Strong third-order Kerr nonlinearity in 2D $PdSe_2$ dichalcogenide films

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Abstract: We characterize the third-order optical nonlinearity in $PdSe_2$ dichalcogenide films via the Z-Scan technique. A strong and negative (self-defocusing) Kerr nonlinearity (n_2) of ~ – 7.65×10^{-16} m^2/W is observed at 800 nm.

1. Introduction

Transition metal dichalcogenides (TMDCs), such as MoS_2[1], $MoSe_2$[2], and WS_2[3] are promising nonlinear optical materials for future photonic devices. Palladium diselenide ($PdSe_2$), a new 2D noble metal dichalcogenide in the TMDC family, has recently become of significant interest. Similar to the puckered structure of black phosphorus (BP), $PdSe_2$ has a puckered pentagonal atomic structure − with one Pd atom bonding to four Se atoms and two adjacent Se covalently bonding with each other [4]. This low-symmetry structure makes $PdSe_2$ possess unique in-plane anisotropic optical and electronic properties, featuring a noncentrosymmetric (pentagonal) structure, in contrast with its cousin $PtSe_2$ [5, 6]. Further, the bandgap of $PdSe_2$ is strongly layer-dependent, varying form 0 eV (bulk) to 1.3 eV (monolayer), a property well suited for photonic and optoelectronic applications [4, 7]. Most significantly, $PdSe_2$ is highly air-stable, indicating its robustness and potential for practical applications, in contrast with BP. The high carrier mobility [4, 7] and anisotropic Raman spectroscopy [8] of 2D $PdSe_2$ layers have been investigated as well as their high performance as photodetectors from the visible to mid-infrared wavelengths [7]. To date, however, its optical Kerr nonlinearity has not been investigated.

In this paper, we report measurements of the third-order nonlinear optical response of 2D $PdSe_2$ films. Experimental results using the Z-scan technique at 800 nm show that $PdSe_2$ films exhibit a strong and negative (self-defocusing) Kerr nonlinearity (n_2) of ~ – 7.65×10^{-16} m^2/W, which is two orders of magnitude higher than that of bulk silicon. Our results show that the extraordinary third-order nonlinear optical properties of $PdSe_2$ have a strong potential for high-performance nonlinear photonic devices.

2. Material preparation and characterization

Fig. 1(a) shows the atomic structure of $PdSe_2$ crystals. Different from other TMDCs like MoS_2 and WS_2, $PdSe_2$ has a unique puckered pentagonal structure, where the Se-Pd-Se layers stack with weak van der Waals interactions to form a layered structure [4, 7]. In each monolayer, the pentagonal rings are formed with one Pd atom bonding to four Se atoms and two adjacent Se covalently bonding with each other, which is similar to the puckered structure of BP and results in the low inversion symmetry properties of $PdSe_2$.

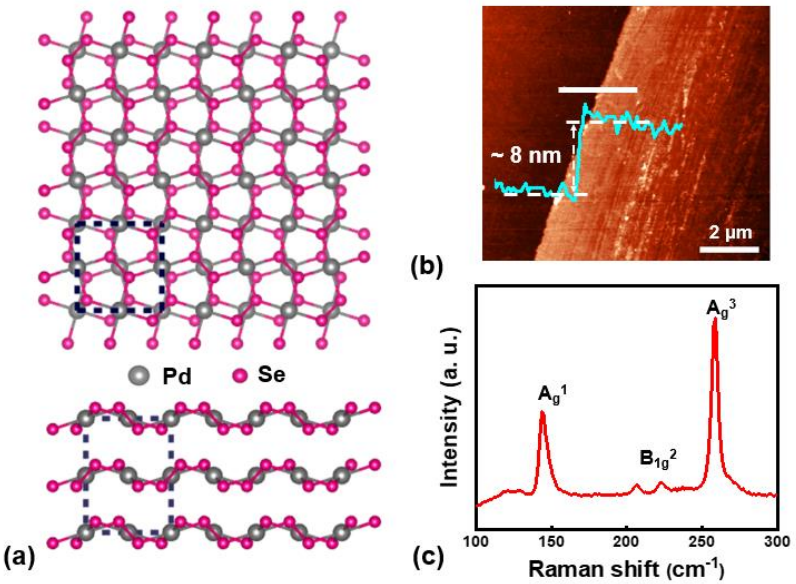

Fig. 1 (a) Schematic atomic structure of $PdSe_2$, (b) AFM height profile and (c) Raman spectrum of multilayer $PdSe_2$ film.

