Black phosphorus as broadband saturable absorber for pulsed lasers from 1 μm to 2.7 μm wavelength

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Received 17 August 2015, revised 21 December 2015
Accepted for publication 22 January 2016
Published 4 March 2016

Abstract
Universal saturable absorbers covering wavelengths from near-infrared to mid-infrared bands have attracted widespread interest. In this contribution, we experimentally demonstrated the broadband saturable absorption of multilayer black phosphorus from 1 μm to 2.7 μm wavelengths. With liquid-phase-exfoliated black phosphorus nanoflakes as the saturable absorber, the Q-switching operation of bulk lasers at 1.03 μm, 1.93 μm, and 2.72 μm was realized, respectively. This work will open up promising optoelectronic applications of black phosphorus for the mid-infrared spectral region.

Keywords: black phosphorus nanoflake, saturable absorber, mid-infrared Q-switched lasers

1. Introduction
Black phosphorus (BP), a layered allotrope of phosphorus, has unique properties. Due to the puckered layer or zigzag direction of intralayer atoms, the BP crystal exhibits highly anisotropic mechanical properties [1]. Moreover, few-layered BP presents anisotropy in both electrical and optical properties [2, 3]. By the use of its high carrier mobility, few-layered BP has been manufactured into fast field-effect transistors (FETs) and opens up its electronic applications [4, 5]. Similar to MoS₂, BP also possesses a thickness-dependent energy bandgap with 1.5–2.0 eV for single layers [6–8], 0.59 eV for five layers [9] and 0.3–0.33 eV for bulk samples [1, 4]. However, MoS₂ shows a transition from direct bandgap to indirect bandgap once it becomes multilayer while BPs always show a direct bandgap property [6]. Such difference would endow multilayer BPs with intrinsically stronger light–matter interaction than multilayer MoS₂. This might lead to some unique applications of multilayer BPs for optoelectronics. Meanwhile, the narrow direct bandgap of multilayer BP results in the strong absorption of photons at the mid-infrared region. Recently multilayer BP with controllable size, acquired by liquid phase exfoliation [10], has been verified to possess optical broadband saturable absorption [11]. Pulsed fiber lasers based on a BP saturable absorber have been demonstrated [3, 12]. These remind us to fabricate a universal saturable absorber covering the near-infrared to mid-infrared bands with multilayer BPs due to their narrow direct bandgap.

Up to now, saturable absorbers based on two-dimensional (2D) materials such as graphene [13–15], topological insulators (TIs) [16–18], and semiconducting transition metal dichalcogenides (TMDs) [19, 20] have been rapidly developed for pulsed lasers of 1 μm to 2 μm wavelengths. But there always exists a bottleneck for saturable absorbers at the longer...
wavelength of ~3 μm. The zero-bandgap structure of graphene weakens absorption at longer wavelengths, while the large bandgap of TMDs prevents photon absorption at longer wavelengths. Fortunately, multilayer BPs, with a direct intrinsic bandgap as narrow as ~0.3 eV for bulk samples [4, 21], should be a suitable candidate for saturable absorbers at the mid-infrared region. In this contribution, we demonstrate that BP can operate as a broadband saturable absorber from 1 μm to 2.7 μm wavelength. By adopting multilayer-BP-coated gold-film mirrors as optical modulating devices in the oscillators, Q-switched bulk lasers at wavelengths of 1.03 μm, 1.94 μm and 2.72 μm were demonstrated, respectively. To the best of our knowledge, this is the widest passive Q-switcher based on 2D materials.

