Photocurrent study of two dimensional materials

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Citations to Published Works

1. Chapter 4 is based on my publication:

B. C. Cao, X. N. Shen, J. Z. Shang, C. X. Cong, W. H. Yang, M. Eginligil and T. Yu, Low temperature photoresponse of monolayer tungsten disulphide, *APL Materials*, **2014**, 2, 116101.

2. Chapter 5 is based on my publication:

M. Eginligil, **B. C. Cao**, Z. L. Wang, X. N. Shen, C. X. Cong, J. Z. Shang, C. Soci, T. Yu, Dichroic spin–valley photocurrent in monolayer molybdenum disulphide, *Nature Communication*, **2015**, 6, 7636.

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Symbols and Abbreviations

2D	Two-dimensional
3D	Three-dimensional
AC	Alternating current
AFM	Atomic Force Microscopy
CNP	Charge neutral point
CPGE	Circular photogalvanic effect
CVD	Chemical vapor deposition
DC	Direct current
DMF	Dimethylformamide
DOS	Density of states
E_F	Fermi energy
FET	Field effect transistor
FWHM	Full-width at half-maximum
HRTEM	High resolution transmission electron microscopy
LPGE	Linear photogalvanic effect
MoS ₂	Molybdenum disulphide
PC	Photocurrent
PDE	Photon-drag effect
PGE	Photogalvanic effect
PL	Photoluminescence
QWP	Quarter-wave plate
SEM	Scanning electron microscopy
SOC	Spin-orbit coupling

TMDs Transition metal dichalcogenides

WS₂ Tungsten disulphide

Abstract

With the discovery of graphene, two dimensional materials have drawn great interest among researchers thanks to their unique properties. Research in graphene optoelectronics is one of the fastest developing platforms to study light-matter interaction. Beyond the active research on new fundamental aspects of this and related systems, the optical and electronic properties of graphene can be employed in numerous applications, such as highly sensitive bolometers, photodetectors, plasmonic or photovoltaic devices, which leverage on photo-induced thermal and electronic effects. Due to the lack of non-trivial band gap in graphene, researchers have explored various two-dimensional materials, among which transition metal dichalcogenide monolayers have shown various interesting properties such as charge density waves, unusual strain and thermal energy dependence, tunable light emission by chemical control and fast photoresponse, which can be used in interdisciplinary device applications. To reveal the intrinsic optical and electronic behavior of the materials mentioned above, photocurrent study turns out to be a powerful tool.

This thesis covers three of my major contributions:

1. Helicity dependent photocurrent in biased bilayer graphene

In this part, we report the experimental determination of the PC response of bilayer graphene as a function of light intensity and state of polarization, as well as carrier density and polarity. The data shows qualitative features in common with the PC that is expected to arise from the photon-drag and the circular photogalvanic effects, as seen in monolayer graphene. In addition, we identify a non-negligible contribution to the PC of different nature, with anomalous dependence on light polarization. These results highlight the richness of bilayer graphene photoresponse, providing an

opportunity to establish light helicity as a means to manipulate the photoconductive behaviour of future optoelectronic graphene devices.

2. Low temperature photoresponse of monolayer tungsten disulphide

High photoresponse can be achieved in monolayers of transition metal dichalcogenides. However, the response times are inconveniently limited by defects. Here, we report low temperature photoresponse of monolayer WS_2 prepared by exfoliation and chemical vapour deposition method. The exfoliated device exhibits n-type behaviour; while the CVD device exhibits intrinsic behaviour. In off state, the CVD device has a photoresponse ratio for laser on/off four times larger than that of the device based on exfoliated WS_2 . And the photoresponse decay-rise time is 0.1s (limited by our setup), compared to few seconds in the exfoliated device. These findings are discussed in terms of charge trapping and localization.

3. Dichroic spin-valley PC in monolayer molybdenum disulphide

The aim of valleytronics is to exploit confinement of charge carriers in local valleys of the energy bands of semiconductors as an additional degree of freedom in optoelectronic devices. Thanks to strong direct excitonic transitions in spin-coupled K valleys, monolayer MoS_2 is a rapidly emerging valleytronic material, with high valley polarization in photoluminescence. Here we elucidate the excitonic physics of this material by light helicity-dependent PC studies of phototransistors. We demonstrate that large PC dichroism (up to 60%) can also be achieved in high-quality MoS_2 monolayers grown by CVD, due to the circular photogalvanic effect on resonant excitations. This opens up new opportunities for valleytronic applications in which selective control of spin-valley-coupled PCs can be used to implement polarization-sensitive light-detection schemes or integrated spintronic devices, as well as biochemical sensors operating at visible frequencies.

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Chapter 1

Introduction

1.1 Rise of the Two-Dimensional World

Ever since the discovery of atomically thin graphene [Figure 1.1] [1], two-dimensional (2D) materials have inspired more and more researchers with their unique properties. The 2D family is growing day by day, from graphene to transition metal dichalcogenides (TMDs) [2,3] and even black phosphorus [4]. Furthermore, there has been over 700 2D materials predicted to be stable [5].

Figure 1.1 (a) Crystal structure of single layer graphene, a honeycomb lattice. (b) Optical image of graphene, mechanically exfoliated on SiO₂/Si substrate.

As the leading member, graphene owns outstanding electronic and optical properties, making it an ideal candidate to explore new aspects of low-dimensional physics and promising applications [6-9]. This part will be further discussed in Chapter 3 of this thesis.

One step forward from gapless graphene, a lot of researchers have move onto 2D TMDs, which have broad range of varieties including metallic, semi-metallic, semiconducting, superconducting and charge density wave [10]. I will give detailed interpretation in Chapter 4 and Chapter 5.

1.2 Photo-response and Photocurrent

1.2.1 Photovoltaic Effect

As the further development of photoelectric effect, demonstrated in Figure 1.2, photovoltaic effect describes the generation of voltage and electric current within a material upon light illumination.

Figure 1.2 (a) Atoms in crystal are surrounded by electrons. (b) An electron absorbs light illumination. (c) This excitation generates electron-hole pair. (d) The recombination of an electron and a hole releases energy.

When two dissimilar materials get contacted, a PN junction or quasi-PN junction will be formed. Electrons in n side and holes in p side diffuse towards each other and get recombined, resulting in a build-in electric field, from n side to p side. This field, in return, drives a reverse current and balances the diffusion, reaching an equilibrium at V_D . Upon light illumination, electron-hole pairs will be generated and enter the build-in

field. Electrons in p side will travel through the depletion area and enter n side, whereas holes in n side behave vice versa. This carrier movement forms a light-induced current I_L . As a consequence, a voltage bias V is established from p to n. and this is called the photovoltaic effect. The potential barrier between the PN junction is thus decreased by V , which drives a positive current I_F from p side to n side. At open circuit condition, I_L equals to I_F , an external voltage is built as V_{OC} . On the other hand, if the PN junction is connected with a load, a DC current will flow through the circuit and the PN junction will act as battery. Figure 1.3 shows the schematic mechanism of the photovoltaic effect.

Figure 1.3 Schematic interpretation of a PN junction at (a) dark condition and (b) light illumination.

1.2.2 Photon-drag Effect

The photon-drag effect (PDE) is a non-linear effect entirely owing to the existence of a photon momentum [11]. When an absorption of electromagnetic radiation is due to free carriers, or due to optical transitions that lead to the formation of free carriers, these carriers would gain a directed motion caused by the absorbed photon momentum, forming a net current in the system. The magnitude of this current conveys rich information about various scattering mechanisms and electron energy spectrum. In 1958, Barlow first considered the low-frequency PDE [12]. In his work, the PDE is described as an ac Hall effect due to the electric and magnetic field vectors of the wave. To simplify the model, the difference between the usual electron mobility μ and the Hall

mobility can be neglected. Thus, in Ref. [11], a schematic model is used to explain the PDE, shown in Figure [1.4]. Assume the medium is isotropic with permittivity ϵ , and a flux Φ of monochromatic photons with energy $\hbar\omega$ and momentum $\hbar q$. Let α be the free-electron absorption coefficient, then $\alpha\Phi\hbar q$ represents the momentum transfer rate per unit volume, which is defined as the drag-force density. The effective electric field E^* can be written as $E^* = -\alpha\Phi\hbar q/eN$, where N is the volume density of free electrons. From this electric field, a current density can be derived as:

$$J = eN\mu E^* = -\alpha\Phi\hbar\mu q = -\frac{\alpha\mu S}{c/\sqrt{\epsilon}} \quad (1.1)$$

where $S = \frac{\Phi}{\hbar\omega}$ is the radiation energy flux.

Figure 1.4 Schematic illustration of a photon-drag effect experiment, adopted from Ref. [11].

Moreover, in degenerate two-dimensional electron gas (2DEG), the PDE will also arise in the presence of a collisional level broadening. Study has shown that in 2D subbands, extra information about the momentum-relaxation kinetics can be revealed by the drag-current spectrum.

1.2.3 Photogalvanic Effect

The spin of electrons and holes has been intensively studied for its interesting

physical phenomena and quantum mechanical properties. Among various approaches to generate and investigate the spin, optical orientation is one of the most powerful methods [13]. The unbalanced spin distribution produced by optical pumping may lead to both spin photoconductive effect and spin photocurrent. Under an external voltage bias, the spin photoconductive effect, in which the spin orientation triggers a change of conductivity, forms a spin-polarized current [14-16]. However, even without any external voltage bias, the spin photocurrents can still occur. They are driven by spin polarization generated by oriented optical pumping.

Light propagating through a semiconductor and acting upon mobile carriers can generate a dc electric current without external bias. The irradiated sample represents a current source. Here we consider photocurrents which appear due to optically induced homogeneous spin orientation of carriers in homogeneous samples. The microscopic origin of these currents is the conversion of spin polarization of carriers into directed motion. The fingerprint of spin photocurrents is their dependence on the helicity of the radiation field. The current reverses its direction by switching the polarization of light from right-handed circular to left-handed circular and vice versa. The experimental data can be described by simple analytical expressions derived from a phenomenological theory which shows that the effect can only be present in gyrotropic media. This requirement rules out effects depending on the helicity of the radiation field in bulk non-optically active materials such as bulk zinc-blende structure and diamond structure crystals. The reduction of dimensionality as realized in QWs makes spin photocurrents possible.

In a homogeneous spin-polarized 2DEG, a new property of the electron spin can be observed, which is able to drive an electric current provided certain requirements for

symmetry are met [17, 18]. This effect is called circular photogalvanic effect (CPGE), belonging to the category of photogalvanic effects (PGEs) which have been systematically studied in semiconductors [19, 20]. To understand the CPGE, it can be seen as a transfer of angular momentum from the photon to the directed motion of a free charge carrier. Imagine a screw thread that transmits rotatory motion into linear motion, which can be considered as a mechanical analogue of the electronic mechanism for CPGE. The microscopic mechanism is illustrated in Figure 1.5. This effect was first predicted in 1978 [21, 22] and then observed in tellurium bulk [23, 24].

Figure 1.5 A schematic picture of the CPGE in the C_s point group, induced by spin orientation for direct transitions. The splitting of subbands in k -space is considered. Arrows represent the currents due to the imbalance of carriers. Currents for only one subband are shown here. σ_+ excitation produces direct transitions (solid arrows) between (a) the valence and conduction band (b) quantized subbands in the conduction band. Due to optical selection rules and spin splitting, an unbalanced occupation of the positive (k_x^+) and the negative (k_x^-) states generate a spin-polarized photocurrent. As for σ_- excitation, the orientations for both the spin current and the spin of the charge

carriers get reversed. This figure is adopted from Ref. [18].

1.3 Organization of the Thesis

This thesis focuses on the investigation of the photo-induced electrical properties of 2D materials, including graphene and TMDs. The full contents are arranged as follows:

In chapter 2, sample preparation, device fabrication, building up experimental systems and some fundamental techniques will be discussed.

