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ARTICLE

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

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In this study, we have successfully demonstrated a method of greatly modifying the nonlinear saturable absorption (SA) properties of WS2 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 Fon and the modulation depth ΔT) with the excitation laser pulse width have been derived and experimentally verified. These studies open up exciting avenues for engineering the SA properties of 2D nanofilms for a wide range of laser photonic devices and applications.

Methods

WS_2 films on quartz substrates were fabricated by using a magnetron sputtering method. The RF power, Ar gas pressure, and substrate temperature were controlled at 60 W, 5 mTorr, and 200°C, respectively, during sputtering. The deposition rate was approx. 5 nm min^{-1}, leading to film thicknesses of ~8.85 nm, ~15.7 nm and ~27.7 nm after deposition times of 1 min, 3 min and 5 min, respectively. To improve the film crystallinity, the as-prepared WS_2 films were annealed in an Ar atmosphere at 800 °C for 120 mins.

As shown in Fig. S1, a Ti:sapphire chirped pulse amplification (CPA) system, consisting of an oscillator, a pulse stretcher, a regenerative amplifier and a pulse compressor, was used to output 200 ps laser pulses before the pulse compressor. Pulses of 100 fs or 10 ps were produced from the compressor by changing the spacing between the pair of gratings that constitute the compressor. The 10 ns laser pulses were generated directly from the Q-switched regenerative amplifier of the CPA system. To avoid laser damage and the effects of heat, a pulse picker was employed to decrease the 1 KHz output pulse repetition rate to 1 Hz. In addition, a motor-driven variable optical attenuator was used to regulate the laser pulse energy. The excitation laser beam was focused at the focus with a beam waist of 29 μm, located at position Z = 0, by a lens with a focal length of 15 cm. The WS_2 film samples were loaded onto a motorized linear stage and translated from Z = −15 to Z = 15 mm along the optical axis (the Z-axis). The pulse energies in front of and behind the sample were measured by two pyroelectric energy meters. The average energy of 10 pulses within the exposure time of 10 seconds was taken for each measurement by using a computer-controlled energy meter and mechanical shutter.

Derivation of analytical expressions for onset fluence F_{on} and the modulation depth ΔT

Eq. (3) was used to derive analytical expressions for the onset fluence F_{on} and the modulation depth ΔT. According to Eq. (3), the additional photonic energy absorbed from the excited pulse due to interband recombination can be expressed as

$$\Delta E = h\nu \cdot \Delta N = h\nu N_{on} \cdot \frac{t}{\tau} \qquad \text{(S1)}$$

Without excitation, the excited state population of the direct band gap semiconductor is almost zero at room temperature. Under the threshold condition, when the input fluence is equal to F_{on}, the energy absorbed by the WS_2 film can be calculated as follows:

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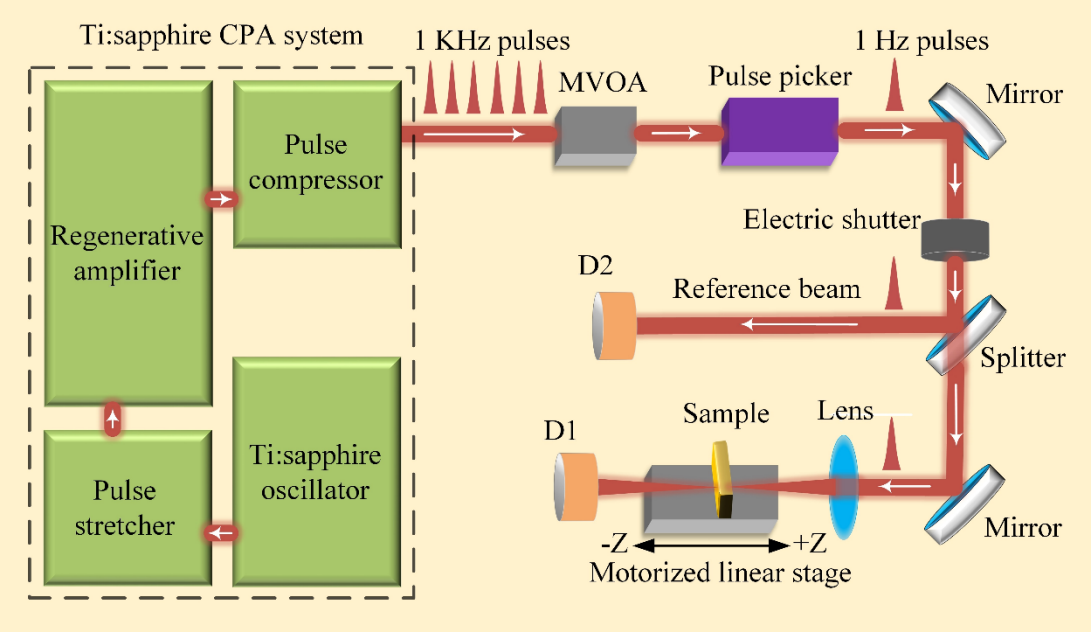

