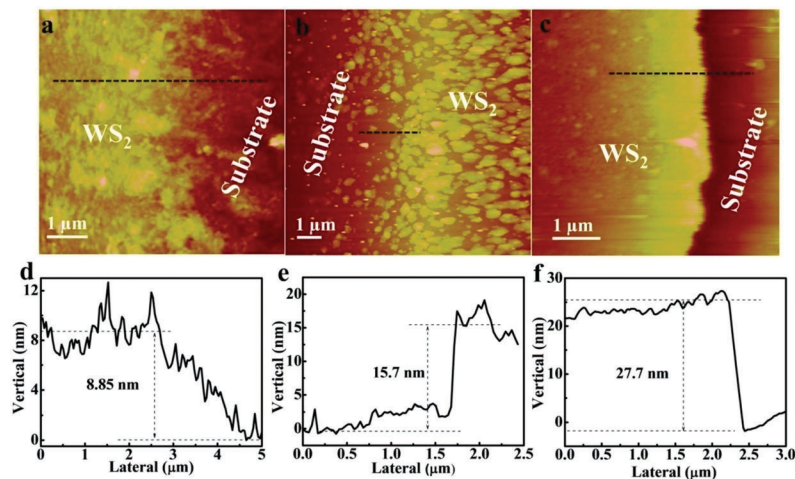


Fig. 2 (a–c) AFM images of WS<sub>2</sub> films; (d–f) height profiles of WS<sub>2</sub> films obtained with 1 min, 3 min and 5 min sputtering time, respectively.

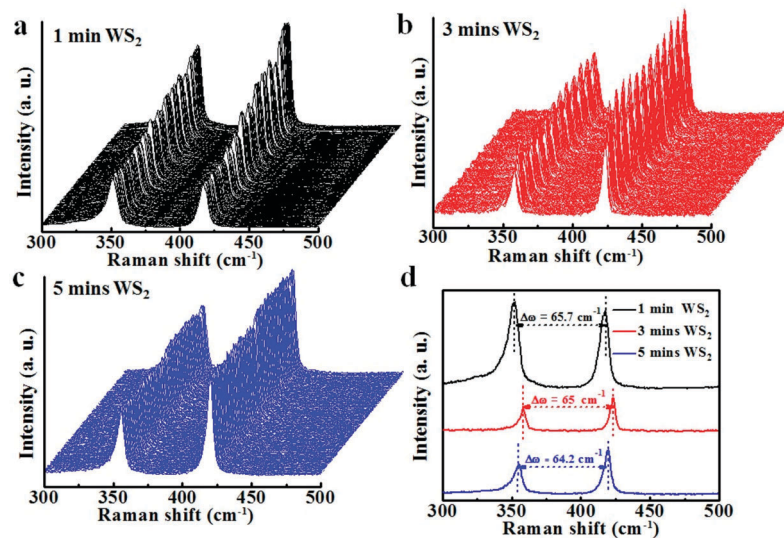


Fig. 3 Raman spectra of WS<sub>2</sub> films extracted from the Raman mapping data obtained in 10 × 10 μm<sup>2</sup> regions of (a) 1 min, (b) 3 min and (c) 5 min WS<sub>2</sub> films. (d) Typical Raman spectra of WS<sub>2</sub> films showing the average frequency difference, Δω.

confirm that the 1 min WS<sub>2</sub> film contained a higher number of layers than the 3 and 5 min films. In conclusion, the layer numbers of WS<sub>2</sub> films fabricated with sputtering times of 3 min and 5 min are similar and are lower than the layer number of 1 min WS<sub>2</sub> film.

Transmission electron microscopy (TEM) was employed to characterize the layer number, crystallinity and structure of the WS<sub>2</sub> samples, as shown in Fig. 4(a, d and g) TEM and Fig. 4(b, e and h) high-resolution transmission electron microscopy (HRTEM) images. The energy-dispersive X-ray spectroscopy (EDS) spectra of three samples are shown in Fig. 4(c, f and i). These results showed that the 1 min WS<sub>2</sub> film consisted of large-area polycrystalline WS<sub>2</sub> film, but countless WS<sub>2</sub> nanosheets were found within the 3 min and 5 min WS<sub>2</sub> films. The results also showed that the 1 min and 3 min WS<sub>2</sub> sheets were mainly horizontally grown, while the 5 min films contained many vertically grown sheets, as shown in Fig. 4(g and h). The change in growth direction from

horizontal to vertical is directly related to the amount of WS<sub>2</sub> deposited on the substrate – the thickness of the precursor WS<sub>2</sub> films. During post-annealing, sulfur vapor diffused into very thin amorphous WS<sub>2</sub> layers; the horizontal growth of large-area WS<sub>2</sub> was more energetically favorable than the growth of vertically aligned layers because WS<sub>2</sub> films with horizontal growth exposed low-surface-energy basal planes. However, when thick amorphous WS<sub>2</sub> films undergo post-annealing, horizontal volume expansion cannot be easily accommodated due to the precursor films anchored to the substrate. In this case, the horizontal growth of a large size and continuous film will produce a great deal of strain energy, and therefore, WS<sub>2</sub> films would grow vertically because of the unconstrained free volume expansion in the vertical direction.<sup>58,59</sup> Moreover, the HRTEM images in Fig. 3(b, e and h) show horizontally grown WS<sub>2</sub> sheets with 0.28 nm interplane spacing and vertically grown WS<sub>2</sub> sheets with layer spacing of 0.64 nm. The EDS spectra of the samples shown