2. Results and discussion

2.1. Material characterization

The multilayer BP sample used in the experiments was fabricated by the liquid phase exfoliation (LPE) method with N-methylpyrrolidone (NMP) as the solvent [11, 22]. For the Raman measurement, TEM and ATM test, the sample was prepared by drop-casting the BP dispersion onto the surface of the quartz substrate and then dried in a vacuum drying oven. The Raman spectrum of the BP flakes is shown in figure 1(a). From the Raman spectrum, it can be seen that there are three Raman peaks located at 361.9 cm⁻¹, 438.1 cm⁻¹ and 465.8 cm⁻¹, which correspond to the BP’s out-of-plane vibration mode A₁ and in-plane vibration modes B₂ and A₂, respectively [23]. To characterize the morphology and thickness of the multilayer BP sample, transmission electron microscopy (TEM) and atomic force microscopy (AFM) measurements were performed. Figure 1(b) shows the TEM image in micron scale. It can be seen that the exfoliated BP is in the form of a layered structure around 4 micrometers in diameter. The thickness parameter of the BP flake is shown in figures 1(c) and (d). The AFM image result shows that the thickness of the BP flake is around 23 nm, indicating this type of BP possesses a comparable bandgap of bulk BP with photon absorption at a wavelength as far as 4.1 μm.

For fabricating a broadband highly reflective saturable absorber as a passive optical modulator, we dropped the BP dispersion onto a gold-film mirror and dried it. Then the BP-coated mirrors were characterized and used for Q-switched lasers. The inset in figure 2(a) shows a photograph of the BP gold-film mirror, and multilayer BP can be clearly seen on the mirror. To verify the broadband absorption of the BP sample, the reflectivity spectrum was measured by using a Lambda 950 PerkinElmer UV/VIS/NIR spectrometer with the result shown in figure 2(a). It can be seen that the BP sample shows strong absorption at the whole spectrum band from ~0.5 μm to 2.5 μm wavelength, implying BP’s ultrabroadband absorption characteristics.
To further characterize the saturable absorption characteristics of the BP-coated gold-film mirror, we perform saturable absorption measurement with a self-built picosecond fiber laser at a 1.94 \( \mu \)m wavelength. The measurement result is shown in figure 2(b). Considering a Gaussian beam of incident light, the effective reflectivity \( R \) of the saturable absorber mirror satisfies:

\[
R(F) = 1 - \alpha_{ns} - \Delta R \left[ 1 - \frac{F_{sat}}{F} \ln \left( 1 + \frac{F}{F_{sat}} \right) \right]
\]

where \( F \) is the incident light fluence, \( \alpha_{ns} \) is the linear loss by the absorber and substrate, \( \Delta R \) is the modulation depth, and \( F_{sat} \) is the saturation fluence of the absorber. Fitting with equation (1), the modulation depth \( \Delta R \) and saturation fluence \( F_{sat} \) of the BP gold-film mirror are determined to be 7.8% and 1.15 \( \mu \)J cm\(^{-2} \), respectively. The linear loss portion \( \alpha_{ns} \) from the BP and gold-film substrate is 20.5%. The large modulation depth and the relatively low saturation fluence indicate that the BP gold-film mirror is suitable as a Q-switcher of bulk lasers.

2.2. Experimental setup

The schematic of the laser cavity used for the three Q-switched lasers is shown in figure 3. A laser diode was used as the pumping source. The pump beam was collimated and focused into gain media by two coupling convex lenses L1 and L2. The three plano-concave mirrors M1, M2, and M3 had the same radius of curvature of \(-100\) mm, and were all highly reflectively coated for the laser wavelength and anti-reflectively coated for the pump wavelength. The output coupling was 2% for the 1.03 \( \mu \)m and 1.93 \( \mu \)m wavelengths, and 1% for the 2.72 \( \mu \)m wavelength. For the 1.03 \( \mu \)m laser, the pump source was a fiber-coupled laser diode at 940 nm and the gain medium was an Yb:LuY AG crystal. For the 1.93 \( \mu \)m laser, the pump source was a single-emitter laser diode at 790 nm and the gain medium was a Tm:CaY AlO\(_4\) crystal. For the 2.72 \( \mu \)m laser, the pump source was a fiber-coupled laser diode at 976 nm with Er:Y\(_2\)O\(_3\) ceramic as the gain medium. The multilayer BP saturable absorber (BP-SA) was used as an end mirror in the cavity.

