Dynamical anisotropic response of black phosphorus under magnetic field

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Abstract

Black phosphorus (BP) has emerged as a promising material candidate for next generation electronic and optoelectronic devices due to its high mobility, tunable band gap and highly anisotropic properties. In this work, polarization resolved ultrafast mid-infrared transient reflection spectroscopy measurements are performed to study the dynamical anisotropic optical properties of BP under magnetic fields up to 9 T. The relaxation dynamics of photoexcited carrier is found to be insensitive to the applied magnetic field due to the broadening of the Landau levels and large effective mass of carriers. While the anisotropic optical response of BP decreases with increasing magnetic field, its enhancement due to the excitation of hot carriers is similar to that without magnetic field. These experimental results can be well interpreted by the magneto-optical conductivity of the Landau levels of BP thin film, based on an effective $k \cdot p$ Hamiltonian and linear response theory. These findings suggest attractive possibilities of multi-dimensional control of anisotropic response (AR) of BP with light, electric and magnetic field, which further introduces BP to the fantastic magnetic field sensitive applications.

1. Introduction

As a two-dimensional (2D) tunable-gap semiconductor with high mobility [1–7], black phosphorus (BP) promises enormous applications in high speed transistors with large on–off ratio [7–13] and mid-IR optoelectronic devices [14–19] surpassing graphene and many other 2D materials [20–23]. Its highly anisotropic response (AR) would lead to interesting transport and optical properties, such as anomalous magneto-optical response [24], highly anisotropic wave-functions of the Landau levels (LLs) [25], and quasi-1D excitonic state with larger binding energy [26, 27], which enables an additional degree of freedom for high performance functional device applications, especially in the applications where angle sensitive operations are desired [3, 5, 26, 28–31]. Investigating the AR of BP under various circumstances such as high field/speed limit or magnetic field are crucial for BP based angle sensitive devices. Although magnetic field is usually much less effective in comparison to electric field in tuning material properties, the recent discoveries on 2D layered ferromagnetic materials, which are conveniently tunable as atomic thin materials, provide an effective route towards magnetic field tuning of other 2D layered materials [32–34] through convenient integration of van der Waals heterostructures [35]. Under these prospective, steady state magneto transport, optical characterization [26, 28, 31] and even high speed transport properties [36] have been applied on BP to characterize its fundamental anisotropy related physical responses. However, despite its importance in fundamental physics and device applications, the dynamical anisotropic optical response of photoexcited carriers under magnetic field, which is vital for any magnetic field related applications, has not been investigated experimentally so far.
In this work, polarization resolved ultrafast mid-infrared transient reflection spectroscopy measurements are performed under magnetic fields up to 9 T to study the dynamical evolution of anisotropic optical properties of BP. The relaxation dynamics of photoexcited carriers, which can be directly correlated to the transient reflection measurements, are found to be insensitive to the applied magnetic field up to 9 T due to the broadening of the LLs and large effective mass of carriers. Through pump polarization dependent magneto-transient reflection measurements, the AR of BP at pump photon transition can be deducted, and it is revealed from these measurements that the anisotropic optical response of BP decreases with increasing magnetic field. By performing the calculation of the magneto-optical conductivity (MOC) of the LLs of BP thin film, based on an effective $k \cdot p$ Hamiltonian and linear response theory, the results indicate the degradation of the AR is an effect of the compression of electron wave-function by magnetic fields. On the other hand, the dynamical evolution of optical conductivity at probe photon transition due to the excitation of hot carriers can be resolved in probe polarization dependent magneto-transient reflection measurements. The results indicate the enhancement of the AR of BP due to the excitation of hot carriers persists under magnetic fields, which is similar to our previous work on the AR of BP under high field/speed operation limit but without magnetic field [36]. Further analysis indicates the relative enhancement of the AR due to hot carrier excitations does not decrease with increasing magnetic field, thus the hot-carrier acceleration either with photoeexcitation or high electric and applying a magnetic field can provide multiple dimensional control of BP’s anisotropic degree of freedom.