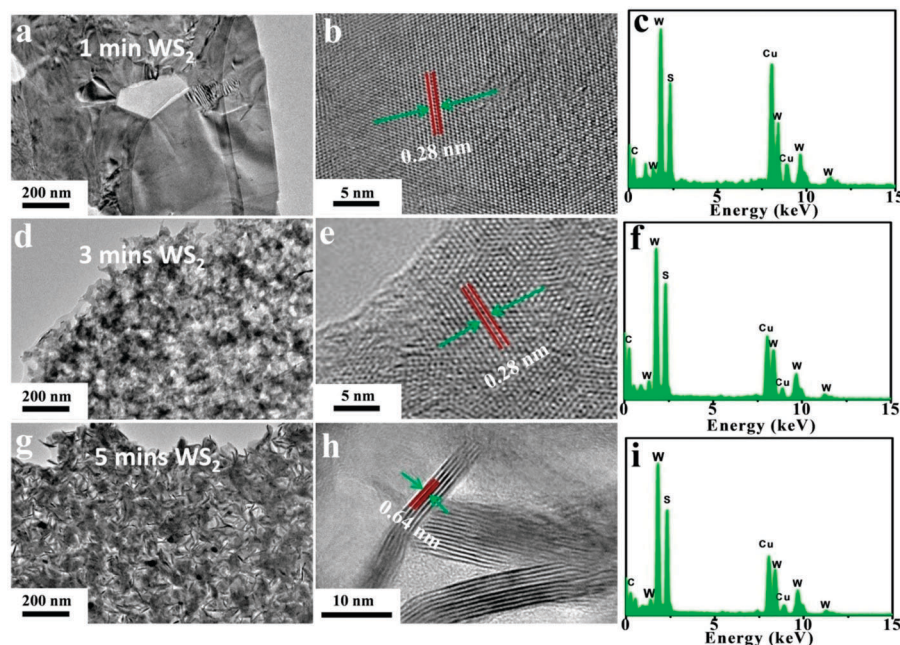


Fig. 4 Transmission electron microscopy (TEM) images of 1 min, 3 min and 5 min  $\text{WS}_2$  films on carbon-coated copper fiber (a, d and g). Top view high-resolution transmission electron microscopy (HRTEM) images (b, e and h) of the vertically grown  $\text{WS}_2$  nanosheets and the horizontally grown nanosheets. The lattice spacing was approximately 0.64 and 0.28 nm for vertically and horizontally grown  $\text{WS}_2$  nanosheets, respectively. Energy-dispersive X-ray spectroscopy (EDS) spectra (c, f and i) of  $\text{WS}_2$  films fabricated with different sputtering times (a–c, 1 min, d–f, 3 min, g–i, 5 min).

in Fig. 4(c, f and i) confirm that both the tungsten (W) and sulfur (S) from  $\text{WS}_2$  were present in all the prepared samples. The detected carbon (C) and copper (Cu) were from the carbon-coated copper substrate used for the TEM measurement.

Cross-sectional TEM images of the three samples were taken for further investigation of the internal structure of the  $\text{WS}_2$  films and are shown in Fig. 5. The cross-sectional TEM images of  $\text{WS}_2$  films with different thicknesses are shown in Fig. 5(a–c). The  $\text{WS}_2$  films deposited with 1 min, 3 min and 5 min sputtering times had uniform thicknesses of approximately 11, 15, and 30 nm, and the numbers of layers estimated from the above cross-sectional TEM images were approximately 18–20, 15–17 and 8–10, respectively. When the sputtering time was increased from 1 min to 3 min, vertically grown nanosheets began to appear. In the sample fabricated with a 5 min deposition time, a large number of vertically grown nanosheets were clearly produced.

To investigate the exciton dynamics of the few-layer  $\text{WS}_2$  films, the exciton radiative lifetime of a  $\text{WS}_2$  film was measured by using an 800 nm (100 fs) excitation laser source. Fig. 6 presents the decay curve for the 5 min  $\text{WS}_2$  film on a linear scale and a logarithmic scale. The decay curve clearly exhibits multi-exponential decay and can be well fitted using the triple exponential decay function  $A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2} + A_3 e^{-t/\tau_3}$ , where  $\tau_1 < \tau_2 < \tau_3$ ;  $\tau_i$  denotes the exponential decay lifetime of each component in the  $\text{WS}_2$  nanofilms; each pre-exponential factor  $A_i$  is the corresponding weight of the  $i$ 'th component; and the subscript  $i$  is equal to 1, 2 or 3. The fitting decay time constants are  $\tau_1 = 512$  ps (67.5% of weight),  $\tau_2 = 1311$  ps (26.2% of weight)

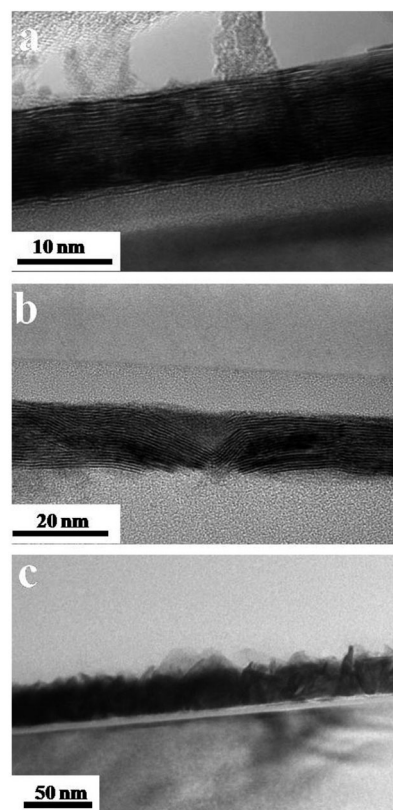


Fig. 5 Cross-sectional HRTEM images of the  $\text{WS}_2$  films. (a) 1 min, (b) 3 min and (c) 5 min.