In chapter 3, the focus is the study on helicity dependent photocurrent in biased bilayer graphene. In this part, the experimental determination of the photocurrent response of bilayer graphene will be presented, as a function of light intensity and state of polarization, as well as carrier density and polarity.

In chapter 4, low temperature photoresponse of monolayer tungsten disulphide is studied. Our focus is the high response ratio and short response time. These findings are discussed in terms of charge trapping and localization.

In chapter 5, dichroic spin-valley photocurrent in monolayer molybdenum disulphide is investigated with phototransistor, elucidating the excitonic underneath. This opens up new opportunities for valleytronics applications in which selective control of spin-valley-coupled photocurrents can be used to implement polarization-sensitive light-detection schemes or integrated spintronic devices, as well as biochemical sensors operating at visible frequencies.

Chapter 6 is conclusion and future perspective of this thesis.

Chapter 2

Experimental Techniques

2.1 Sample Preparation

There are various methods to acquire atomically thin two-dimensional materials, among which mechanical exfoliation and chemical vapor deposition stand as the most widely adopted.

2.1.1 Mechanical Exfoliation

Commonly known as “scotch tape” [Figure 2.1] method, mechanical exfoliation of 2D materials from bulk was first introduced by Novoselov et al. in 2004 [1]. Take graphene as an example. The bulk graphite is constructed with stacking of graphene layers, held by weak van der Waals interaction. Therefore, when placed in between two slides of sticky tapes, layers of the high-quality bulk graphite will be detached by gently pulling apart the tapes. This process will be repeated several times until graphene layers with desired thickness are left on the tape, which can be tell by experience. Afterwards, the tape with leftover graphene is stick onto certain substrate, usually silicon wafer with silicon dioxide coating. Usually the tape will be held for a certain period of time, and proper force may also apply. Then, remove the tape from the wafer by smooth peeling off. According to Ref. [25, 26], the 300 nm thick SiO_2 can enhance the optical contrast of graphene against the substrate. Thus, we can locate our target graphene under optical microscope. Graphene layers, as well as other 2D materials, obtained by this method generally possess relatively high crystal quality. In this thesis, graphene and other 2D TMDs prepared by mechanical exfoliation are used for experiments.

Figure 2.1 Scotch tape and dicing tape, also known as “the blue tape”.

2.1.2 Bottom-Up Growth by Chemical Vapor Deposition

Although 2D materials obtained by mechanical exfoliation is easy to acquire and usually exhibit good quality, it is only applicable for lab research with almost no control of sample quantity and geometry. In order to realize the application of 2D materials, utilizing their superior mechanical, electronical and optical properties, large-scale synthesis becomes necessary.

Chemical vapor deposition (CVD) technique has been deeply developed and widely used for mass production in industry. In 2D area, CVD growth of graphene has been well studied and is quite mature [27]. Based on this, the CVD growth of TMDs are thus developed and optimized by various control of conditions and precursors [28-30]. For instance, a traditional method to synthesis single layer MoS₂ is to use MoO₃ power as precursor, and to sulfurize at high temperature [31]. Alternatively, Mo thin film, grown on Si substrate, can also be used as growth source, treated with heat, together with sulfur powder [30, 32].

In our work, we have successfully designed a CVD system for controllable growth of atomically thin WS₂ flakes, using WO₃ power and pure sulfur source [33].

Figure 2.2 shows the experimental set-up for CVD growth of WS_2 . The WO_3 (> 99.5%) and sulfur (> 99.95%) are commercially available from Sigma Aldrich. As the first step, WO_3 powder is well distributed on Si/SiO₂ substrate, which is then loaded into the center of the quartz tube. Sulfur powder is filled in a ceramic boat and place at the entrance of the tube. After evacuation, ultra-high-quality Ar flow is constantly steamed into the tube with a flow rate of 200 sccm, kept through the whole growth process. Then the heating-up begins, increasing the temperature from room temperature to 550 °C. The heating rate is 18 °C/min. Sulfur starts to vaporize at 550 °C. The heating rate is thus set to 5 °C/min, raising the temperature up to 800 °C. After that, the tube is kept at this temperature for 10 min before naturally cooling down to room temperature. By this method, the WS_2 monolayers with triangular shape can be obtained. The following optical and electrical characterizations show the high quality of these samples. Detailed discussion will be given in Chapter 4.

Figure 2.2 Illustration of the CVD set-up for growth of TMDs.

2.2 Device Fabrication

In order to investigate the electrical and opto-electrical properties of 2D materials, back-gated field effect transistors (FETs) are fabricated. Figure 2.3 shows the schematic flow chart for device fabrication process.

Figure 2.3 Schematic flow chart for FET device fabrication.

CVD grown or mechanically exfoliated 2D materials are placed on Si/SiO₂ wafer for further treatment. A thin layer of electronic photoresist, Poly (methyl methacrylate) (PMMA), is spin-coated and then the substrate is post-baked on a hot plate at 175 °C for 1 min. The post-bake helps hardening the resist and improves the e-beam lithography resolution. After locating the desired sample position under optical microscope, e-beam lithography is carried out with Zeiss Auriga system, an integrated system consists of field emission scanning electron microscope (SEM) and nano-patterning visualization engine (NPVE). We developed a precise point-to-point positioning method that can write e-beam patterns down to 500 nm with convenient approach. Subsequently, the wafer is immersed in a mixed solution of isopropanol alcohol (IPA) and methyl isobutyl ketone (MIBK) to develop the exposed area. Rinsed in IPA and blow-dried with N₂, the wafer is deposited with metal contacts, for instance 5 nm / 100 nm of Ni/Au, by thermal evaporation. After taken out, the wafer is immersed

in acetone for several hours as lift-off to remove the undesired metal film. Sometimes ultrasonic cleaning is needed to assist the removal process. Optical images of selected procedures are shown in Figure 2.4.

Figure 2.4 (a) Original image of CVD grown WS_2 . (b) Spin-coated with PMMA and patterned with marks. (c) Developed for metal deposition. (d) Final image after lift-off.

2.3 Instrumentation

In this part, I will introduce several instruments used in this thesis. Among them, my major contribution is to help design and build an integrated magneto-opto-electronics system, which will be demonstrated in Chapter 2.3.2.

2.3.1 Basic Characterization Facilities

2.3.1.1 Optical Systems

In this thesis, optical images are taken with an Olympus BX-51 optical

microscope, shown in Figure 2.5 (a). Thanks to the high-resolution camera, images with optimized quality can be taken conveniently. Additionally, a burner lamp attachment provides the ability of fluorescence excitation. This is a useful feature for us to primarily determine the optical quality of the sample.

Another powerful facility we use for sample morphology characterization is the Zeiss Auriga system, shown in Figure 2.5 (b). The field emission SEM supports nanometer grade imaging as well as the capability of e-beam lithography. Besides, the open-slot design allows further upgrade of the system with advanced features like focus ion beam (FIB), scanning transmission electron microscope (STEM) and energy dispersive spectroscopy (EDS) probe.

Figure 2.5 (a) Olympus BX-51 microscope with fluorescence attachment. (b) Zeiss Auriga system.

For the characterization of sample qualities in terms of crystal and electronical structure, Raman and photo-luminescence (PL) are commonly adopted approaches. In this thesis, micro in-situ Raman and PL measurements are conducted by a Witec CRM-200 system with a backscattering configuration. Figure 2.6 shows the configuration of the system. Initially, the sample is placed on an XYZ stage and located by manual manipulation and fine movement of a piezo stage. The piezo stage has a moving range of 100 μm by 100 μm , enabling a large area mapping for the sample. Three laser lines (457 nm, 532 nm and 633 nm) are couple with the system via single mode fibers. The

system is equipped with three gratings, 600, 1800 and 2400 grooves/mm, respectively.

Besides, combined with a Linkam Stage, spectra from 80 to 400 K can be collected.

Figure 2.6 Configuration of Witec CRM-200 system. Image adopted from Witec.

2.3.1.2 Electrical Measurement Facilities

Crucial properties of a 2D material including resistivity, carrier density, carrier mobility and Fermi level can be acquired through electrical transport measurement. This can be quickly carried out right after FET device fabrication by a probe station [Figure 2.7 (a)]. However, this is only rough measurement in ambient atmosphere and room temperature, which may exhibit inaccurate information or even damage the sample. Thus, contacts are usually connected with chip carrier by wire-bonder [Figure 2.7 (b)], and then put into vacuum chamber for further tests. This can effectively prevent the device from oxidation and burn-down during measurements, and avoid the risk of being physically damaged by the probes.

Figure 2.7 (a) Probe station. (b) Wire-bonder.

Electrical characterizations are conducted with Keithley Semiconductor Characterization Station 4200-SCS, shown as the bottom of Figure 2.8 (a). It provides a variety of built-in measurement program and the ability of customization. Additionally, to provide a constant voltage bias, Keithley 2612A sourcemeter is also used [Figure 2.8 (a), top right]. To measure photocurrent generation, lock-in amplifiers [Figure 2.8 (b)] are also utilized to illuminate the DC signal. Nevertheless, photocurrent response is usually in the order of pico-Amperes, which is way too small for common instruments to detect. Thus, a current preamplifier [Figure 2.8 (a), top left]. is applied to transfer the photocurrent signal into amplified voltage output.

Figure 2.8 (a) Top left: Stanford SR570 low-noise current preamplifier. Top right: Keithley 2612A sourcemeter. Bottom: Keithley Semiconductor Characterization Station 4200-SCS. (b) SR-830 Lock-In Amplifiers.

2.3.2 Integrated Magneto-Opto-Electronics System

A customized system is developed, integrated with liquid helium cryostat, magnet up to 9 T, high vacuum chamber, scanning table, white light illumination, laser excitation, optical chopper, optical spectrometer, Keithley 4200-SCS, sourcemeter, preamplifier and lock-in amplifier.

2.3.2.1 Attocube Magneto-Raman System

With the help from Attocube, we designed a magneto-Raman system, consisting of a cryostat, a 9 T magnet and optical spectrometer provided by Witec. A schematic view and the optical image of the system are given in Figure 2.9. With liquid helium (LHe) bath and a heater plate underneath the sample stage, the system can operate from 4.3 K up to 100 K, with a programmable temperature controller. The magnetic field, which is in vertical direction, changing from -9 T to 9 T, is generated by superconducting loops. The sample stage is an integration of an XYZ positioner and a fine-scan piezo actuator, which enables a mapping function up to 30 μm by 30 μm . In terms of excitation laser source, we have two options of 532 nm and 633 nm. The spectrometer contains two gratings, 600 and 1800 grooves/mm, suitable for Raman and PL measurements.

Figure 2.10 shows the characterization tests on the system. As can be seen, the square patterns of the test sample (Anfatec-UMG02) make it ideal for planar calibration. According to calculation based on the test results, our system can reach a spatial resolution of about 1 μm .

Figure 2.9 (a) Schematic view of the magneto-Raman system. (1) Raman system. (2) Cryostat. (3) 9 T magnet, the magnetic field is in vertical direction. (4) Piezo stage. (b) The optical image of the system.

Figure 2.10 (a) SEM image of the test sample. (b) Rayleigh mapping image at room temperature. (c) Rayleigh mapping image at 5 K.

2.3.2.2 Design and Build-Up of the Optical Component

A crucial part of the system is the optical head component [Figure 2.11 (a)] which is placed on top of the vacuum tube. The operational principle is shown in Figure 2.11 (b). This optical head requires extremely fine adjustment to optimize its performance, including laser spot size, signal intensity and coherence, CCD

visualization and white light illumination.

Figure 2.11 (a) The optical head. (b) Schematic principle of the optical head.

2.3.2.3 Combination of Electrical, Optical and Magnetic Instruments

To fully take advantage of the instruments, an integrated system is built up.

Based on the existing magneto-Raman system, an optical chopper is added to change the excitation frequency. The laser is break apart and re-aligned as shown in Figure 2.12.