Fig. S1 Schematic diagram for the setup of open-aperture Z-scanning. The MVOA is a motor-driven variable optical attenuator, the pulse picker consists of a Pockels cell and a Glan-Taylor prism, and D1 and D2 are pyroelectric energy meters for the signal pulses and the reference pulses, respectively.

$$F_{on} \cdot a = h\nu N_{on} + \Delta E \qquad \text{(S2)}$$

where $a = 1\text{-}T_L$ is the linear absorption. Substituting (S1) into (S2) and simplifying produces

$$F_{on} = \frac{1}{a} \cdot h\nu N_{on}\left(1+\frac{t}{\tau}\right), \qquad \text{(S3)}$$

where $1/\tau = A_1 \cdot 1/\tau_1 + A_2 \cdot 1/\tau_2 + A_3 \cdot 1/\tau_3$. According to the exciton dynamics fitting outcomes shown in the text, A_1 = 67.5 %, τ_1 = 512 ps, A_2 = 26.2 %, τ_2 = 1311 ps, A_3 = 6.3, and τ_3 = 2883 ps. Then, Eq. (S3) becomes

$$F_{on} = \frac{1}{a} \cdot h\nu N_{on}\left(1+\frac{t}{650}\right). \qquad \text{(S4)}$$

For t = 0.1 ps (100 fs), $\frac{t}{650} = 0.000153$ is a very small value that can be ignored. We define F'_{on} to be the value of F_{on} for t = 0.1 ps and can thereby obtain

$$F'_{on} \approx \frac{1}{a} \cdot h\nu N_{on}. \qquad \text{(S5)}$$

Then, expression (S3) can be rewritten as follows:

$$F_{on} \approx F'_{on}\left(1+\frac{t}{\tau}\right). \qquad \text{(S6)}$$

Therefore, the analytical expression (4) has been verified.

Next, the analytical expression of the modulation depth ΔT in terms of the pulse width t is derived. The SA modulation depth ΔT is defined as follows:

$$\Delta T = \frac{T_0}{T_L} - 1 \qquad \text{(S7)}$$

where T_L is the linear transmittance of the WS2 film, and T_0 is the maximum transmittance of the WS_2 film at z = 0 for the Z-scan measurement. T_0 is given by $T_0 = F'_0/F_0$, where F_0 and F'_0 are the laser fluences in front of and behind the WS2 film at the position z = 0. Then, equation S8 can be obtained:

$$T_0 = \frac{F'_M - \Delta E}{F_0} \qquad \text{(S8)}$$

where F'_M is the maximum value of F'_0 for the excited pulse width $t \to 0$, and the additional optical energy absorbed because of interband recombination $\Delta E \to 0$. Combining equation (S1) and (S5), we can obtain

$$\Delta E \approx aF'_{on} \cdot \frac{t}{\tau} \qquad \text{(S9)}$$

For t = 0.1 ps (100 fs), $\Delta E \approx 0.000163 mJ/cm^2$. This value is very small value and can be ignored. Thus T'_0 is constant and equal to T_0 (t = 0.1 ps), and therefore $F'_M \approx T'_0 \cdot F_0$. Then, equation (S8) can be rewritten as

$$T_0 \approx \frac{T'_0 F_0 - aF'_{on} \cdot \frac{t}{\tau}}{F_0}. \qquad \text{(S10)}$$

Inserting this expression into (S7) produces

$$\Delta T \approx \frac{T'_0 F_0 - aF'_{on} \cdot \frac{t}{\tau}}{T_L F_0} - 1. \qquad \text{(S11)}$$

(S11) can be further simplified as follows:

$$\Delta T \approx \Delta T' - \frac{(1-T_L)F'_{on}}{T_L F_0} \cdot \frac{t}{\tau}, \qquad \text{(S12)}$$

where $\Delta T'$ is constant and equal to ΔT (t = 0.1 ps). In summary, the analytical expressions (S6) and (S11) can be deduced. These expressions describe the regular variation of the SA parameters F_{on} and ΔT with the pulse width. By utilizing these two expressions and the measured parameters for 100 fs pulse excitation, other values of F_{on} and ΔT with respect to different pulse widths can be calculated for any other TMD material.