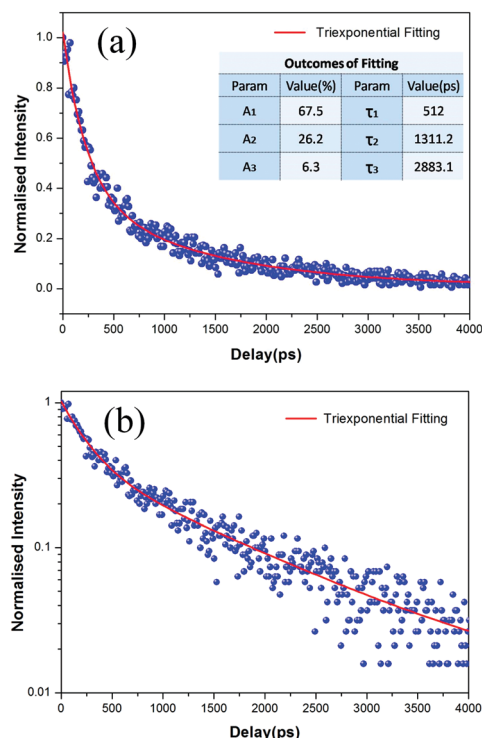


Fig. 6 Exciton dynamics for 5 min  $\text{WS}_2$  film with a pump wavelength of 800 nm on a linear scale (a) and a logarithmic scale (b), revealing multi-exponential decay. The solid line is fitted using a triexponential decay function, and the outcomes of the fitting are presented in the inset table.

and  $\tau_3 = 2883$  ps (6.3% of weight). Thus, the corresponding mean decay time ( $\tau_m$ ) of the  $\text{WS}_2$  film is 870.71 ps. This result is essentially consistent with the decay time of  $\text{WS}_2$  nanosheets ( $\sim 1$  ns) presented in previous research works.<sup>60,61</sup>

### 3 Experimental results

Two sets of Z-scan experimental data are presented to examine the relationship between the nonlinear optical (NLO) properties of  $\text{WS}_2$  samples fabricated with different sputtering times (1 min, 3 min and 5 min) under condition (A), a constant pulse width (100 fs) but varying pump pulse energies (1  $\mu\text{J}$ , 1.5  $\mu\text{J}$  and 2  $\mu\text{J}$ ), and condition (B), a constant pump pulse energy (2  $\mu\text{J}$ ) but varying pulse durations (100 fs, 200 ps, 10 ps and 10 ns). The Ti-sapphire excitation laser source was operated at 800 nm for all the experiments. A schematic diagram of the experimental setup of the open aperture Z-scan is shown in the ESI:† Fig. S1. The Z-scan experimental data marked with squares, circles, triangles and rhombuses are shown in Fig. 7 and 8, and all the related theoretical fittings shown by solid lines were calculated by eqn (2).

#### 3.1 Condition (A) a constant pulse width (100 fs) but various pump pulse energies (1 $\mu\text{J}$ , 1.5 $\mu\text{J}$ and 2 $\mu\text{J}$ )

Only SA was observed for all samples under excitation by a 100 fs pulse with various pulse energies, as shown in Fig. 7. The NLO effect grew stronger as the pulse energy increased.

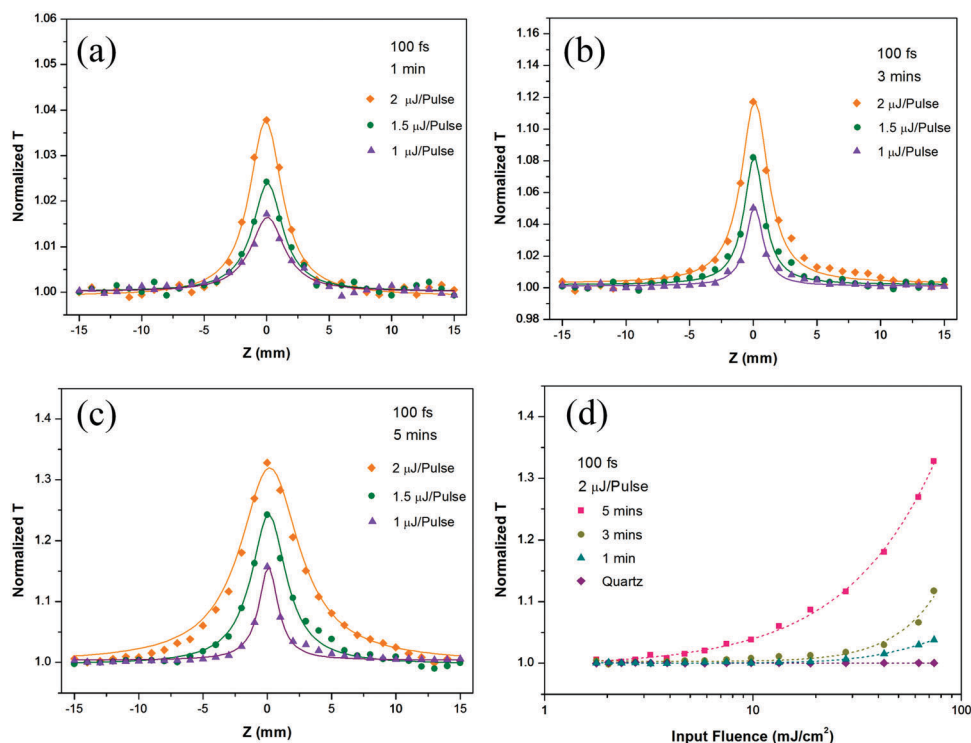


Fig. 7 Open aperture Z-scan results for few-layer  $\text{WS}_2$  films fabricated with different magnetron sputtering times (a, 1 min; b, 3 min; c, 5 min) at a 100 fs (800 nm) laser pulse with different energies. (d) Normalized transmittance versus input fluence for 1 min, 3 min, and 5 min  $\text{WS}_2$  films and the pure quartz substrate under 2  $\mu\text{J}$  laser pulse excitation.