The chopper provides tunable control of the incidence frequency, which is fed into the lock-in amplifier.

Figure 2.12 *Laser coupler with optical chopper.*

At the electrical terminal, the sourcemeter is connected to provide a constant voltage bias. The current signal is then transmitted into the preamplifier and thus converted to voltage output, which goes into the lock-amplifier for further amplification, based on the frequency determined by the chopper. Finally, the 4200-SCS collects the signal and records over time.

This powerful system greatly expands our ability to carry out experiments, with multiple degrees of freedom. We are able to apply a strong magnetic field, change the temperature, apply voltage or inject current, tune the polarization of the incident light, etc. On the other hand, in-situ Raman/PL can be measured as well as electrical transport and photoelectric response.

Chapter 3

Helicity Dependent Photocurrent in Biased Bilayer Graphene

Research on graphene optoelectronics is one of the fastest developing platforms to study light-matter interaction [34]. Beyond the rich fundamental physics, unique optical and electronic properties of graphene can be employed in many applications. Some examples are highly sensitive bolometers [35], photo-detectors, plasmonic devices [36] and photovoltaic devices [37] in which mainly photo-induced thermal and electronic effects are prominent.

There have been extensive studies of photo-response in graphene to elaborate its origin and significant components by using various device configurations, such as p-n junctions [38-40] and metal/graphene interfaces [41]. By varying gate voltage and drain-source bias, and tuning light frequency and pulse widths, it is possible to distinguish thermoelectric, photovoltaic and bolometric effects in observed photocurrent and photoconductivity [42]. These are major parameters to be modulated on the material side of light-matter interaction rather than the nature of illuminating light.

Another degree of freedom is light polarization. Helicity of incident radiation has been shown to be a crucial tool to link the state of polarization of radiation to the allowed Drude transitions and transitions between π and σ orbitals in graphene,

giving rise to photocurrent contributions based on the photon-drag effects (PDE), the linear photogalvanic effect (LPGE) and the circular photogalvanic effect (CPGE) [43]. Photon-drag effects (the transfer of momentum of light to the free carriers) and photogalvanic effects (quantum interference between Drude transitions and indirect intra-band transitions with states located in $P3+$ band) take place as a result of point group symmetry arguments, under oblique incidence of radiation (breaking of rotational symmetry). Particular attention has been given to the CPGE which is even at time reversal.

Here, we experimentally identify the PDE and the CPGE contributions to photocurrent via circularly polarized light in globally backgated bilayer graphene (BLG). Our findings also reveal, for the first time, an additional non-negligible component of photocurrent with anomalous dependence on light polarization, which cannot be explained in terms of quadratic response theory up to second order. These results highlight the richness of BLG photo-response, providing an opportunity to establish light helicity as an approach to manipulate the photoconductive behaviour of future optoelectronic graphene devices.

3.1 Introduction to Graphene

In 2010, the Nobel Prize of Physics went to Andre Geim and Konstantin Novoselov, for “groundbreaking experiments regarding the two-dimensional (2D) material graphene” [45]. Ever since then, graphene has attracted great interests across various areas thanks to its unique fundamental physical properties and promising applications, opening a new era for low-dimensional physics [6].

3.1.1 The Crystal Structure of Graphene Layers

Graphene, a single sheet of carbon atoms arranged in the form of a honeycomb lattice, was firstly discovered by mechanical exfoliation of graphite on top of a Si/ SiO₂ wafer in late 2004 [1]. This discovery is well acknowledged to be a great breakthrough in the nanotechnology area, bringing the concept of single atomic layer structure closer to reality [46] and leading the world into a new age for fundamental physics studies as well as high-tech applications.

The lattice structure of single layer graphene (SLG) is shown in Figure 3.1 (a). The unit cell of SLG contains two carbon atoms: A and B . The primitive lattice vectors of SLG $\mathbf{a}_1$ and $\mathbf{a}_2$ can be written as [47]:

$$\mathbf{a}_1 = \frac{a}{2}(3\hat{x} + \sqrt{3}\hat{y}), \quad \mathbf{a}_2 = \frac{a}{2}(3\hat{x} - \sqrt{3}\hat{y}) \quad (3.1)$$

where $a \approx 1.42 \text{ \AA}$, is the nearest carbon-carbon distance. The reciprocal lattice of graphene is shown in Figure 3.1(b). The Brillouin zone (BZ) unit vectors $\mathbf{b}_1$ and $\mathbf{b}_2$ are given by [47]:

$$\mathbf{b}_1 = \frac{2\pi}{3a}(\hat{k}_x + \sqrt{3}\hat{k}_y), \quad \mathbf{b}_2 = \frac{2\pi}{3a}(\hat{k}_x - \sqrt{3}\hat{k}_y). \quad (3.2)$$

Figure 3.1 (b) also shows some high-symmetry points within the first BZ of SLG. The K and K' points are two inequivalent points called Dirac Cones, located at the corners of the 2D hexagonal BZ. The M point is in the middle of K and K' points and the Γ point is at the zone center.

Figure 3.1 Honeycomb lattice and its Brillouin zone. (a) The lattice structure of single layer graphene. a_1 and a_2 are the lattice unit vectors, and δ_i , $i=1,2,3$ are the nearest-neighbour vectors. (b) The Brillouin zone of single layer graphene and reciprocal-lattice vectors b_1 and b_2 . The Dirac cones are located at the K and K' points.

As a member of the carbon family, graphene is the basic building block for all sp^2 carbon structures [47]. As demonstrated in figure 3.2, wrapping-up graphene forms zero-dimensional fullerene, rolling graphene layers along a given direction and reconnecting the carbon bonds results in one-dimensional carbon nanotube, and stacking-up graphene layers constructs three-dimensional (3D) graphite.

Figure 3.2 Top left: graphene. Top right: graphite. Bottom left: carbon nanotube. Bottom right: fullerene.

The stacking order of the individual graphene layers provides an additional degree of freedom in stacking SLG to acquire BLG, trilayer graphene (TLG) and few-layer graphene (FLG). Figure 3.3 shows the crystal structures of BLG and TLG with different stacking orders. Normally, as shown in Figure 3.2 (b), mechanically exfoliated BLG exhibits an AB (or Bernal) stacking arrangement. On the other hand, AA stacked BLG, which is energetically unstable, can be produced when Li intercalates into graphene layers of AB stacked graphite [48] or appear in carbon nanofilms fabricated by oxidation of natural graphite [49], epitaxial graphene layers on SiC (0001) [50], or diamond (111) [51]. There are two crystallographically stable configurations for TLG: ABA and ABC stacking, as shown in Figures 3.3 (d) and (e). These two stacking orders naturally coexist in graphite, having an ABA to ABC ratio around 85:15 [52].

Figure 3.3 Stacking structure for graphene layers. (a) single layer, (b) AB bilayer, (c) AA bilayer, (d) ABA trilayer, and (e) ABC trilayer. Right side is the top view along the c -axis corresponding to each stacking structure.

3.1.2 The Electronic Band Structure of SLG and BLG

Pristine single layer graphene is a zero-gap semiconductor with a linear energy dispersion relation for low energies around the six corners of the 2D hexagonal Brillouin zone, which was firstly achieved as early as 1947 by P. R. Wallace [53]. It is now well known that the linear energy dispersion of the electrons and holes near these six points makes them behave as massless Dirac fermions [54], thus these six corners of the Brillouin zone are called the Dirac points.

Considering that electrons can hop to both nearest- and next-nearest-neighbour atoms, the tight-binding Hamiltonian for electrons in graphene can be written as [47]:

$$H = -t \sum_{\langle i,j \rangle, \sigma} (a_{\sigma,i}^\dagger b_{\sigma,j} + \text{H. c.}) - t' \sum_{\langle\langle i,j \rangle\rangle, \sigma} (a_{\sigma,i}^\dagger a_{\sigma,j} + b_{\sigma,i}^\dagger b_{\sigma,j} + \text{H. c.}) \quad (3.3)$$

Here, t is the nearest-neighbour hopping energy (electrons hop between different sublattices), and t' is the next nearest-neighbour hopping energy (electrons hop in the

same sublattice). Derived from this Hamiltonian, the energy bands have the form [47]:

$$E_{\pm}(k) = \pm t \sqrt{3 + f(k)} - t'(k),$$

$$\text{here } f(k) = 2 \cos(\sqrt{3}k_y a) + 4 \cos(\frac{\sqrt{3}}{2}k_y a) \cos(\frac{3}{2}k_x a) \quad (3.4)$$

In this equation, the plus sign applies to the π^* conduction band and the minus sign is for the π valence band. By expanding the electronic band dispersion around K (K') point, for electron momentum q (with $|q|$ is much smaller than $|K(K')|$, which is measured from K (K') point), a linear dispersion equation is obtained:

$$E_{\pm}(q) \approx \pm v_F |q| + O[(q/K)^2] \quad (3.5)$$

Here, v_F is the Fermi velocity given by $v_F = \frac{3ta}{2}$ with a value of approximately 1.0×10^6 m/s, which is about 1/300 velocity of a photon.

Figure 3.4 shows the 3D electronic dispersion of graphene with $t = 2.7$ eV and $t' = -0.2t$. A linear dispersion of electronic band structure located around K (K') point could be seen, giving rise to a variety of fascinating electronic properties in graphene.

Figure 3.4 Left: The 3D image of the band structure of single layer graphene. Right: The zoom-in image of band dispersion around one of the Dirac points. Adopted from

Ref. [47].

Unlike SLG, which has only one conduction band and one valence band with linear dispersion around the K point, AB stacked BLG has two valence bands and two conduction bands with parabolic shape around K point, as shown in Figure 3.5 (a) [55]. However, as can be seen from Figure 3.5 (b), for the AA stacked BLG, two linear low-energy bands intersect each other and are almost isotropic near the K point. Moreover, its Fermi energy change from the K point to the neighbouring two points due to the interlayer coupling [56].

Figure 3.5 (a) Band structure of AB stacked BLG near K point, adopted from Ref. [55].

(b) Band structure of AA stacked BLG near K point, adopted from Ref. [56].

At energies near the charge neutrality point (CNP), the elementary electronic excitations in SLG behave as massless Dirac fermions, characterized by a Berry phase of π as observed in the anomalous quantum Hall effect (QHE) [57]. The absence of a band gap in the electronic spectrum of SLG limits its direct utilization in many electronic applications that rely on semiconducting characteristics of the underlying material, although interesting broadband applications are possible, such as non-equilibrium hot carrier extraction by photo-excited currents [58]. This limitation can be overcome, in principle, with BLG since electrons in BLG turn into massive chiral fermions due to the coupling between two layers, giving rise to an unconventional QHE [67]. A band gap can be opened and tuned by driving a potential difference between the two layers [59-61]. This electrostatic

breaking of the layer symmetry can be achieved with chemical doping [62], a direct utilization of independent top and bottom gates [63-66], or a combination of both [61], and thus obtain a continuously tunable bandgap of up to 250 meV. Electrons in BLG have intrinsically different properties than SLG, such as the different energy-momentum relation, $E_p = p^2/2m$ with effective mass m , different chirality, and a different Berry phase of 2π [67, 68].