The schematic diagram of transient magneto-optical measurements is shown in figure 1(a) and more experimental details and basic BP sample characterizations are described in the methods section. The effect of magnetic field on the AR of BP is determined by transient measurements with two different configurations of pump/probe wavelengths: 800 nm/1940 nm and 1940 nm/4000 nm with the magnetic field applied perpendicular to the BP $xy$-plane. Figures 1(b) and (c) show the optical and atomic force microscopy images of a typical BP sample that is mechanically exfoliated from synthesized bulk BP crystal. The $x$- and $y$-axis are along the armchair and zigzag direction, respectively, which is identified by the polarization-resolved reflection spectroscopy described in reference [36]. Thickness of this BP sample measured by atomic force scanning along the white dotted line shown in figure 1(d) is about 101 nm, from which we can deduce that the sample contains around 190 layers, using a layer spac-
ing of 0.53 nm. The thick sample is insusceptible to the degradation of surface layers compared to few-layers, and the mid-IR gap of the bulk directly connects to the appealing mid-IR optoelectronics. The synthesized BP crystal is found to be p-doped with bulk doping density of $4.2 \times 10^{18} \text{cm}^{-3}$ by Hall measurement, which converts to $4.24 \times 10^{13} \text{cm}^{-2}$ for 101 nm thick BP flake. The typical pump fluence for 800 nm and 1940 nm excitation is $8.1 \times 10^{14}$ and $5.4 \times 10^{15}$ photons cm$^{-2}$ respectively, which converts to $3.27 \times 10^{14}$ and $2.18 \times 10^{15}$ cm$^{-2}$ electron–hole pairs after the excitation assuming a 0.4%/nm linear absorption rate at both wavelengths [2]. Figure 1(e) shows the band structure of bulk BP and the difference of dispersion relation along $\Gamma$–X and $\Gamma$–Y direction indicating that the effective masses are also anisotropic. The probe photon energy, either 1940 nm or 4000 nm, involves the transition from the highest valence band and lowest conduction band only. To measure the dynamic evolution of the AR, polarization resolved 1.55 eV (0.8 $\mu$m)/0.64 eV (1.94 $\mu$m) and 0.64 eV (1.94 $\mu$m)/0.31 eV (4 $\mu$m) probe photon arriving at various delay time ($t$) with respect to pump pulse is used and the pump induced probe reflection change is recorded.

2. Methods

2.1. Sample preparation
Bulk BP was grown by chemical vapor deposition as described before [37]. Red phosphorus (500 mg, 99.999 + %), AuSn (364 mg) and SnI$_4$ were sealed in an evacuated quartz ampule of about 12 cm length and 1 cm diameter (pressures lower than $10^{-3}$ mbar). Then this ampule was placed horizontally at the center of a single zone tube furnace chamber. The ampule was slowly heated to 873 K in 10 h and maintained at this temperature for 24 h. In a next step the temperature was reduced to 773 K applying a cooling rate of 40 K h$^{-1}$ and maintained this temperature before switching off the oven. Using this method, BP with crystal sizes larger than 1 cm can be obtained. The thin BP flake was mechanically exfoliated from synthesized bulk BP crystal on 285 nm SiO$_2$ substrate.

2.2. Transient reflection spectroscopy
To perform transient reflection spectroscopy measurement, a 250 kHz Ti-sapphire amplifier (RegA) system [38], an optical parametric amplifier (OPA), and a homemade difference frequency generator (DFG) were used. Laser pulses at 800 nm (1.55 eV) wavelength with 60 fs pulse width generated by RegA were injected into the OPA to generate 1350 nm (signal) and 1940 nm (idler) pulses. The 1940 nm pulse (~150 fs) was used as either pump in 1940 nm/4000 nm measurement or probe in 800 nm/1940 nm measurement. The dispersion-compensated residual 800 nm of the OPA was used as the pump. The OPA signal and idler can also be injected into the DFG to generate 4 $\mu$m pulse which is used as probe in 1940 nm pump experiment. The pump and probe are both linearly polarized and two half-wave plates are used to alter their polarization angle, respectively. A 40 $\times$ transmissive or reflective objective lens was used to focus the co-propagating pump and probe beams onto the sample that was placed in a liquid helium-cooled cryostat for temperature control. A liquid cryogen-free superconducting magnet system was used to generate a magnetic field up to 9 T perpendicular to the sample. The reflected probe beam was collected by the same reflective lens and detected by an InGaAs detector. The detected signal was read by lock-in amplifier referenced to 1.4 kHz mechanically chopped pump. The probe spot size is about 4 $\mu$m for 1940 nm probe and 8 $\mu$m for 4000 nm probe and the pump spot size is slightly larger.