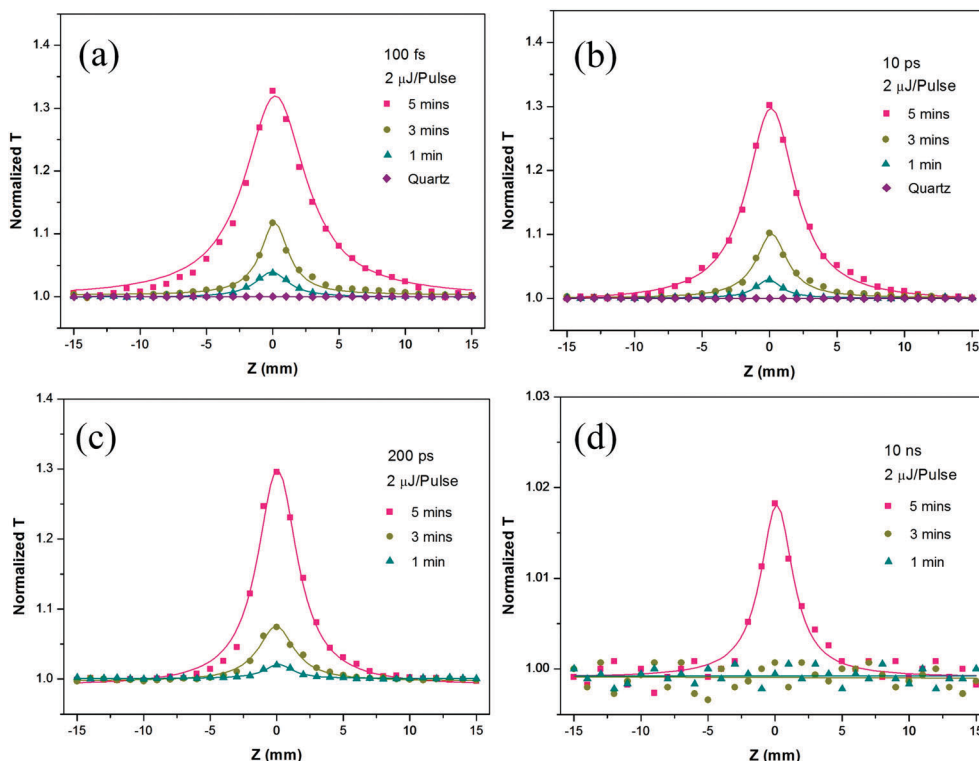


Fig. 8 Z-scan results of 1 min, 3 min and 5 min  $\text{WS}_2$  films for (a) 100 fs, (b) 10 ps, (c) 200 ps and (d) 10 ns laser pulses at 800 nm. The response for the pure substrate is also included.

The measured normalized transmission increased to its maximum as the sample position approached the focus. The  $Z$  position shown in Fig. 7(a)–(c) can be translated into input fluence, which can be calculated by dividing the input pulse energy by the measured beam spot area at different  $Z$  positions. An example is given in Fig. 7(d), which shows the normalized transmission with respect to different input fluences under excitation by a  $2\ \mu\text{J}$  100 fs pulse. No NLO effect was observed from the quartz substrate alone. Therefore, the NLO properties were derived from the deposited  $\text{WS}_2$  materials. These results indicate that the 5 min sample with the larger pulse energy ( $2\ \mu\text{J}$ ) exhibited the strongest SA properties among the various samples and excitation pulse energies. The observed results are reasonable, as the SA effect depends on the amount of nonlinear materials and the pulse energy. To ensure the NLO properties were not the results of nonlinear optical damage, the sample was examined under a microscope after each experiment. No laser damage was observed for all samples under excitation by a pulse energy of  $2\ \mu\text{J}$ .

### 3.2 Condition (B) the same pump pulse energy ( $2\ \mu\text{J}$ ) but various pulse duration (100 fs, 200 ps, 10 ps and 10 ns)

This section presents the experimental data for various  $\text{WS}_2$  film samples under excitation by the same pulse energy  $2\ \mu\text{J}$  with different pulse widths. This information will give us a deeper understanding of the NLO properties of these materials changes with respect to pulse width modulation.

As shown in Fig. 7 and 8, all the samples exhibited a prominent ultrafast SA response or no NLO response. The SA behaviors observed for the three  $\text{WS}_2$  films implied that their band gap energies were all smaller than 1.55 eV (the one-photon energy of the 800 nm exciting laser). The band gap of the few-layer  $\text{WS}_2$  films was approximately 1.3 eV based on the previous reports.<sup>33,62,63</sup> Therefore, the NLO effects of the three  $\text{WS}_2$  nanofilms can be attributed to the strong single photon absorption and Pauli blocking in semiconductor materials.<sup>64</sup>

## 4 Nonlinear absorption model and discussion

The following nonlinear absorption model was widely used to fit all the Z-scan data and to quantitatively analyze the corresponding NLO coefficients:<sup>65,66</sup>

$$\alpha(I) = \alpha_0 - \alpha_{\text{NL}}I \quad (1)$$

where  $\alpha(I) = -dI/(I \cdot dz')$  is the total absorption coefficient, including the linear absorption term  $\alpha_0$  and the nonlinear absorption coefficient  $\alpha_{\text{NL}}$ ;  $I = I(z')$  is the intensity distribution within the sample; and  $z'$  is the propagation length within the sample. We can solve eqn (1) exactly and obtain the normalized power transmission as follows:

$$T(z) = \frac{\ln[1 + q_0(z)]}{q_0(z)} \quad (2)$$



**Table 1** Optical parameters of linear transmittance ( $T_L$ ), linear absorption coefficient ( $\alpha_0$ ), nonlinear absorption coefficient ( $\alpha_{NL}$ ), saturation irradiance ( $I_s$ ), NLO onset fluence ( $F_{on}$ ), and NLO modulation depth ( $\Delta T$ ) for few-layer WS<sub>2</sub> films. The calculation details of the different parameters are given in the ESI