3.1.3 The Berry's phase and the Berry's curvature in graphene

The Berry's phase, which manifests as a phase shift in transport measurements, originates from an adiabatic evolution on a closed path, either in real space or, in the case of periodic systems, in reciprocal space [82, 83]. In periodic systems with n bands, the canonical momentum $\mathbf{q}$, and the basis function $u_n(\mathbf{q})$, the phase can be expressed $\oint d\mathbf{q} \langle u_n(\mathbf{q}) | i\nabla_{\mathbf{q}} | u_n(\mathbf{q}) \rangle$ and the associated curvature as $\boldsymbol{\Omega}_n(\mathbf{k}) = \nabla_{\mathbf{q}} \times \langle u_n(\mathbf{q}) | i\nabla_{\mathbf{q}} | u_n(\mathbf{q}) \rangle$. For strictly 2D materials, such as graphene, the Berry's curvature is a vector normal to the 2D plane, because the wave-vector is only defined in the 2D plane. Consequently, in general the Berry's curvature will only manifest by coupling with another out-of-plane quantity, i.e. the gap terms in the Hamiltonian $H = |E_p| \hat{\mathbf{n}}_p \cdot \boldsymbol{\sigma}$ [54]; where $\mathbf{p} = \hbar\mathbf{k}$ is the momentum, $\hat{\mathbf{n}}_p$ is the unit vector, and $\boldsymbol{\sigma}$ are the spin-Pauli matrices. Then, the $\boldsymbol{\Omega}(\mathbf{k})$ leads to the anomalous velocity which is the product of the Berry's curvature $\boldsymbol{\Omega}(\mathbf{k})$ and the time derivative of the quasi-particle wavevector's component $\frac{d\mathbf{k}}{dt}$, where $\mathbf{k}$ is the Bloch wave vector [83]. The simplest "tools" to generate a closed path in reciprocal space are either magnetic or electric fields. The former induces a cyclotron motion, defining a closed path in the momentum space, hence generating the Berry's phase. The latter uses an electric field to move an electron from one Brillion zone to another, such that the momentum variation is $\mathbf{q} \rightarrow \mathbf{q} + \mathbf{G}$, where $\mathbf{G}$

is reciprocal lattice vector, hence acquiring also a Berry's phase.

3.2 Recent Study on Photocurrent with an Excitation of Helicity

As a great candidate to study light-matter interaction, graphene has drawn much research interest, among which photocurrent turns out to be quite powerful. Furthermore, the state of polarization adds another dimension to the parameter space available to control the photocurrent. It would be crucial for spintronic and photonic device concepts to understand these effects and how to harness the consequences.

3.2.1 Linear and Non-Linear Photo-response of Graphene

The non-linear DC electrical response of electrons to the light field can be generically written, to second order, as:

$$j_\alpha = S_{\alpha\beta\gamma} \frac{E_\beta E_\gamma^* + E_\beta^* E_\gamma}{2} + A_{\alpha\beta\gamma} \frac{E_\beta E_\gamma^* - E_\beta^* E_\gamma}{2} \quad (3.6)$$

where $S_{\alpha\beta\gamma}$ and $A_{\alpha\beta\gamma}$ are symmetric and anti-symmetric tensors of rank three [18]. This splitting of the quadratic response is advantageous because (i) the anti-symmetric combination of fields in the second term is directly proportional to the degree of circular polarization of the incoming light, and (ii) the symmetric and anti-symmetric character of $S_{\alpha\beta\gamma}$ and $A_{\alpha\beta\gamma}$ assists in identifying which terms survive for a given point symmetry of the target system. This current is strongly-dependent on the polarization and orientation of the incoming radiation, and effects such as the photogalvanic effect (PGE) and the photon-drag effect (PDE), are intrinsically associated with specific polarization states [70] (e.g. the so-called linear PDE, the linear PGE, and the circular PGE). The motivation for making this distinction among the various contributions to the photocurrent explicit lies in the distinct signatures that they display, namely a

symmetry/anti-symmetry with the inversion of helicity for linear and circular contributions to photocurrent, respectively. This behaviour can be probed by measuring the photocurrent as a function of the polarization state (phase angle) of the incident light, which can be readily achieved by passing linearly polarized light through a quarter wave plate ($\lambda/4$ plate). The plate's optical axis with respect to the incoming linear polarization, φ , defines the helicity of the outgoing light, afterwards directed at the sample. Expressing the electric field amplitudes in Equation (3.6) in terms of this quarter-wave plate angle φ , the photocurrent can be cast generically as

$$j_{\alpha} = (L_1 \sin 4\varphi + L_2 \cos 4\varphi) + (C_1 \sin 2\varphi) + D. \quad (3.7)$$

This expression encodes the most general dependence of the photocurrent on the polarization state arising from Equation (3.6), and defines the so-called linear (L_1 and L_2) and circular (C_1) contributions to the photocurrent [18]. These can be readily identified through their different periodicity on the angle φ . This is a purely geometric consequence of Equation (3.6) and, hence, holds independently of the microscopic details at play determining the coefficients L_1 , L_2 , and C_1 (these are also explicit functions of the incidence angles, which we omitted for ease of notation). It is also worth noticing that the linear contributions L_1 and L_2 are different in polarization direction. Whether such quadratic response terms are permitted is determined microscopically by the dependence of the allowed optical transitions on the polarization, as well as by symmetry constraints that require, foremost, the absence or breaking of inversion symmetry, and as well as other constraints imposed by the 6-fold (3-fold) and horizontal plane symmetries of graphene (BLG).

3.2.2 Photocurrent Study on Graphene with Infrared Laser Excitation

The linear PGE (LPGE) and circular PGE (CPGE) are two particular cases of the photocurrent that is induced under general elliptic polarization and oblique incidence

of radiation [43]. As shown in Figure 3.6, single layer graphene exhibits clear polarization dependence. In Ref. [43], the authors fitted their data according to the phenomenological equations:

$$\vec{j}_y = \vec{j}_{yA} \sin 2\varphi + \vec{j}_{yB} \sin 4\varphi + \xi \quad (3.8)$$

$$\vec{j}_x = \vec{j}_{xB'} \cos 4\varphi + \vec{j}_{xC} \quad (3.9)$$

They interpreted the equation by photogalvanic effect and photon-drag effect. The directions and magnitudes of the photocurrents depend on the radiation polarization state. Meanwhile, the major contribution to the photocurrent changes its sign when reversing the radiation helicity. First of all, the photocurrent may generate due to the combined action of the electric and magnetic fields of the laser wave (or transfer of the radiation wave vector to the electron ensemble). Secondly, the current may arise due to the photogalvanic effects which become possible when the presence of the substrate breaks the inversion symmetry.

Figure 3.6 Photocurrent response as a function of the angle φ , defining radiation helicity. $\vec{j}(\varphi)$ is measured at room temperature. Solid lines show fits according to Eq. (3.8) and Eq. (3.9). Adopted from Ref. [43].

3.2.3 Helicity Dependent Photocurrent in Topological Insulators

Recently, novel applications of the CPGE were reported that polarization was shown to allow control over of photocurrents arising from the topological surface states in a topological insulator [44]. The photocurrent generated by illuminating the TI Bi_2Se_3 with circularly polarized light reverses the current direction while reversing the helicity of the light. As shown in Their result agrees well with the phenomenological expression:

$$j_y(\alpha) = C \sin 2\alpha + L_1 \sin 4\alpha + L_2 \cos 4\alpha + D \quad (3.10)$$

Fig 3.7 Surface photocurrent originating from helical Dirac fermions, adopted from Ref. [44].

This opens new prospects of harnessing helicity-dependent photocurrents for technological use.

3.3 Materials and Methods

3.3.1 Sample Preparation

The BLG flake was obtained from highly ordered pyrolytic graphite by mechanical exfoliation [1], on top of a silicon wafer with SiO_2 coating. The 300 nm thickness of the oxide enhanced the visual contrast to locate the graphene through an

optical microscope and to estimate its layer number. We carried out Raman measurement to further confirm the thickness of our BLG sample [71, 72] by calculating the G/G' ratio of intensity and the full width half maximum (FWHM) of G/G' peak, as shown in Figure 3.8 (b). The flake was then fabricated into device by standard EBL and thermal deposition of Ti (5 nm) / Au (60 nm) as contacts.

3.3.2 Photocurrent Measurements

The photocurrent is measured at room temperature in ambient conditions, by illumination of graphene and BLG phototransistors under a continuous wave laser with $\hbar\omega = 2.33$ eV and a focus spot 200 μm in diameter. A schematic diagram of the setup is given in Figure 3.8 (a). The linearly polarized laser was tuned from 0.5 mW to 20 mW and chopped at 137 Hz before passing through a $\lambda/4$ retarder, and is subsequently directed obliquely (incidence angle θ) towards the sample in such a way as to keep the spot center aligned with the geometrical center of the sample. The photocurrent at the chopping frequency is measured with a lock-in amplifier. This experimental setup allows one to vary continuously the helicity of the radiation reaching the device by rotating the wave plate, and we use the angle φ between the plate's fast axis and the initial linear polarization as the parameter that identifies a particular helicity.

As illustrated in Figure 3.8 (a), light impinges on the sample of BLG at a constant $\theta = 50^\circ$ oblique incidence and the current is measured perpendicularly to the plane of incidence. An electric field is applied perpendicularly via a global back-gate provided by the doped-Si portion of the substrate, which allows the variation of the carrier density by field effect. The BLG device has a mobility of $1850 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, determined by a linear fit to the drain current vs back-gate voltage data.

Figure 3.8 The photocurrent setup and photocurrent of BLG. In (a) we schematically depict the measurement layout. The centre of the BLG phototransistor device with Ti/Au electrodes defines the origin ($y = 0$, $x = 0$) of the coordinates in the plane. The laser frequency is $\hbar\omega = 2.33 \text{ eV}$. (b) Raman spectrum of the BLG sample, taken by 532 nm incident laser, showing G peak (1580 cm^{-1}) and G' peak (2700 cm^{-1}). (c) Characterization of the photocurrent as a function of laser intensity (points), and the best linear fit (line). Polarization-dependence studies were performed at 8 Wcm^{-2} . (d) photocurrent measured under oblique incidence, at an angle $\theta = 50^\circ$ in the Oxz plane, as a function of the position of the centre of the focused beam along the length of the device.

3.4 Results

Figure 3.8 (c) shows that the measured photocurrent varies linearly with laser

intensity, establishing it as arising from the quadratic response to the electromagnetic field. All the measurements discussed below are performed at a constant intensity of 8 W/cm². It is important to note that the magnitude and sign of the photocurrent induced in the sample generally depends on the position of the centre of the spot within the channel, as can be seen explicitly in Figure 3.8 (d), and thermoelectric contributions must be carefully eliminated [44]. For this reason, the analysis of the polarization dependence of the photocurrent was performed with the laser spot at the geometrical centre of the sample, corresponding to the longitudinal position $y=0$ in Figure 3.8 (d).

Figure 3.9 photocurrent measurements for elliptically polarized light. The data are acquired at fixed oblique incidence ($\theta = 50^\circ$) with two different azimuthal alignments. (a) and (b) represent the two alignments considered, with the plane of incidence parallel to the Oxz and Oyz planes, respectively. In (c) and (d), we plot the respective photocurrent as a function of the angle of the quarter-wave plate, φ . Data are represented by the black circles. The three lines correspond to three different fitting

schemes: the one represented by the dashed (violet) line takes all the constants in (3) (i.e., C_1 , L_1 , L_2 , D , and E) as fitting parameters; the solid (blue) line explicitly constrains $L_1 = 0$; the dotted (blue) fit explicitly forces $E = 0$. Scale bars in each graph mark the vertical (current) scale. The insets show the magnitude of the fitted parameters and the horizontal bar is 300 pA.