Multilayer $PdSe_2$ large-scale films used in our experiment were synthesized on the transparent sapphire substrate via the chemical vapor deposition (CVD) method. The morphology image and height profile of the $PdSe_2$ film was characterized by the atomic force microscopy (AFM), as shown in Fig. 1(b). The measured thickness is ~ 8 nm. Fig. 1(c) shows the Raman spectrum of $PdSe_2$ film with an excitation laser wavelength at 514 nm. Three

typical phonon modes of A_g^1 (~145.5 cm^{-1}), B_{1g}^2 (~222.5 cm^{-1}), and A_g^3 (~ 258.8 cm^{-1}) are observed, where the A_g^1 and B_{1g}^2 vibrational modes correspond to the movement of Se atoms and the A_g^3 mode relates to the relative movements between Pd and Se atoms [7, 8].

3. Z-scan measurements

The third-order optical nonlinear response of the $PdSe_2$ films was characterized via the open- (OA) and closed-aperture (CA) Z-scan methods [9]. A femtosecond laser source at 800 nm wavelength was used to excite the samples, with a laser pulse duration of ~140 fs. Fig. 2(a) shows the OA Z-scan curve for the $PdSe_2$ film at the (incident) laser intensity of 17.15 GW/cm^2. Typical reverse saturation absorption (RSA) can be observed, with the transmission decreasing as the $PdSe_2$ sample was moved through the focal point. Various mechanisms, including two-photon absorption (TPA) and free carrier absorption (FCA), may contribute to the RSA behavior [9, 10]. By fitting the OA data, the nonlinear absorption coefficient α_{NL} is measured to be ~ 2.82×10^{-8} m/W, which is comparable to the values of graphene [11] and WS_2 [3].

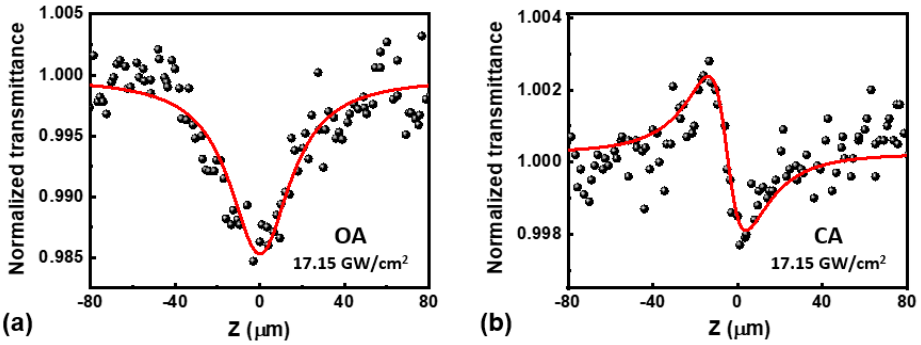

Fig. 2 Measured (a) OA and (b) CA curves of $PdSe_2$ film at laser intensity of 17.15 GW/cm^2.

We also characterize the Kerr nonlinearity of $PdSe_2$ films via the CA Z-scan method. Fig. 2(b) displays the CA data of the multilayer $PdSe_2$ film. Obviously, the normalized transmittance of sample exhibits a transition from peak to valley when the sample passes the focal plane. The typical peak-valley CA configuration reflects a negative Kerr coefficient n_2, indicating the optical self-defocusing effect in 8 nm-$PdSe_2$ film. The measured n_2 of $PdSe_2$ is ~ -7.65×10^{-16} m^2/W at an intensity of 17.15 GW/cm^2. Compared with other 2D materials (Table 1), n_2 for $PdSe_2$ is lower than graphene and BP, but still two orders of magnitude higher than bulk silicon [12-14], which demonstrates the high potential of $PdSe_2$ as a new optical material for nonlinear photonic applications. Further, like Si-Ge heterostructures, [15] $PdSe_2$ may also offer interesting possibilities for second order nonlinear effects courtesy of its complex anisotropic nonlinear optical characteristics.

Table 1. Comparison of α_{NL} and n_2 of various 2D layered materials

Material	Laser parameter	Thickness	α_{NL} (m/W)	n_2 (m^2/W)	Reference
Graphene	1150 nm, 100 fs	5-7 layers	3.8×10^{-8}	-5.5×10^{-14}	[11]
MoS_2	1064 nm, 25 ps	25 μm	$(-3.8\pm0.59)\times10^{-11}$	$(1.88\pm0.48)\times10^{-16}$	[1]
WS_2	1040 nm, 340 fs	57.9 nm	$(1.81\pm0.08)\times10^{-8}$	$(-3.36\pm0.27)\times10^{-16}$	[3]
$PtSe_2$	800 nm, 150 fs	4.6 nm	-8.80×10^{-8}	–	[5]
$PtSe_2$	1030 nm, 340 fs	17 layers	–	$(-3.76\pm0.46)\times10^{-15}$	[6]
$PdSe_2$	800 nm, 140 fs	8 nm	$(2.82\pm0.16)\times10^{-8}$	$(-7.65\pm0.83)\times10^{-16}$	This work

4. References

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