Sample	800 nm laser	$T_L$ (%)	$\alpha_0$ (cm <sup>-1</sup> )	$\alpha_{NL}$ (cm GW <sup>-1</sup> )	$I_s$ (GW cm <sup>-2</sup> )	$F_{on}$ (mJ cm <sup>-2</sup> )	$\Delta T$ (%)
1 min WS <sub>2</sub>	100 fs	94.84	$6.97 \times 10^4$	$97.55 \pm 8.83$	$306.16 \pm 25.41$	18.86	3.8
	10 ps			$(9.63 \pm 0.18) \times 10^3$	$3.1 \pm 0.06$	27.9	2.9
	200 ps			$(1.66 \pm 0.33) \times 10^5$	$0.18 \pm 0.03$	42.5	1.9
3 min WS <sub>2</sub>	100 fs	79.25	$1.58 \times 10^5$	$162.96 \pm 15.70$	$455.07 \pm 39.99$	7.47	11.7
	10 ps			$(1.67 \pm 0.02) \times 10^4$	$4.45 \pm 0.05$	9.8	10.2
	200 ps			$(2.77 \pm 0.40) \times 10^5$	$0.27 \pm 0.03$	13.32	7.4
5 min WS <sub>2</sub>	100 fs	60.97	$1.91 \times 10^5$	$314.67 \pm 5.43$	$282.63 \pm 4.8$	2.73	32.1
	10 ps			$(2.87 \pm 0.01) \times 10^4$	$3.09 \pm 0.01$	3.87	30.2
	200 ps			$(5.71 \pm 0.40) \times 10^5$	$0.16 \pm 0.01$	5.86	28.5
	10 ns			$(2.20 \pm 0.42) \times 10^6$	$0.04 \pm 0.006$	42.5	1.8

where  $q_0(z) = \alpha_{NL} I_0 L_{eff} / (1 + z^2/z_0^2)$ ,  $L_{eff} = (1 - e^{-\alpha_0 L})/\alpha_0$ ;  $I_0$  is the on-axis intensity at the focus of the beam (*i.e.*,  $z = 0$ ); and  $z_0$  is the beam diffraction length. The linear transmittance ( $T_L$ ) and absorption coefficient ( $\alpha_0$ ) of the WS<sub>2</sub> films were measured and are given in Table 1. The reflectance of the quartz substrate of the sample has been taken into account in the measurement. Then, eqn (2) was used to generate the solid fitting lines for the Z-scan experimental data shown in Fig. 7 and 8. The fitting lines agree well with the measured Z-scan experimental data. The measurement precision was improved by averaging ten measurements. For the 100 fs laser pulses, the corresponding fitted  $\alpha_{NL}$  values used for the 1 min, 3 min and 5 min WS<sub>2</sub> films were approximately 97.55 cm GW<sup>-1</sup>, 162.96 cm GW<sup>-1</sup> and 314.67 cm GW<sup>-1</sup>, respectively, as given in Table 1. The increasing values of  $\alpha_{NL}$  indicate that the NLO absorption increases continuously for samples with longer sputtering times. The saturation intensity  $I_s$  is also widely adopted to evaluate the performance of SA materials and is critical for evaluating the pulse-shortening effect in the pulse generation.  $I_s$  is generally defined by  $\alpha(I) = \alpha_0 / (1 + I/I_s)$ , which means that the absorption coefficient  $\alpha(I)$  will be reduced to half of its original value  $\alpha_0$  for the incident intensity  $I = I_s$ . By setting  $\alpha(I) = \alpha_0/2$  in eqn (1), we obtain  $I_s = \alpha_0/(2\alpha_{NL})$ , and then the values of  $I_s$  for the WS<sub>2</sub> films with 100 fs pulses can be calculated and are shown in Table 1. In contrast to the other SA nanomaterials presented in previous works with 800 nm (100 fs) pulses, *e.g.*, TMD dispersions or films,<sup>67,68</sup> graphene oxide (GO) films<sup>69</sup> and graphene,<sup>29,70,71</sup> the 5 min WS<sub>2</sub> film exhibited relatively low  $I_s$  values of 282.63 GW cm<sup>-2</sup>.

Table 1 shows that the linear transmittance,  $T_L$ , decreases and the linear absorption coefficient,  $\alpha_0$ , increases with the sputtering time as more WS<sub>2</sub> is deposited on the substrate. The value of  $\alpha_{NL}$  also increases with sputtering time. This result implies that the nonlinear absorption will increase with increasing deposition time. For instance,  $\alpha_{NL}$  of the 5 min film is approximately three times higher than that of the 1 min film for 100 fs, 10 ps and 200 ps pulses. However,  $I_s$  of all the three WS<sub>2</sub> films did not change greatly with respect to sputtering time but decreased rapidly for increasing pulse duration, *e.g.*,  $I_s$  of the 5 min sample decreased from 282.63 GW cm<sup>-2</sup> for 100 fs to 0.16 GW cm<sup>-2</sup> for 200 ps, which, to the best of our knowledge, is the lowest  $I_s$  among TMDs in the ps region.<sup>29,66,68</sup>