Figures 3.9 (c) and Figures 3.9 (d) show the photocurrent measured in the transverse and longitudinal geometries depicted in Figures 3.9 (a) and Figures 3.9 (b) respectively. At zero back-gate voltage and no bias, the transverse photocurrent (i.e., perpendicular to the incidence plane) of the sample can be best fit by the formula,

$$j_y = C_1 \sin 2\varphi + L_1 \sin 4\varphi + L_2 \cos 4\varphi + D + E \cos \varphi \quad (3.11)$$

where C_1 is the coefficient associated with the circular component of the incoming light, L_1 and L_2 with the linear components, and D is a polarization-independent term. The inclusion of the last term, varying with $\cos\varphi$ and in principle not anticipated according to Equation (3.11), is found necessary to accurately describe the dependence of the photocurrent on the polarization state over the full range of variation of the polarization. This is illustrated by the three different fits to the measured photocurrent in Figure 3.9 (c), which highlight the need for a finite E to capture the large-scale modulation of the photocurrent signal with φ . The photocurrent magnitude is in the sub nano-Ampere range and, for selected polarization states, has values: 300.9 pA at $\varphi = 45^\circ$ (left-circularly polarized light, $\oslash$), 283.9 pA at $\varphi = 135^\circ$ (right-circularly polarized light, $\otimes$), 286.6 pA at $\varphi = 225^\circ$ ($\oslash$), and 302.2 pA at $\varphi = 315^\circ$ ($\otimes$). In the longitudinal configuration, the solid fitting curve in Figure 3.9 (d) yields photocurrent amplitudes for $\varphi = 45^\circ$, 135° , 225° , and 315° of 287.9, 291.8, 286.7, and 291.1 pA, respectively. Note that the anomalous behaviour proportional to $\cos \varphi$ is absent in this geometry where the current is measured parallel to the incidence plane. Also, the photocurrent exhibits a

similar polarization dependence in the longitudinal and transverse geometries, in particular, the currents has similar magnitude and sign for both left and right circular polarizations. Except for this anomalous photocurrent contribution, the polarization dependence of the terms proportional to L_1 , L_2 , C_1 , D follows directly from the DC response to an electromagnetic field in second order [18].

Control measurements of the photogalvanic response under the same experimental conditions were performed on a SLG flake. Figure 3.10 shows the power dependent photocurrent response. Similar to the BLG, the data of SLG FET sample are taken at 8 Wcm^{-2} , which is in the linear regime of photocurrent vs. laser intensity.

Figure 3.10 Photocurrent vs. laser intensity of the single layer graphene FET sample is shown. The arrow indicates the power used in all helicity dependent photocurrent measurements which is 8 Wcm^{-2} .

At zero backgate voltage, the photocurrent amplitude and phase are measured as a function of incident light polarization in Figure 3.11 (a) and (b), respectively. The oscillations in the data are similar to the p-type SLG reported previously.

Figure 3.11 Photocurrent amplitude and phase of the single layer graphene FET. Photocurrent of graphene as a function of the angle of photon polarization at zero backgate voltage, is shown. Black spheres in (a) are the photocurrent amplitude measured, blue solid curve is the fitting function based on the photocurrent formula. The coefficients, C_1 , L_1 , L_2 , D , and E are determined from this fitting. (b) The signal is $\sim 180^\circ$ and out-of-phase.

The photocurrent formula $j_y = C_1 \sin 2\varphi + L_1 \sin 4\varphi + L_2 \cos 4\varphi + D + E \cos \varphi$ to determine the photocurrent contributions is fitted to the data. The coefficients C_1 , L_1 , L_2 , D , and E are extracted and used in Figure 3.12 together with values determined at other backgate voltages. The values of the photocurrent anomaly term, E ($\cos \varphi$ term), are very small and there is no clear backgate voltage dependence of this term, unlike BLG. This evidences that the mechanism in BLG is different than SLG. This is possibly because, as a function of backgate voltage, it is possible to obtain a current which is most probably due to the asymmetry in BLG structure which is absent in SLG.

Figure 3.12 Photocurrent amplitudes as a function of backgate voltage in single layer graphene (a) the CPGE component C_1 fully filled spheres, L_1 half filled spheres, (b) the $\cos \varphi$ term, E , (c) polarization dependent PDE component L_2 , and (d) polarization independent PDE component D . Spheres are data points determined from PC formula fittings of the data at specific backgate voltages. Based on theory, the data for C_1 , L_2 and D behave as the Fermi-Dirac functions, which fits well, particularly around the charge neutrality point. In single layer graphene, there is no noticeable E term dependent photocurrent as a function of backgate voltage as shown in (b).

The SLG results demonstrate no noticeable photocurrent anomaly, suggesting that the anomalous photocurrent contribution might be characteristic of the BLG.

Figure 3.13 Dependence of the resistance and photocurrent on the back-gate voltage for BLG at $\varphi = 0^\circ$. The colour gradient drawn in the background of the resistance (a) and photocurrent (b) graphs represents the carrier density at a given back-gate voltage. The charge neutrality point is identified by the peak in the resistance circa 32 V, which coincides with the voltage at which the photocurrent changes sign as a result of the modification of carrier type.

To study the sensitivity of the photocurrent to the character and density of the charge carriers, the same measurements were repeated at different back-gate voltages (V_{bg}). Figure 3.13 (a) presents the resistance as a function of V_{bg} characteristic of our BLG sample, which is hole-doped at zero V_{bg} and has the CNP at around 32 V where the resistance reaches its maximum value. The corresponding back-gate dependent photocurrent signal measured at $\varphi = 0^\circ$ is shown in Figure 3.13 (b): it is characterized

by a monotonic increase in magnitude from $V_{bg} \approx -50$ V to $V_{bg} \approx 5$ V (in this range the photocurrent increases by 110 pA), followed by a fast decrease in magnitude and sign change at the CNP associated with the transition from hole to electron conduction. The gate voltage corresponding to zero photocurrent coincides with the CNP extracted from the resistance characteristic. This behaviour of the photocurrent in BLG is similar to the one reported for SLG, in which photovoltaic effects were seen to dominate [73]. With the ability of varying the back-gate voltage, the coefficients of the different terms in Equation (3.11) can be studied as a function of carrier sign and density, n . We carried out such a study by extracting $j_y(n, \varphi)$ in the full range of φ and fitting to Equation (3.11) for each density. The result is summarized in Figure 3.14, which shows the variation of the coefficients $C_1 - E$ with density.

Figure 3.14 Selected photocurrent contributions as a function of back-gate voltage for elliptically polarized light propagating in the Oxz plane. Each graph represents one of the coefficients introduced in (3). Circles represent the numerical value obtained from a data fitting similar to the one described in Figure 3.9 at each back-gate voltage. In panels (a), (c), and (d) dashed lines are the Fermi-Dirac functions that best fit the data. In panel (b) a straight line is drawn in the range $10 \text{ V} < V_{bg} < 50 \text{ V}$ around the charge neutrality point for reference.

3.5 Discussion

In Ref. [43], the low-frequency (THz) photocurrent response of monolayer graphene was studied, and its behaviour as a function of frequency, polarization and incidence angles has been attributed to the interplay between the so-called AC Hall effect, a type of photon-drag effect whereby momentum transfer occurs between the radiation field and the electrons and dominates at low frequency, and photogalvanic

contributions that are possible if the substrate interaction is enough to break the inversion symmetry, and was seen to dominate at higher frequencies [43]. In contrast with the results reported in this reference for monolayer graphene, for which the photocurrent is seen to be dominated by the contribution proportional to the light helicity ($\sim \sin \varphi$), our photocurrent fits show that the current is dominated by the polarization-independent contribution in both geometries, followed by the linear and anomalous terms in order of importance/magnitude (the latter only present in the transverse geometry). From this perspective, the photocurrent response seen here in BLG shares greater similarity to that found in the three-dimensional topological insulator Bi_2Se_3 at high frequency [44], than the photocurrent response of SLG at low frequencies.

The most important question with regards to our data refers to the origin of the photocurrent in the first place. An intrinsic photocurrent will be possible if inversion symmetry is broken and a band gap is induced in the BLG's electronic structure. In this situation, a non-zero Berry curvature arises [74] which enables a non-zero quadratic response to the electromagnetic field [75] in the absence of any scattering mechanism. However, by computing this intrinsic photocurrent explicitly, we found that its magnitude is much smaller than the photocurrent measured at the excitation frequencies used experimentally. This can be seen in Figure 3.15, where the typical magnitude at the relevant frequencies is much smaller than the average 300 pA that are measured experimentally. In Figure 3.15, we plot the only independent and non-vanishing component of the second order conductivity tensor for optical rectification in gapped BLG, i.e. $\sigma_{222}(\omega)$. The point group of AB stacked BLG contains the C_3 rotation symmetry, implying that any rank three tensor contains only four non-zero in-plane elements related by $\sigma_{222} = \sigma_{211} = \sigma_{121} = \sigma_{122}$ [76].

Figure 3.15 Second order conductivity for optical rectification in gapped BLG. The curves represent the dependence of the only independent second order conductivity tensor σ_{222} on photon frequency. The conductivity is presented in units of $\sigma^{(2)} \equiv \frac{e^3 a_0}{4\gamma_0 \hbar} = 2.88 \times 10^{-15} \text{ m}^{-2} \text{ A}^3 \text{ kg}^{-2} \text{ m}^{-1} \text{ s}^6$, and the tight-binding parameters used in this calculation are discussed in the main text. The main panel shows the intrinsic photogalvanic response in the low to mid energy range, whereas the inset highlights the region of higher frequencies relevant for the experiments, and where $\sigma_{222}(\omega)$ is a monotonous function of frequency.

The main plot shows the response in the infrared range, while the inset focused on the vicinity of the laser energy used in our experiments. In the infrared range the response shows clear features associated with vertical transitions from valence to conduction bands at 0.179 and 0.512 eV. For this calculation we approximate the electronic structure of BLG within the standard four-band tight-binding framework [47] with the following parameterization: in-plane hopping $\gamma_0 = 3.0$ eV, out-of-plane hopping $\gamma_1 = 0.4$ eV, external bias $V = \Delta/2 = 0.2$ eV, chemical potential $\mu = 0$ eV (in

the middle of the gap), and $T = 300\text{K}$. To obtain the quadratic conductivity tensor, we compute the intrinsic second order response to the electric field in the framework proposed by Aversa and Sipe [77]. The intrinsic processes that lead to the photocurrent are associated with mixed intra and inter-band electronic transitions [77]. At the laser energy used in our experiments, this intrinsic quadratic conductivity has a magnitude of $\sigma_{222}^{(2)} \approx 0.2 \sigma^{(2)}$, where $\sigma^{(2)} \equiv \frac{e^3 a_0}{4\gamma_0 \hbar} = 2.88 \times 10^{-15} \text{ m}^{-2} \text{ A}^3 \text{ kg}^{-2} \text{ m}^{-1} \text{ s}^6$. Considering our device dimension and geometry, a simple estimate of the order of magnitude of the photocurrent associated with this value of $\sigma_{222}^{(2)}$ for linearly polarized light perpendicular to the current yields $I^{(2)} \approx 4 \times 10^{-2} \text{ pA}$. Moreover, such intrinsic response requires a finite and sizable gap, which, although possible in our doped back-gated samples (the high peak, $\sim 40 \text{ k}\Omega$, in resistance vs V_{bg} seen in Figure 3.13 (a) at the CNP suggests that our samples might be gapped.), would not explain the order of magnitude of the measured currents. This indicates that other photogalvanic or photon-drag effects are responsible for the observed photocurrent.

At the microscopic level, the linear PDE (LPDE) can be characterized on general grounds in terms of the transition rate $M_{b,a}^{\mathbf{k}}$ from an initial electronic state a to a final state b of the electron due to illumination with photons having wave vector $\mathbf{k}$ and simultaneous scattering by impurities or phonons. The second-order DC response can be written as [18]:

$$j_{\text{LPDE}} = \frac{8\pi e}{\hbar} \sum_{a,b} [\nu_b \tau(\varepsilon_b) - \nu_a \tau(\varepsilon_a)] |M_{b,a}^{\mathbf{k}}|^2 [f(\varepsilon_a) - f(\varepsilon_b)] \delta(\varepsilon_b - \varepsilon_a - \hbar\omega) \quad (3.12)$$

where ν is the magnitude of the electron velocity, $\tau(\varepsilon)$ the momentum relaxation time, and $f(\varepsilon)$ the Fermi-Dirac distribution function. In Figure 3.14 (c) and Figure 3.14 (d), we observe a step-like behaviour of the photocurrent with respect to V_{bg} , i.e. with respect to the chemical potential of the device. Both L_2 and D exhibit a similar behaviour near

the CNP. They both fit well to a Fermi-Dirac function (the dashed curve) that shows saturation at 20 V (on negative values of photocurrent) and 45 V (where it saturates at positive photocurrent). The L_2 coefficient symmetrically saturates at -15 pA and 15 pA, while D saturates at -300 pA under hole doping. Under electron doping, D seems to saturate at 100 pA, although we cannot be definitive with regards to the behaviour here given that the CNP is relatively close to our operational maximum positive back-gate voltages. This asymmetry with respect to the CNP in the saturation values of photocurrent for the coefficient D strengthens the hypothesis of graphene-substrate interaction, while the symmetry seen in the saturation of L_2 in the hole- and electron-doped regimes is consistent with the associated photocurrent contribution arising from the graphene sample alone, which has particle-hole symmetry [43]. From the values of L_2 and D deep in the electron and hole-doped regimes, we estimate that $D/L_2 \sim 20$ and 6 in p-type and n-type samples, respectively.