3. Results

3.1. Photoexcited carrier dynamics under magnetic field
Figure 1(f) shows typical magneto-transient reflection kinetics with pump and probe polarization marked in the figure. In either cases, the transient reflection signals $\Delta R/R$ are negative at timezero and then the signal evolves differently with different probe polarizations, which has been discussed extensively in our previous work [36]. Interestingly, in the present study, it is observed that the perpendicular magnetic field does not have any influence on the dynamical evolution of $\Delta R/R$ of BP up to 9 T with either 800 nm/1940 nm or 1940 nm/4000 nm pump probe configurations. Usually, the discrete LLs that are induced in high magnetic fields will increase the photoexcited carrier relaxation time compared to continuous band, as the relaxation between discrete energy level has to fulfill more rigorous energy and momentum scattering process [39]. However, the observed dependence of the dynamic evolution of $\Delta R/R$ on magnetic field (up to 9 T) indicates that the photoexcited carrier relaxation time of BP is not influenced by the magnetic field.

3.2. Degradation of AR under magnetic field
Though the magnetic field does not influence the photoexcited relaxation time of BP, it has a profound impact on the wave-function of BP and thus affects its AR. Effect of magnetic field on the AR of BP can be determined by measuring the transient reflection amplitude at different pump polarization as shown in figure 2. It is clearly evident from figure 2 that the amplitude of transient reflection $\Delta R/R$ varies with pump polarization, while the shape of their kinetics remains the same (figure 2(a)). In our previous work, it has been shown that the amplitude of transient reflection at timezero ($\Delta R/R|_{t=0}$) has linear dependence on photoexcited carrier density based on the pump power dependent measurement [36] and the $\Delta R/R|_{t=0}(\alpha_3)$ is proportional to pump polarization angle ($\alpha_3$), respective to crystal x-axis as marked...
in figure 1(a)) dependent absorption coefficient $A(\alpha_1)$. Based on this, we can simply fit $\Delta R/R|_{\alpha=0}(\alpha_1)$ as function of $\alpha_1$ (see section S1 (stacks.iop.org/TDM/5/025010/mmedia), supporting information for derivation):

$$\Delta R/R|_{\alpha=0}(\alpha_1) \sim A(\alpha_1)$$

$$= 4\sqrt{\epsilon_1(\epsilon_1 + \epsilon_2)}$$

$$\epsilon_0(\sqrt{\epsilon_2} + \sqrt{\epsilon_1})$$

$$= \epsilon_0(\sqrt{\epsilon_2} + \sqrt{\epsilon_1})$$

$$\sim \epsilon_0(\sqrt{\epsilon_2} + \sqrt{\epsilon_1})$$

(1)

where, $\epsilon_1$ and $\epsilon_2$ are dielectric constants of substrate and air, respectively, $\epsilon_0$ is the free-space permittivity, $c$ is the speed of light, $\sigma_{xx}$ and $\sigma_{yy}$ are non-zero diagonal component of optical conductivity tensor.

According to equation (1), $\Delta R/R|_{\alpha=0}(\alpha_1 = 0^\circ)$ is fitted by the function $A_1 \cos^2(\alpha_1 + \phi_1) + A_2 \sin^2(\alpha_1 + \phi_2)$. The relative change of real part of conductivity $Re(\sigma_1)/[Re(\sigma_1)]_{\alpha=0}$ is $x$ or $y$. The black and red circles represent conductivity change in $x$ and $y$-axis, respectively. (c) The anisotropy of conductivity ellipse: $Re(\sigma_{xx})/Re(\sigma_{yy})$ as a function of magnetic field. The red solid line is a linear fitting. All experiments are taken at 78 K.

3.3. Magnetic field enhanced relative anisotropy increment with hot carriers

Furthermore, the hot carrier induced anisotropy change under magnetic field is also investigated from probe polarization dependent transient reflection measurements. In the absence of magnetic field, the photoexcited hot carriers can enhance the AR of BP, which has been systematically studied in our previous
work [36]. Figure 3(a) shows the probe polarization dependence of transient reflection kinetics under 9 T magnetic field. The dynamical evolution of the transient reflection signal with different probe polarization angle is similar to the one in the absence of magnetic field. At fixed pump-probe delay, $\Delta R/R$ demonstrates sinusoidal oscillation as a function of probe polarization (figure 3(b)). Except for the initial non-equilibrium state, this periodic oscillation is robust and persists during the whole decay process (figure 3(b)). After the initial relaxation of highly excited states, the measured $\Delta R/R$ can be converted to optical conductivity change $\Delta \text{Re}(\sigma)$ through the following relation (see section S4, supporting information for derivation):

$$\frac{\Delta R}{R} \left|_{\alpha_2} \right. \approx \frac{0.03}{\sigma_0} (\Delta \text{Re}(\sigma_{xx}) \cos^2 \alpha_2 + \Delta \text{Re}(\sigma_{yy}) \sin^2 \alpha_2)$$