The onset fluence ( $F_{on}$ ) denotes the NLO onset threshold, defined as the input fluence point at which the normalized transmittance of SA materials begins to increase. The modulation depth ( $\Delta T$ ) is the maximum possible change in transmittance induced by incident laser pulses.  $F_{on}$  and  $\Delta T$  are two important SA parameters which are widely used to evaluate the practical performance of saturable absorbers. In general, for a saturable absorber used in passive mode-locking or Q-switching lasers, a lower  $F_{on}$  means lower laser threshold for the onset of pulse operation and a larger  $\Delta T$  leads to shorter pulse generation and more reliable self-starting of mode-locking.<sup>50–53</sup> For easy comparison, the onset fluence  $F_{on}$  and modulation depth  $\Delta T$  are plotted against the sputtering times of samples for different pulse width at the same excitation energy of 2  $\mu$ J in Fig. 9(a and b) respectively. As shown in Fig. 9 and Table 1, generally, as the magnetron sputtering time increased from 1 min to 5 min, the onset fluence  $F_{on}$  of the SA response dropped, and the modulation depth  $\Delta T$  of SA increased. This indicates that  $F_{on}$  decreases and  $\Delta T$  increases with increasing film thickness, decreasing numbers of layers, and increasing amount of vertically grown WS<sub>2</sub> nanosheet. For various pulse duration, the key SA parameters, modulation depth  $\Delta T$  and onset fluence  $F_{on}$ , have been demonstrated to be greatly modifiable by controlling the film thickness and structure *via* adjusting the magnetron sputtering time during the fabrication process.

In this section, the modulation of  $F_{on}$  and  $\Delta T$  by changing the sputtering time at various pulse widths will be discussed. Generally, the modulation of  $F_{on}$  and  $\Delta T$  is quite large: (1)  $F_{on}$  was reduced by  $\sim 86\%$  for all three pulse durations (100 fs, 10 ps and 200 ps). (2) The value of  $\Delta T$  was also greatly enhanced by 840%, 1040% and 1500% for 100 fs, 10 ps and 200 ps pulses. These enhancements were achieved by increasing the sputtering time from 1 min to 5 min. Therefore, we can conclude that the values of  $F_{on}$  and  $\Delta T$  can be modified greatly by changing the sputtering time. Compared with other WS<sub>2</sub> films used in previous studies under the same excitation wavelength and duration of 800 nm and 100 fs, respectively, the WS<sub>2</sub> films used in this work exhibited larger modulation depth  $\Delta T$ . With a similar value of  $T_L \approx 95\%$ , the  $\Delta T$  value obtained for the 1 min sample was 3.8%, which was approximately 50% larger than the previous record.<sup>67</sup>





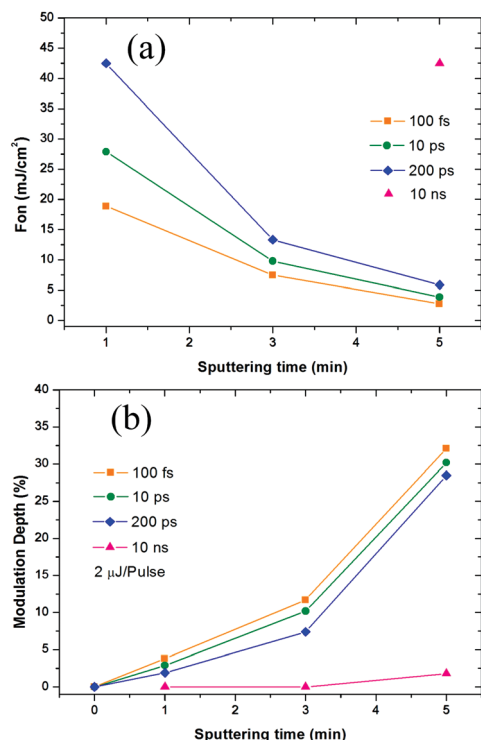


Fig. 9 Onset fluence  $F_{on}$  (a) and modulation depth  $\Delta T$  (b) of WS<sub>2</sub> films fabricated with different sputtering times for 100 fs, 10 ps, 200 ps and 10 ns laser pulses (800 nm, 2  $\mu$ J).

Additionally, Fig. 9 and Table 1 reveal that the changes in  $F_{on}$  and  $\Delta T$  with respect to the changing pulse width can also be quantified.  $F_{on}$  approximately doubled ( $\sim 100\%$ ) for all three samples as the pulse duration was changed from 100 fs to 200 ps (1000 times). The value of  $\Delta T$  decreased by 50% for the 1 min, 36.7% for the 3 min and 11.2% for the 5 min sample as the pulse width increased from 100 fs to 200 ps. The reduction in  $\Delta T$  was smaller for WS<sub>2</sub> samples with longer sputtering times. Fig. 8(d) and 9 show weak SA for the 5 min sample under the excitation of a 10 ns pulse and no SA for the other two samples. For this reason, only a single data point for the 10 ns pulse is shown in Fig. 9(a and b). Overall, the WS<sub>2</sub> films prepared for this work possess prominent ultrafast SA parameters in both the fs and ps regions and can fully satisfy various ultrafast SA device applications, including passive mode-locks, passive Q-switchers, optical switches, etc. These results confirm that the 5 min sample offers the strongest NLO properties, and therefore, Fig. 10(a–c) were plotted for the detailed comparison of various pulse widths.