2.3. Q-switched lasers

In order to further verify the broadband saturable absorption of the BP sample, we conducted the Q-switching experiment in bulk lasers at 1.03 \( \mu \)m, 1.93 \( \mu \)m and 2.72 \( \mu \)m wavelengths, respectively. The typical Q-switched pulse trains, pulse durations and laser spectra at the three wavelengths are summarized in figure 4.

Firstly, we tested the Q-switching performance of the BP gold-film mirror in the Yb:LuY AG bulk laser at a 1 \( \mu \)m wavelength. Under an incident pumping power of 4.0 W, stable Q-switched pulses were achieved with an average output power of 6 mW, a pulse width of 1.73 \( \mu \)s, a repetition rate of 63.9 KHz, and pulse energy of 0.09 \( \mu \)J at a wavelength of 1029 nm. The low output power was mainly attributed to the large linear loss of the BP gold-film mirror.

The Q-switching performance of the BP mirror was also tested in the Tm: CaYAlO\(_4\) bulk laser at a 2 \( \mu \)m wavelength. With an incident pumping power of 5.1 W, the laser emitted stable Q-switched pulses with an average output power of 6 mW, a pulse width of 1.73 \( \mu \)s, a repetition rate of 17.7 KHz, a pulse width of 3.1 \( \mu \)s, and pulse energy of 0.68 \( \mu \)J at 1930 nm. The obtained pulse energy and pulse duration are comparable to the 2 \( \mu \)m Q-switching results with graphene as the saturable absorber [24].

To verify the saturable absorption of the multilayer BP at longer wavelength, a Q-switching experiment at a 2.7 \( \mu \)m wavelength was also implemented in Er:Y\(_2\)O\(_3\) ceramic laser. Due to the long lower-level lifetime of Er:Y\(_2\)O\(_3\) and the large vapor absorption loss in atmosphere, Er:Y\(_2\)O\(_3\) ceramic
laser at a 2.72 μm wavelength generally has a high laser threshold. For reducing the loss induced by the BP mirror, in the experiment we adopted a BP gold-film mirror with fewer BP layers, which had a reflectivity of ∼90%. With the thin BP mirror as the saturable absorber, Q-switching operation at a 2.72 μm wavelength was realized with an average output power of 6 mW, a pulse width of 4.47 μs, a pulse repetition rate of 12.6 kHz and pulse energy of 0.48 μJ. The results demonstrate that BP is a promising saturable absorber as a passive optical modulator in the mid-infrared spectral band.

3. Conclusions

In summary, we have experimentally demonstrated the broadband saturable absorption of BP from 1 μm to 2.7 μm wavelengths. The saturable absorption measurement at 1.94 μm demonstrates the as-fabricated BP gold-film mirror has a modulation depth of 7.8% and saturation fluence of 1.15 μJ cm⁻². With the BP sample as the saturable absorber, Q-switched lasers at 1.03 μm, 1.93 μm and 2.72 μm by using different gain media have been realized. The results show that BP has potential as a universal saturable absorber with an ultrawide absorption band. Considering the bandgap (∼0.3 eV) of multilayer BP, saturable absorption at a 2.72 μm wavelength approaches its absorption limit at the mid-infrared region. The easy fabrication, broadband absorption and low saturation fluence of multilayer BP would promote optoelectronic applications towards the unexplored mid-infrared region.

Acknowledgments

We are grateful to Prof Yuzhi Zhang and Prof. Lingnan Wu of the Shanghai Institute of Ceramics for measuring the reflection spectrum of the BP gold-film mirror. We are also grateful to Prof Jian Zhang and Prof Xiaodong Xu of Jiangsu Normal University for providing the laser crystals. The work is...
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