For the excitation energies used in our experiments and the proximity to the CNP we expect the photocurrent to be dominated by electronic processes in the vicinity of the $\mathbf{K}$ and $-\mathbf{K}$ points (or valleys) in the Brillouin zone. This is analogous to the spin-orientation induced CPGE which takes place as a result of two different hole spin states in semiconductor quantum wells with the Cs symmetry [39]. In the present case, instead of spin states, there are two different valleys, which leads to a modified optical transition matrix at $\mathbf{k} = \pm\mathbf{K}$, $M_{b,a}^{k=\pm K}$, in Equation (3.12). The photocurrent contribution due the CPGE can then be expressed as [18]:

$$j_{\text{CPGE}} = \frac{8\pi e}{\hbar} \sum_{a,b} [v_b \tau(\varepsilon_b) - v_a \tau(\varepsilon_a)] |M_{b,a}^{k=\pm K}|^2 [f(\varepsilon_a) - f(\varepsilon_b)] \delta(\varepsilon_b - \varepsilon_a - \hbar\omega). \quad (3.13)$$

From here, j_{CPGE} is expected to be smaller than j_{LPDE} , since $|M_{b,a}^{k=\pm K}|^2$ is smaller than $|M_{b,a}^k|^2$. In Figure 3.14 (a), the C_1 term due to the CPGE is plotted as a function of

V_{bg} . The values fluctuate slightly for $V_{bg} < 20$ V, but there is an increasing trend from 20 V to 50 V. Comparison of panels (a) and (c) in this figure shows that C_1 is smaller than L_2 by a factor of ~ 5 in the hole-doped regime, and by ~ 2 at the highest electron doping that we could achieve. The asymmetry in the V_{bg} dependence of the C_1 term can be due to processes influenced by electron-hole asymmetry [47], as observed in Figure 3.13.

Although we cannot provide a phenomenological justification for the anomalous contribution to the photocurrent, our data are seen to be best fitted with the inclusion of the term proportional to $\cos \varphi$ in Equation (3.11). Inspection of Figure 3.14 (b) shows that in the vicinity of the CNP ($10 \text{ V} < V_{bg} < 50 \text{ V}$), the coefficient E is approximately linear in V_{bg} , hence in carrier density, and is most pronounced at 10 V and 50 V, as demonstrated in Figure 3.16. This contribution is then progressively suppressed upon entering the deep hole-doped regime, becoming zero at around -50 V.

Figure 3.16 Photocurrent vs. angle of photon polarization at (a) 10 V, (b) 50V backgate voltage. Grey spheres are the data. Blue solid curve is the fitting function based on the photocurrent formula. The inset shows the coefficients. The coefficient E is well pronounced.

Interestingly, if one considers a finite Berry curvature [74] in BLG given by

$\Omega(\mathbf{k}) = \frac{\eta \xi \Delta 2k^2}{\lambda_k^3} \hat{\mathbf{e}}_z$ (here $\xi = 1(-1)$ for valley $\mathbf{K}(-\mathbf{K})$, $\eta = \pm 1$ for right- and left-circularly polarized light, Δ is the bandgap, and λ_k is related to the gap and wave vector), its contribution to the photocurrent can be written semi-classically as [78]:

$$j_{\Omega(k)} = e \int \frac{d^2k}{4\pi} [\mathbf{k} \times \Omega(\mathbf{k})] g(\mathbf{k}) \quad (3.14)$$

where $\mathbf{k} = (e\mathbf{E}/\hbar)$, $\Omega(\mathbf{k}) = \Omega(k, \theta)\hat{\mathbf{z}}$, and $g(\mathbf{k}) \propto (e\mathbf{E} \cdot \mathbf{v}_\mathbf{k}) \cdot \tau_\mathbf{k} |(df/d\varepsilon)|_{\varepsilon=\varepsilon(\mathbf{k})}$, reflects the deviation from the equilibrium distribution of the charge carriers within a relaxation time $\tau_\mathbf{k}$. In the limit of small gap, one can show that the term in Equation (3.13) that survives under circular polarization can be cast as:

$$j_{\Omega(k)circ} \propto \frac{2e^3}{\pi^2} \frac{\Delta\tau}{\hbar^2} \varepsilon_F \quad (3.15)$$

For each valley, where $\varepsilon_F = \frac{\pi\hbar^2 n}{m}$ is the chemical potential, with n the charge carrier density. The asymmetry expected in the valley population under circular light polarization could then yield a net photocurrent directly related to the non-trivial Berry curvature and the degree of circular polarization. In other words, one would obtain a photocurrent contribution linear in density, as the one observed for the anomalous term in the vicinity of the Dirac point [Figure 3.14 (b)]. We note, however, that any non-trivial contributions to the quadratic response arising from a finite Berry curvature in BLG would be expected to contribute to one of the coefficients C_1 , L_2 or D in Equation (3.11), but not to the anomalous amplitude E [78].

3.6 Conclusion

We studied the spontaneous generation of a DC electrical current in a graphene bilayer under illumination by a monochromatic laser field, with a particular emphasis on its sensitivity upon the polarization state of the incoming light and the density and

type of carriers in the system. The dependence on the polarization allowed us to identify different contributions to the photocurrent: one due to the LPDE, one from the CPGE, as well as a polarization-independent contribution. While the LPDE in BLG is similar to that in the monolayer counterpart, the CPGE is expected to be larger in BLG, since the response can be enhanced as the thickness increases. However, there is no such pronounced enhancement of the CPGE in our data which may be attributed to the low effective number of electrons per atom for polarization in the Oxy plane than for polarization in $\hat{z}$ direction [78], or to the high excitation energy used. Nevertheless, photocurrents arising from the CPGE can, in principle, be enhanced with the integration of tailored plasmonic structures, as the higher absorption that they promote should lead to a more pronounced photocurrent response [79].

The origin of the anomalous contribution to the photocurrent proportional to $\cos \varphi$ remains unclear. On the one hand, various control experiments done on SLG show that such a term is absent [Figure 3.12], as one expects on the most general grounds, following Equation (3.10). Nevertheless, in all our transverse measurements in BLG, the polarization dependence of the photocurrent seems to require such an additional dependence to be best fitted. In addition, position dependence of photocurrent contributions in BLG is also considered. In Figure 3.17, extracted photocurrent contributions are plotted as a function of y position at zero backgate voltage. Helicity dependent photocurrent fittings obtained at various y positions show that C_1 , L_2 and E are largest around the centre ($y = 0$), and become smaller towards contacts. On the other hand, the polarization independent contribution changes sign around the centre of the sample, similar to the behaviour of the total measured photocurrent.

Figure 3.17 Photocurrent contributions at various y positions at zero backgate voltage. The data are extracted from helicity dependent photocurrent fittings. All the polarization dependent contributions are largest around $y = 0$, while the polarization independent component changes sign as expected.

Except for the polarization-independent contribution, all the other terms in the photocurrent (including the anomalous E term) are largest for $y = 0$, and decay towards the contacts. This suggests that the $\cos \varphi$ anomaly in the photocurrent stems from the same mechanisms driving the emergence of the other (regular) polarization-dependent terms. Thus, this warrants further experimental and theoretical investigation in the future to identify its prevalence across other electronic systems, and the underlying conditions and microscopic mechanism.

Finally, there is much interest in characterizing the photogalvanic response beyond that of isolated graphene and its derivatives. The ultrasensitive and fast photo-response of TMDs motivates the future study of valley-dependent photogalvanic effects in heterostructures combining graphene and TMDs [80, 81]. A platform based on the control of electrical currents and valley polarization by combining light helicity and electrostatic gates, such as the system we studied here, stands to open the door for opto-

valleytronic device applications based on graphene.

Chapter 4

Low Temperature Photoresponse of Monolayer Transition Metal Dichalcogenide

The remarkable properties of graphene and the recent availability of preparation methods have triggered the research community to further explore other 2D materials. With the great research of graphene [6-8], various classes of 2D materials have attracted considerable attention from the research community of both fundamental sciences and developing applications [141-143]. Recently, transition metal dichalcogenides (TMDs), possessing analogous structure to graphene, have attracted considerable attention due their broad range of optical, electronic and mechanical properties. Monolayers of semiconducting TMDs, such as 2H-MoS₂, 2H-MoSe₂, 2H-WS₂ and 2H-WSe₂, which are the direct band gap materials, have demonstrated the striking light emission ranging from the visible to near infrared region and unique electric properties [124, 126, 144-147]. 2D TMD materials have various classes of electrical properties including semiconducting, metallic, half-metallic, superconducting, and charge density wave characteristic [2]. Here we will focus on semiconducting TMDs, which own intrinsic band gaps in the visible to the near-infrared spectral range and become fascinating materials for electronic and optoelectronic applications.

4.1 Introduction

The family of TMDs has members which have many technologically important

properties and physically interesting states [84]. When they are thinned to few layers and become 2D materials [10], they may present new phases of charge density waves [85] and superconductors [86], or semiconductors [87]. Among these, 2D semiconductor TMDs, as well as their heterostructures [88, 89] and hybrid structures [3, 90], are promising for a variety of potential optoelectronic applications owing to their direct band gap at K valley in monolayers [91]. Some applications can be named as high on and off ratio phototransistors and fast photodetectors [92], as well as future devices based on spin-valley coupling [93]. In order to make standardized, effective, and dynamic optoelectronic devices based on TMDs, there are three major issues to elaborate: (i) to produce single crystal, large area samples with strong homogeneous luminescence, (ii) to fabricate devices with high but tunable photoresponse, and (iii) to find the right TMDs for rapid yet well-defined response and detection reflecting intrinsic semiconducting properties.

There has been important advance in dealing with the first issue by mastering on growth techniques. Over the last few years, strong excitonic photoluminescence of monolayer TMDs, such as MoS₂, and WS₂, has been demonstrated, particularly in mechanically exfoliated single crystal flakes with sizes less than 10 μm [94]. Interesting strain [95] and thermal conductance [96] properties were observed in these exfoliated samples. Growth of large-area, while maintaining similar high quality, flakes of MoS₂ and WS₂ on SiO₂ and WS₂ on sapphire substrates, was succeeded by chemical vapour deposition (CVD) methods [97-99]. Recently, by utilizing an advanced CVD method, triangular flakes of WS₂ with size exceeding 250 μm were grown [33]. By this method, it is possible to obtain monolayer WS₂ flakes with homogeneous, high crystalline quality, and nonblinking luminescence [100] which are stronger than their exfoliated counterparts and their cousin MoS₂. Tunable emission by electrical gating [101] and

chemical doping [102] has been demonstrated for these CVD grown flakes.