Fig. 10 summarizes the SA responses of the 5 min sample. The SA of the sample decayed slowly when the pulse width increased from fs to ps but was sharply weakened by the ns pulse excitation, as shown in Fig. 10(a)–(c). The corresponding pulse width dependences of the SA modulation depth  $\Delta T$  and the onset fluence  $F_{on}$  are shown in Fig. 10(c). Fig. 10(c) shows that  $\Delta T$  decreased and  $F_{on}$  increased slowly when the pulse width was increased from 100 fs to 200 ps. However, the changes accelerated as the pulse width increased further from 200 ps to 10 ns.  $F_{on}$  increased dramatically from 5.86 mJ cm<sup>−2</sup>

to 42.5 mJ cm<sup>−2</sup> (725%) as the pulse duration changed from 200 ps to 10 ns. A dramatic reduction from 28.5% to 1.8% (1583%) in  $\Delta T$  of the 5 min WS<sub>2</sub> sample occurred as the pulse duration changed from 200 ps to 10 ns. Notably, as the duration of the laser pulses increased from 100 fs to 200 ps, the peak power of the laser pulses decreased by 2000 times, but the values of  $\Delta T$  and  $F_{on}$  showed no obvious changes. As far as we know, no interpretation or theoretical analysis of this phenomenon exists. The mechanism by which the SA parameters of such TMDs varied with the pulse width thus far remains unclear.

In this section, a pulse width-dependent SA theoretical model that considers the effects of the interband exciton recombination is first proposed to understand and analyze the mechanism by which the SA properties of WS<sub>2</sub> vary with the excitation pulse width. Then, two analytical expressions for the key SA parameters ( $F_{on}$  and  $\Delta T$ ) in term of pulse width are deduced by using the energy band theory and exciton dynamics of the WS<sub>2</sub> nanofilms. As shown in Fig. 10(d), a large number of free carriers are excited from the valence band to level C of the conduction band. These photoexcited electrons consequently decay to lower energy levels by intraband relaxation ( $< 500$  fs).<sup>60,72</sup> When the input fluence is greater than or equal to the SA onset fluence  $F_{on}$ , the states below the energy level C in the conduction band are fully filled. Then, further absorption is blocked (*i.e.*, Pauli-blocking), and saturated absorption occurs.<sup>73</sup> Interband charge recombination has usually been ignored in previous research works.<sup>29,67,68</sup> In fact, the excitons at the bottom of the conduction band relax by interband recombination at the speed  $1/\tau$ , where  $\tau$  is the exciton radiative decay lifetime of the material. However, within the pump pulse duration, the decayed electrons reabsorb another photon and jump back into the conduction band to refill the unfilled states. This process is dynamic. The ratio between pulse duration,  $t$ , and the exciton radiative decay lifetime plays a critical role in SA properties. The exciton radiative decay is generally believed to be negligible if it is much longer than the pump pulse duration. However, as mentioned previously, decay will always occur even within the exciton decay lifetime. Based on our experimental data shown in Table 1, even within the decay lifetime ( $\sim 0.87$  ns), a longer excitation pump pulse (200 ps) will still exhibit a higher  $F_{on}$  than that of 100 fs, although by only 2 times. However, if the pulse width is much longer than the decay lifetime,  $F_{on}$  is expected to become much higher as the exciton decay becomes more significant. Thus, if the sample is pumped within its lifetime, energy can be efficiently absorbed for the SA effect. The duration of the 10 ns pulse is much longer than the WS<sub>2</sub> decay lifetime, which implies that the decay of excited electrons becomes significant and that, therefore, more pumping energy is needed to saturate the sample. Accordingly, the following new theoretical model based on the ratio of  $t$  and  $\tau$  was developed to account for interband recombination.

During this process, the maximum excited state population,  $N_{on}$ , was kept constant, and then the total number of the recombination excitons,  $\Delta N$ , could be calculated by