(2)

where $\alpha_2$ is probe polarization angle respective to crystal x-axis as marked in figure 1(a). As can be seen in figures 3(c) and (d), under high magnetic field at 9 T, the conductivity ellipse is stretched at pump-probe delay around 5 ps and later on gradually recovers as the delay time between pump and probe increases. The stretch of conductivity ellipse is similar to that in the absence of magnetic field, which is a result of photoexcitation of hot carriers. This behavior persists over the subsequent relaxation process and completely recovers after the relaxation and recombination of the photoexcited hot carriers. We can conclude from these results that the enhancement of AR in presence of hot carrier is well preserved under high magnetic field.

To analyze the magnetic field dependence of hot carrier's enhancement on AR, we further analyze the enhancement of AR $\Delta(B) = \left| \frac{\text{Re}(\sigma_{xx}) + \Delta \text{Re}(\sigma_{xx})}{\text{Re}(\sigma_{yy}) + \Delta \text{Re}(\sigma_{yy})} \right| - \left| \frac{\text{Re}(\sigma_{xx})}{\text{Re}(\sigma_{yy})} \right|$ due to the presence of hot carriers at fixed delay as a function of magnetic field. To account for the degradation of anisotropy under magnetic field, the relative change $\Delta \% (B) = \Delta(B) / \left| \frac{\text{Re}(\sigma_{xx})}{\text{Re}(\sigma_{yy})} \right|$ is plotted in figure 3(e).

We note that $\Delta \%$ increases as magnetic field increases at all fixed pump-probe delays. Although the effect is not unambiguous considering the larger synthetic error bar of $\Delta \%$, however, it is safe to conclude that the magnetic field effect obviously does not degrade the relative enhancement of AR due to the presence of hot carriers.

Figure 3. Hot carrier induces anisotropy change under magnetic field. (a) 1940 nm probe polarization dependence of transient reflection kinetics with 800 nm pump polarization fixed along x-axis under 9 T magnetic field. (b) Transient reflection spectra with different probe polarization at fixed delays marked in figure (a). The angle dependence is fit by function $\Delta R/R = a \cos^2 \alpha_2 + b \sin^2 \alpha_2$. (c) Dynamic evolution of $\text{Re}(\sigma_{xx})/\text{Re}(\sigma_{yy})$ at different delays at 9 T. The black dash line marks value of $\text{Re}(\sigma_{xx})/\text{Re}(\sigma_{yy})$ prior to pumping at 9 T. (d) Dynamical evolution of $\text{Re}(\sigma)$ ellipse at different delays under 9 T magnetic field. $\text{Re}(\sigma)$ is doubled for clarity. Inset: enlarged plot of area marked by red rectangle. (e) The relative change ($\Delta \%$) of anisotropy induced by photoexcited hot carriers at different magnetic fields with fixed pump-probe delay times. All experiments are performed at 78 K.
4. Discussion

The experimentally observed magnetic field effect on dynamic evolution of photoexcited carriers can be phenomenologically described by calculating the LL splitting and density of states around the probe photon transitions. To account for the temperature and inhomogeneous broadening of LLs in the sample, an anisotropic two-band $k \cdot p$ Hamiltonian of BP coupled with a perpendicular magnetic field $B$ and a Gaussian broadening $\Gamma$ of the LLs is incorporated into the calculation. The details of this calculation are described in the section S8, supporting information.