Solutions to the issues related to optoelectronic device performance have been guided by the extensive knowledge of graphene, which is the leading 2D material without a natural band gap. High photoresponsivity (8.61 A/W) of graphene was reported [103], when graphene is lithographically designed into graphene quantum dots, which is about three orders of magnitude higher than that of graphene photoresponse reported previously [104]. The main reason for this was defects in the mid-gap band. However, control over defects as well as the origin of the photocurrent is not well understood [103]. Instead of artificially created gaps and such structures it would be more beneficial to use natural semiconductors, such as 2D TMDs which could be precisely controlled by tuning the device both electrically and optically. Recently, a phototransistor based on monolayer MoS₂ in off state and with sub-micro watt illumination intensity showed a photoresponse of 880 A/W [80]. A photoresponse of four orders of magnitude higher than that of MoS₂ phototransistors was reported for graphene/MoS₂ heterostructures [105]. However, in both cases, charge trapping either in MoS₂ or in the interface of MoS₂ and the substrate cause to slow down the response.

Although ultra-high-gain photoresponse has been obtained in 2D heterostructures, one of the most important components of future's technology, fast and reliable photodiodes require high speed response and detection. Since trapped charges, which are mainly due to natural defects in MoS₂, are the reason for slow carrier recombination [105], alternative 2D TMDs such as WS₂ and WSe₂ which are relatively more intrinsic and less defective [106] have attracted attention. In order to investigate TMD device photoresponse independent of the interface effects, low temperature characterizations are needed in which phonon assisted processes are expected to be negligible [107]. Although, a field effect transistor (FET) device based on 20 nm thick

mechanically exfoliated WS₂ with photoresponsivity of 0.86 A/W [108], a photosensor based on few layer WS₂ [109], and electrical measurements of monolayer WS₂ FET at room temperature [99, 110], have been reported; there are no photoresponse of monolayer WS₂ FET studies up to date.

4.1.1 Structure of TMD Materials

In the TMDs family, although over 40 different compounds exist, not all of them are in layered structures [3]. An individual layer of TMD materials comprises of three layers of atoms, which is formed in X-M-X structure, where X represents a chalcogen and M is transition metal element from group IV, V and VI. In monolayer, metal atom is arranged between two layers of hexagonally packed chalcogen atoms and each TMD layer weakly stacks by van der Waals interaction. Bulk TMDs include diverse polytypes depending on the stacking sequences of the layers, whereas two stacking polytypes are found in a monolayer, which are trigonal prismatic and octahedral [2, 3, 121-123]. Trigonal prismatic phase [Figure 4.1, left], which is also referred to 2H (1H for monolayer), belong to D_{3h} point group, while octahedral [Figure 4.1, right] belongs to D_{3d} point group (1T phase). For the 2H phase, the position of S atom in upper layer is exactly on top of that on lower layer, whereas the S atoms in upper and lower layers are offset from each other in the 1T phase. Generally, MoX₂ and WX₂ compounds such as MoS₂, MoSe₂, WS₂, WSe₂ are semiconductors, and have been found predominately as the 2H polytype [123]. However, fabrication of these semiconducting TMDs using chemical exfoliating methods leads to the conversion to the 1T polytype [124]. The difference between the 1T and 2H phases has been distinguished by high-resolution scanning transmission electron microscopy [121]. Difference in crystal symmetry substantially changes the electronic structure of TMDs as revealed by recent studies that 2H-MoS₂ exhibits semiconducting, while 1T-MoS₂ is metallic [121, 124].

Figure 4.1 Schematic structures of monolayer TMD with trigonal prismatic coordination (left) and octahedral coordination (right). The purple atoms represent metal and the chalcogen atoms are shown in yellow. Adopted from Ref. [3].

4.1.2 Electronic Structure of TMDs

MoS₂ and its counterpart structures such as WSe₂, WS₂, and MoSe₂ are regarded as semiconductors. The band structures of bulk and monolayer MoS₂ calculated from first-principle density functional theory (DFT) are presented in Figure 4.2 [125]. For bulk, the excitonic transition is indirect band gap transition. When the MoS₂ layers are thinned down to a monolayer, it becomes direct band gap material and the transition occurs at the K point of Brillouin zone [125, 126]. It is found that the direct excitonic transition (K-K) rarely changes with the TMD thickness. However, indirect band gap substantially increases with increasing thickness. Note that various TMDs have similar overall features in their band structures [125, 127]. The varying electronic structures of TMD materials with number of layers arise from quantum confinement effect and the alteration in hybridization between p_z orbitals of chalcogen atom and d orbitals of metal atom [126, 87]. DFT calculation of MoS₂ layers demonstrates that the conduction band states around the K point predominately originate from localized d orbitals of Mo atoms. Mo atom is arranged at the center of S-Mo-S slab and thus, it experiences less impact from the interlayer coupling [126]. In contrast, the states near the Γ point associating the indirect band gap transition arise from the combining effects from both d orbitals of Mo and antibonding p_z orbitals of S [126]. Therefore, the states near the Γ point remarkably

change with the number of TMD layers. The band gaps of bulk and monolayer semiconducting TMDs have been predicted to be ~ 1.1 -2 eV in the visible and near infrared range [125, 127, 128].

Figure 4.2 Band structures of bulk and monolayer MoS₂. The lowest energy transitions are represented by arrows. In bulk MoS₂, the lowest energy transition is indirect band gap transition, while monolayer MoS₂ is direct band gap transition. Adopted from Ref. [110].

4.1.3 Recent Progress in TMD Studies

Abundant efforts have been devoted to fabrication of monolayer 2D semiconducting TMDs with good quality and scalable size. It has been reported that monolayer TMDs can be obtained by various techniques such as mechanical cleavage [129], chemical exfoliation [124] and CVD [133]. Substantial band gaps in TMD family make them interesting channel materials for FETs. Several works have demonstrated the utilizing monolayer MoS₂ as FETs, which exhibit excellent on/off ratio and low sub-threshold swing (~ 70 mV/dec) [134]. These characteristics are crucial for the development of low-power electronic circuits. In addition, breaking of inversion symmetry in monolayer TMDs such as MoS₂ associating with strong spin-orbit interaction lead to the coupling between the spin and valley degree of freedom. Thus,

charge carriers can be selectively confined in different valleys (K and K', as experimentally demonstrated by using circularly polarized light [135, 136]. Moreover, the tunable band gaps in such materials have been achieved by strain, electrical/chemical doping and intercalation of ions or molecules [132, 137-140], which is necessary for optoelectronic applications. The unique physical and electrical properties make 2D TMDs worth for exploring their new physics and developing for broad range applications from nanoelectronics to optoelectronics including solar cells, photodetectors, light emitting diodes, and a new field of valleytronic devices [3, 110].

4.2 Experimental

4.2.1 Sample Preparation

In this work, we conducted low temperature photoresponse measurements with two types of monolayer WS₂ FET devices, one obtained by mechanical exfoliation and the other grown by CVD.

The mechanical exfoliation method is introduced in Chapter 2.1.1.

As for CVD growth, the process has been adapted with two different heating conditions, resulting in two types of CVD WS₂: Group A and Group B. Commercial WO₃ (> 99.5%) and sulfur powder (> 99.95%) from Sigma Aldrich are used as reactant sources for both processes. For Group A, 1 mg of WO₃ was placed onto SiO₂/Si substrate, which was placed in the center of the quartz tube, and sulfur powder (200 mg) was put upstream of ultrahigh-purity Ar, as shown in Figure 4.3 (a). The flow rate was maintained at 200 sccm during the entire process. Subsequently, the furnace was heated at a rate of 18°C/min to 550°C in Ar environment. The sulfur started to melt at this temperature, which is similar to previous reports [65]. Subsequently, the furnace temperature was then heated to 800°C at a ramping rate of 5 °C/min and

maintained at the setting temperature for 10 min before cooling down naturally to room temperature in Ar environment. For Group B, sulfur powder (200 mg) was placed at the inlet, outside of the furnace heating zone, and it was heated independently at 250°C by an additional heater, as demonstrated in Figure 4.2 (b). Other growth conditions used for group B samples are the same as those used for group A.

Figure 4.3 Experimental setups for CVD growth for group A (a) and group B (b) WS_2 samples. WO_3 power is placed on the SiO_2/Si substrates.

The WS_2 flakes are fabricated into FETs by method introduced in Chapter 2.2.

4.2.2 Characterization

In absorption and time-resolved PL measurements, two groups of samples were transferred onto the quartz substrates using a modified transfer technique reported previously [28]. Moreover, the exfoliated 1L- WS_2 samples on the SiO_2/Si substrate were used for comparison, which were obtained from the synthesized bulk crystals from 2D semiconductors Inc. Fluorescence and optical micrographs were

obtained by using an Olympus microscope (BX51) integrated with a fluorescence component (U-RFL-T). Number of layers and morphology of as-grown samples were identified using AFM (Veeco, Nanoscope V). The samples were then characterized by a Raman/PL microscope with 532 nm laser excitation.

Electrical properties are measured with Keithley 4200-SCS and all the low temperature experiments are carried out in the Magneto-Raman system as in Chapter 2.3.2.1.

4.3 Optical Characterization of Monolayer WS₂

Figure 4.4 (a) Optical image of triangular 1 L-WS₂ on SiO₂/Si substrate. (b) Optical image of an individual WS₂ triangle and thicker layers grown on top of the 1L flake. (c) AFM image of the marked region in (b) and its corresponding line scanning profile (d).

The majority of obtained samples are individual triangular islands of 1L-WS₂ as shown in Figure 4.4 (a). However, some triangular WS₂ flakes containing thicker layers grown at the center as demonstrated in Figure 4.4 (b) have also been observed.

Figure 4.4 (c) presents AFM image of an indicated area in Figure 4.4 (b). The line scan profile in Figure 4.4 (d) shows the height of ~ 0.7 nm for the thinnest region, which is an indicative of 1L, corresponding with the previous studies [144, 145].

Figure 4.5 (a) Raman spectrum of 1 L WS₂ showing multiple-peak Lorentzian fitting where the prominent peaks are indicated. (b) Raman spectra from WS₂ flakes including 1 to 3 L and bulk. Dashed line indicates peak position from Si. (c) Variation of the A_{1g} and E_{2g}¹ peak frequencies with number of layers and the difference of frequencies between the two peaks.

Figure 4.5 (a) shows Raman spectrum of 1L-WS₂ with the laser excitation wavelength (λ_{ex}) of 532 nm. The pronounced peak at ~ 350 cm⁻¹ consists of three sub-peaks, which are obtained by Lorentzian fitting. These three sub-peaks located at 343, 350 and 355 cm⁻¹ are attributed to E_{2g}¹(M), 2LA (M) and E_{2g}¹(I) modes,

respectively referring to previous experimental studies [31, 148-150] and the calculated phonon dispersion [151] of 1L WS₂. The other prominent peak is the A_{1g} mode appearing at $\sim 417 \text{ cm}^{-1}$, related to the out-of-plane vibration of S atoms. In addition, weak Raman peaks observed at 296 and 320 cm^{-1} are the combination modes corresponding to the 2LA-2E_{2g} and 2LA-E_{2g} modes, respectively. Figure 4.5 (b) presents Raman spectra of 1 to 3 L and bulk WS₂. The thickness of WS₂ flakes can be determined from the peak frequencies of the A_{1g} (Γ) and E_{12g} (Γ) modes and their frequency differences as presented in Figure 4.5 (c).

Furthermore, the thickness of WS₂ flakes can be identified by contrast spectroscopy, which has been found to be rapid and effective method for identifying the number of layers of graphene [152] and MoS₂ [153]. Contrast spectra collected from WS₂ including 1 to 3 L are shown in Figure 4.6 (a). In 1 L-WS₂, the contrast spectrum contains one peak appearing at $\sim 635 \text{ nm}$, originating from the superposition of absorbed, reflected, and emitted light from the WS₂/SiO₂/Si system. With increase of thickness, the peak red-shifts corresponding with the A exciton emission, which will be discussed in the following part. Figure 4.6 (b) shows the contrast values at 600 nm and at peak maxima linear change with number of WS₂ layers.

Figure 4.6 (a) Contrast spectra of 1 to 3 L WS₂. (b) Contrast value as a function of thickness at 600 nm (square) and at the peak maximum (circle).