$$\Delta N = N_{on} \cdot \frac{t}{\tau} \quad (3)$$



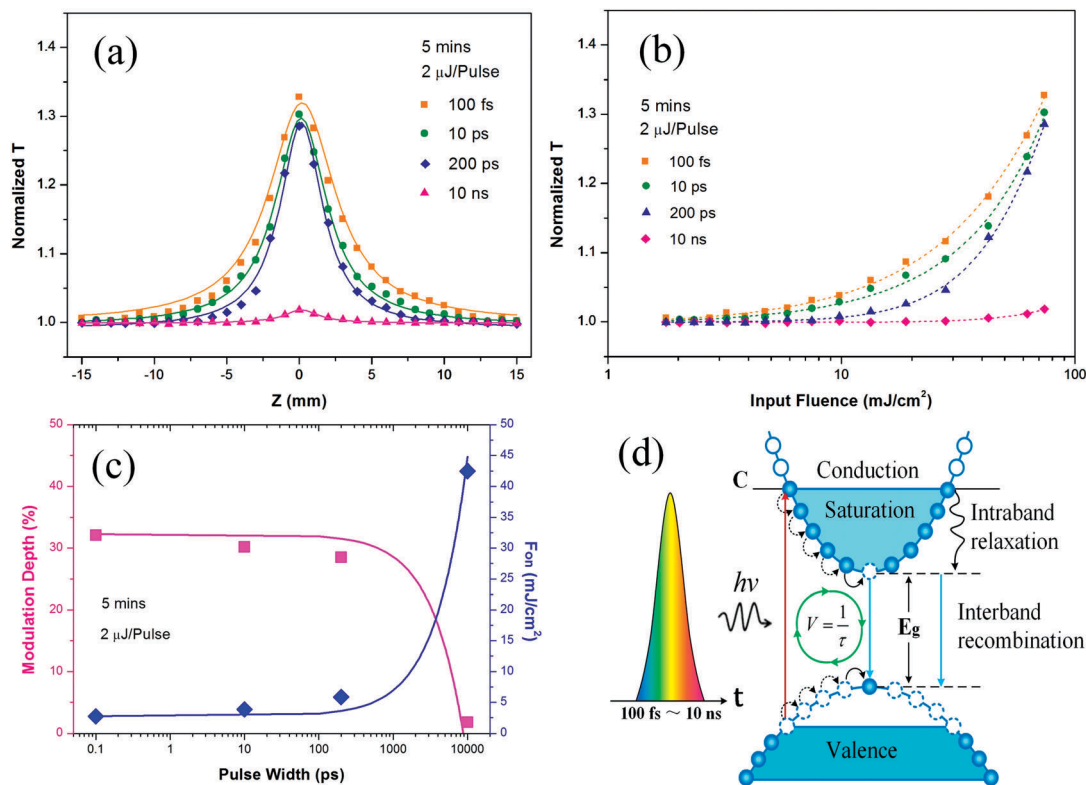


Fig. 10 Comparison of SA responses (normalized transmittance versus  $Z$  position (a) and input fluence (b)) of the 5 min WS<sub>2</sub> film for 100 fs, 10 ps, 200 ps and 10 ns laser pulses with 2 μJ energy. (c) Corresponding SA modulation depth  $\Delta T$  and onset fluence  $F_{\text{on}}$  as a function of excitation pulse width. The solid curves were plotted to show the conclusions of our theoretical model. Square – modulation depth; diamond –  $F_{\text{on}}$ . (d) Schematic of SA and relaxation processes in WS<sub>2</sub> film excited by ultrashort laser pulses.

For the exciton dynamics described above,  $1/\tau$  is the interband recombination speed of the WS<sub>2</sub> nanofilms, and  $1/\tau = A_1 \cdot 1/\tau_1 + A_2 \cdot 1/\tau_2 + A_3 \cdot 1/\tau_3$ ;  $\tau_i$  denotes the exponential decay lifetime of each component in the WS<sub>2</sub> nanofilms; and  $A_i$  denotes the corresponding weights. The subscript  $i$  can equal 1, 2 or 3. After a few steps (the detailed derivation is given in the ESI†), eqn (4) and (5) can be obtained:

$$F_{\text{on}} \approx F_{\text{on}}' \left( 1 + \frac{t}{\tau} \right) \quad (4)$$

and

$$\Delta T \approx \Delta T' - \frac{(1 - T_L) F_{\text{on}}'}{T_L F_0} \cdot \frac{t}{\tau}, \quad (5)$$

where  $F_{\text{on}}$  and  $\Delta T$  represent the onset fluence and modulation depth, respectively.  $F_0$  is the laser fluence at  $z = 0$ , and  $F_{\text{on}}'$  and  $\Delta T'$  are the values of  $F_{\text{on}}$  and  $\Delta T$  for the pulse width  $t = 100$  fs. The analytical expressions (4) and (5) show the regular variation of the SA parameters  $F_{\text{on}}$  and  $\Delta T$  with the excitation pulse width  $t$ . For the 5 min WS<sub>2</sub> film,  $T_L = 60.97\%$ ,  $a = 0.3903$ ,  $F_{\text{on}}' = 2.73 \text{ mJ cm}^{-2}$ ,  $F_0 = 73.9 \text{ mJ cm}^{-2}$ ,  $T_0' = 80.54\%$ ,  $A_1 = 67.5\%$ ,  $\tau_1 = 512 \text{ ps}$ ,  $A_2 = 26.2\%$ ,  $\tau_2 = 1311 \text{ ps}$ ,  $A_3 = 6.3\%$ , and  $\tau_3 = 2883 \text{ ps}$ . Substituting these parameters into eqn (4) and (5) produces the two solid curves shown in Fig. 10(c) to describe the relationship between the key parameters ( $F_{\text{on}}$ ,  $\Delta T$ ) and the pulse duration,  $t$ , for the 5 min WS<sub>2</sub> sample. Both theoretical

curves agree well with the experimental data. Thus, the dramatic change of the SA properties of these samples in the fs, ps and ns regions can be well described by the SA theoretical model and analytical expressions developed here. Overall, the newly developed theoretical model and the experimental data confirmed that the SA parameters of these WS<sub>2</sub> films can be modified by controlling the sputtering time. These research findings are vital for the design and engineering of TMD-based nonlinear materials for various applications, *e.g.*, ultrafast lasers, nanosecond lasers, ultrafast pulse shaping, optical switching, optical communications, and optical computing.

## 5 Conclusions

In summary, large-area samples of WS<sub>2</sub> nanofilms with different thicknesses and morphologies deposited on quartz were fabricated by magnetron sputtering for various deposition times. The 1 min and 3 min WS<sub>2</sub> films contained mainly horizontally grown WS<sub>2</sub>, while the 5 min films contained many vertically grown few-layered WS<sub>2</sub> nanosheets. The characteristics and the ultrafast NLO properties of these nanofilms were investigated systematically by  $Z$ -scan. The WS<sub>2</sub> films were found to possess prominent ultrafast SA properties under excitation by an 800 nm pulsed laser with energy up to 2 μJ and varying pulse durations in the fs, ps and ns regions. Some key SA parameters, *e.g.*, the onset fluence  $F_{\text{on}}$  and

the modulation depth  $\Delta T$ , can be greatly modified by adjusting the thickness and morphology *via* controlling the magnetron sputtering time. A pulse width-dependent SA model that considers the effects of interband exciton recombination was proposed for the first time. The ratio between the decay lifetime and pulse width is critical for the SA effect. Laser pulses with the same pulse energy but a duration shorter than the decay lifetime produce a stronger SA effect. Two analytical expressions for the variation of the onset fluence  $F_{\text{on}}$  and the modulation depth  $\Delta T$  with the excitation laser pulse width are derived. Our experimental results were in good agreement with the analytical predictions. These expressions can be employed to calculate the values of  $F_{\text{on}}$  and  $\Delta T$  for various pulse widths for the TMD materials and further develop various ultrafast lasers and nanosecond lasers. These research findings have great value for both basic science and practical applications.

## Conflicts of interest

There are no conflicts to declare.

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