The LLs without the broadening which get involved into the 1940 nm and 4000 nm probe transitions with $k_z = 0$ are shown in figure 4(a). Due to the large effective mass, the LLs are quite dense, and it’s splitting at probe transition of 0.64 eV (1940 nm) and 0.31 eV (4000 nm) are only 4.3 (3.4) meV and 3.8 (2.8) meV, respectively, for valence (conduction) band under 9 T magnetic field. These tiny splittings can be smeared out by temperature ($T = 78$ K, $kT \sim 6.72$ meV) and inhomogeneous broadening due to disorder effect caused by impurities and defects. Figure 4(c) shows the density of states taking different LL broadening $\Gamma$. With $\Gamma = 1$ meV the LL splittings are barely visible in 9 T magnetic field and the peaks of the density of states are completely quenched by LL broadening ($\Gamma = 1$ meV, figure 4(d)). Hence, the relaxation of photoexcited carriers from highly excited states to probe photon transition experiences continuous state instead of discrete Landau levels even under 9 T magnetic field, because of which the dynamics of photoexcited carrier relaxation (as observed in figure 1(f)) is not influenced by the applied magnetic field.

The AR under magnetic field could be described approximately by MOC of BP. From the $k \cdot p$ Hamiltonian of BP coupled with a perpendicular magnetic field $B$ and Kubo Formula [24], we can evaluate the longitudinal optical conductivities and plot the wave-function as functions of the photon energy and magnetic field (see section S8, supporting information). The spatial distribution of the wave-function for the LLs in the valence band at the excitation photon transition of 0.64 eV at $k_z = 0$ are shown in figure S8, supporting information. Comparing to the wave-function at weaker magnetic field ($B = 6$ T), the wave-function under 9 T magnetic field is less anisotropic. Quantitatively, if we plot the $\text{Re}(\sigma_{xx})/\text{Re}(\sigma_{yy})$ as a function of magnetic field which is shown in figure 4(b), $\text{Re}(\sigma_{xx})/\text{Re}(\sigma_{yy})$ gradually decreases with increasing magnetic field, which is consistent with experimental observation. However, there are two major discrepancies comparing with experimental results: First, $\text{Re}(\sigma_{xx})/\text{Re}(\sigma_{yy})$...
oscillates with magnetic field in figure 4(b), which is not observed in the experiment. Measurement of \(\text{Re}(\sigma_{xx})/\text{Re}(\sigma_{yy})\) with fine tuning of magnetic field does not show clear oscillatory behavior (figure S6, supporting information), this is due to the quenching of the Landau level splittings at transitions corresponding to the pump photon energy as shown in figure 4(a). Second, the absolute magnitude of \(\text{Re}(\sigma_{xx})/\text{Re}(\sigma_{yy})\) is far larger than those observed in the experiment. Theoretically, the \(\text{Re}(\sigma_{xx})/\text{Re}(\sigma_{yy})\) highly depends on the temperature and doping intensity as shown in figure S7, supporting information. As the experiment is performed with femtosecond pulse, the absorption of falling edge of the pulse is strongly affected by the highly excited nonequilibrium state of BP that are excited by the rising edge of the pulse, thus experimentally observed \(\text{Re}(\sigma_{xx})/\text{Re}(\sigma_{yy})\) is strongly modified because the excited carriers and the magnitude is significantly different from our theory which is based on quasi-equilibrium state. Although the magnetic field significantly degrades the AR of BP, the hot carrier enhancement effect on AR is preserved under magnetic field as verified in probe polarization dependent measurement. These experimental results further extend the tuning capability on AR with hot carriers under magnetic field. Thus, in addition to magnetic field, excitation of hot carriers provides another tuning knob of the AR of BP which stays robust under high magnetic field. The hot carriers excitation with light or high electric field together with applying magnetic field provide multiple dimensional control of AR for high performance device with BP. Though the magnetic field control is usually considered not as convenient as electric field, recent introduction of 2D ferromagnetic semiconductor materials [32, 33] and the easy van der Waals integration with other layered 2D materials could greatly facilitate the magnetic field tuning of BP. Furthermore, large range bandgap tuning of few-layer BP by electrical gating has also been realized experimentally [40–42], this dynamic tuning of bandgap may further realize electrically tunable topological insulators and semimetals with BP [43–45]. Together with other tuning knobs, such as strain, pressure [46, 47], BP is becoming a very versatile materials platform that can be easily tuned between different condensed matter phases. Based on the above, the AR is adding another controllable degree of freedom to BP, which can be used for applications when angle sensitive application is desired. The experimental verification of the multiple dimensional control of this degree of freedom with high electric field acceleration of hot carriers and magnetic field will further pave the way for future multiple functional high performance devices based on BP.

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