The PL spectra of 1-3 L WS₂ ranging between 570 and 725 nm are shown in Figure 4.7 (a), and the corresponding spectra are presented in log scale for Y for clarification [Figure 4.7 (b)]. The peak maxima are observed in the range of 630-640 nm, and this peak mainly arises from the emission of the A exciton, which is the direct excitonic transition emerging at the highest valance band and the lowest conduction band at the same K point [154]. It is worth noting that charged and bound excitons may contribute in the emission spectra, and further investigation is needed in the future. When the thickness is thinned to 1 L, PL intensity considerably increases, demonstrating the conversion from indirect to direct band transitions. Figure 4.7 (c) shows that PL peak position red-shifts and the line shape broadens with increase of the WS₂ layers. The observed red-shifts of PL peak energy with increase of thickness of our as-grown samples is similar to previous reports [144, 149], however, in some work, the reversed trend is observed [146]. The discrepancy is probably owing to the varying electronic structures caused by different fabrication processes. It has been found in previous studies different stacking sequences

occurring in graphene samples prepared by mechanical exfoliation [155, 52], CVD [176] and epitaxial [177] techniques have resulted in varying electronic transitions/structures. In Figure 4.7 (d), the absorption spectrum of 1 L-WS₂ transferred onto quartz substrate shows A and B excitons located at 615 (2.02 eV) and 517 (2.40 eV) nm, respectively, and the corresponding FWHMs are 47 and 133 meV. In addition, the estimation of the PL quantum yield of 1 L-WS₂ can be achieved when rhodamine 6G (R6G) film is used as calibration by referring to the previous reported method for 1L-MoS₂ [87].

Figure 4.7 (a) PL spectra of WS₂ with different number of layers. (b) PL in (a) presenting in log scale for y-axis. (c) PL peak energy and FWHMs as a function of number of layers. (d) Absorption spectrum of 1 L-WS₂ on quartz showing A and B excitonic transitions.

There are two groups of CVD grown 1 L-WS₂ samples, named as group A and group B, respectively, which can be acquired using different heating conditions (see details in Chapter 4.2.1). Optical and fluorescence images of 1 L-WS₂ and -MoS₂ flakes prepared by both mechanical exfoliation and CVD method on SiO₂/Si substrates are shown in Figure 4.9 (a-d), adopted from a separate work from our group [100]. Note that fluorescence images and PL spectra of all samples shown in Figure 4.9 were obtained under the same conditions.

Figure 4.9 (a-d) upper panel: optical images and lower panel: fluorescence images of 1 L-WS₂ triangular flakes (group-A), a 1 L-WS₂ (group B), 1 L-MoS₂ mechanically exfoliated from bulk crystals, and 1 L-MoS₂ grown by CVD, respectively (e) PL spectra from WS₂ and MoS₂ samples presented in (a-d) at $\lambda_{\text{ex}} = 532$ nm taken under the same conditions. (f) Comparison of integrated PL intensity of 1 L-WS₂ and -MoS₂ fabricated by different techniques where each value is normalized to that of

exfoliated 1 L-MoS₂. Scale bars: 5 μ m. Adopted from Ref. [100].

In Figure 4.9 (a), light emission from 1 L-WS₂ triangular flakes from group A exhibits inhomogeneous features i.e. the brightness is more intense around the edge and gradually decreases from edge to inner regions. 1 L-WS₂ sample from group B [Figure 4.9 (b)] samples, on the contrary, shows strong and uniform fluorescence throughout the flake and the intensity is the most intense than the other samples. A fluorescence image of exfoliated MoS₂ in Figure 4.9 (c) show that the 1 L region exhibits a homogenous contrast, while the neighbouring bulk region is not observable because the dominant emission band shifts to infrared spectral region, which is not detectable by our system. As shown in Figure 4.9 (d), fluorescence image of 1 L-MoS₂ grown by CVD method could not be seen under this condition. PL spectra from 1 L-WS₂ and -MoS₂ samples (with $\lambda_{\text{ex}} = 532$ nm) ranging between 550 to 750 nm are shown in Figure 4.9 (e), and their relative integrated intensities with respect to that of 1 L-MoS₂ prepared by mechanical exfoliation is presented in Figure 4.9 (f). For $\lambda_{\text{ex}} = 532$ nm, the integrated PL intensity of 1 L-WS₂ from Group-B is more than 50 times higher than that of an exfoliated MoS₂ sample. It is worth noticing that the relative intensity ratio is related to λ_{ex} due to the discrepancy of the absorbance changes of 1 L-WS₂ and 1 L-MoS₂ under different laser excitation wavelengths. For instance, this intensity ratio becomes ~ 45 times for $\lambda_{\text{ex}} = 457$ nm [Figure 4.10]. According to previous report [144], the PL intensity from 1 L-WS₂ peeled off from the synthetic bulk crystals exhibits ~ 20 -30 times of that the exfoliated 1L-MoS₂ at $\lambda_{\text{ex}} = 473$ nm.

Figure 4.10 PL intensities of 1 L-WS₂ and MoS₂ samples (normalized by intensity of exfoliated MoS₂) fabricated by CVD and exfoliation techniques with $\lambda_{\text{ex}}=457$ nm.

Experimentally, the emerging difference in PL characteristics of group A and group B samples are correlated with the different growth conditions described in experimental section. Specifically, in the case of group A, the sulfur powder was melted and evaporated due to rising temperature of furnace ranging from room temperature to ~ 300 °C during heating up and naturally cooling of the furnace. For group B samples, on the other hand, the sulfur powder was placed outside the heating zone of furnace, which was then steadily heated by an extra heater at 250° during the growth process as demonstrated in Figure 4.3 (b). We attribute the inhomogeneous features of PL observed in group A sample to the relatively inconstant supply of sulfur caused by the alteration of the temperature, and vice versa for group B sample. Particularly, supply of sulfur source for the group A sample may be insufficient in the beginning of the growth when the furnace temperature is rising from room temperature. This would result in relatively more structural defects around the inner part of the triangles than the edge, such as sulfur vacancies, which have been found to be major defects in 2D MoS₂ grown by the CVD technique due

to their low formation energy [178]. However, for the group B, the sulfur vapor is sufficiently supplied, leading to the better sample quality. In our work, the commercially available WO_3 powder was utilized as the tungsten precursor, while the other group [146] used in the form of WO_3 films grown by thermal evaporation method. Compared with the seed-initialed growth of MoS_2 as reported previously [31], we did not use extra seed layer, while an extra heater was used separately to vaporize the sulfur powder for group B samples. It is worth noticing that the growth of TMD materials and PL signals can be influenced by several possible factors such as the cooling rate, the excess supply of sulfur, the substrate effect (the dielectric environment) and the edge structures. For the growth of MoS_2 , when the sulfur was not adequately provided, the oxysulfide rectangular flakes were grown, while hexagonal and triangular islands of MoS_2 were formed when enough and excess sulfur sources were supplied, respectively [29]. In our work, during the growth the excess sulfur source was supplied. As shown by previous studies, the high quality MoS_2 samples can be achieved when both natural [29] and fast cooling conditions [28] have been used to grow the samples. Specifically, CVD growth of MoS_2 with a fast cooling rate resulted in the large-grain size of triangular islands (usually larger than $100\text{ }\mu\text{m}$) [28]. We adopted the natural cooling in our CVD growth of WS_2 for the facile and repeatable functioning of the furnace. Moreover, the emission signals can be influenced by the edge geometries and chemical composition. For example, the second layer of MoS_2 trends to grow around the edge of the sample flakes or substrates [29], which may lead to the weakening of PL around the edge of sample.

Recent studies showed that variation of the PL intensity of TMD with different types of substrates, and even on the same type of substrate, the fluctuation of PL signals was also observed [179].

In our following work, we choose CVD WS₂ from Group B to conduct further experiments for its high uniformity and better optical behaviour.

4.4 Photoresponse of Monolayer WS₂

FET devices made from both mechanical exfoliation (S1-EXF) and CVD growth (S2-CVD) are measured in this part. Figure 4.11 shows the original images and fluorescence of the two samples.

Micro-PL of S1-EXF and S2-CVD, by 532 nm laser excitation at room temperature, in Figure 4.12 (a) and (b), respectively, demonstrates the quality of the flakes after device fabrication. There is a single neutral exciton peak at 1.965 eV in intrinsic S2-CVD. However, as a result of n-type doping, there is a blueshift in the neutral exciton peak in S1-EXF of 50 meV (2.015 eV). Also, there is an additional peak at 1.98 eV, which is attributed to charged exciton with relatively lower PL intensity [100]. In the upper part of the insets to Figure 4.12 (a) and (b), the optical images of S1-EXF (S2-CVD) are shown. Bright fluorescence images corresponding to the optical images, in the lower parts of the insets to Figure 4.12 (a) and (b), are in agreement with the PL data for S1-EXF and S2-CVD.

Figure 4.11 (a) Optical image of S1-EXF. (b) Optical image of S2-CVD. (c) Fluorescence image of S1-EXF. (d) Fluorescence image of S2-CVD.

Figure 4.12 Spectra for (a) exfoliated sample S1 and (b) CVD sample S2 for 532 nm laser excitation. Insets show the corresponding optical and fluorescence images of the devices. Drain current vs. drain voltage for S1-EXF and S2-CVD (c) at room temperature (d) 4.2 K are shown. Gate voltage dependence of drain current for S1-EXF at 5 V drain voltage and S2-CVD at 16 V drain voltage (e) at room temperature (f) at 4.2 K are shown. Results suggest S1-EXF is n-type doped, while S2-CVD is intrinsic.

Initial electrical measurements of these FET devices are performed at room temperature and 4.2 K, at dark. At zero gate voltage, drain current vs. drain voltage of S1-EXF and S2-CVD are compared in Figure 4.12 (c) up to 5 V. Both devices show similar behavior up to 2 V, but current is about twice at 5 V in S1-EXF. This voltage is sufficient to observe the device activation in S1-EXF without device heating. When the temperature is lowered to 4.2 K, 10 nA of current at room temperature at 5 V drain voltage in S1-EXF improves to 350 nA by overcoming the Schottky barrier at ~ 2.5 V [Figure 4.12 (d)], while there is almost constant current of less than 1 nA in S2-CVD. Higher conductance at lower temperatures is typical for a heavily doped semiconductor [180], which is the case for S1-EXF. On the other hand, an intrinsic and thermally activated semiconductor is expected to have lower conductance at lower temperatures, as observed by the change from an activated S2-EXF in room temperature to deactivation at 4.2 K. Furthermore, gate voltage is varied from -40 V to 40 V, for 5 V (16 V) applied drain voltage for S1-EXF (S2-CVD). According to room temperature data shown in Figure 4.12 (e), S1-EXF FET needs 25 V gate voltage to overcome the threshold, while S2-CVD FET can turn on at about 0 V. At 4.2 K [Figure 4.12 (f)], the threshold drops below 0 V gate voltage in S1-EXF FET, as an indication of the Fermi level moving into the conduction band when temperature is lowered; while S2-CVD FET is off for the all applied gate voltages at 4.2 K, which is due to the suppression of thermally activated processes at low temperatures. The overall picture of high and low temperature drain current vs. drain voltage for geometrically similar devices, as well as drain current vs. gate voltage behaviour, is

consistent for the argument of S1-EXF being n-type doped and S2-CVD being more intrinsic.

In order to investigate the response of these two samples with different electrical transport properties, the rest of the measurements are performed at 4.2 K, in the absence and existence of 532 nm laser excitation. In Figure 4.13 (a), for S1-EXF, drain current vs. drain voltage characteristics at zero gate voltage reveal a nonlinear increase of the current with increasing laser powers for drain voltages over the Schottky potential. This nonlinear dependence in S1-EXF may be due to light doping as in the case of CdSe nanobelts [181], and recombinations taking place in defect centers and traps [107]. On the other hand, the intrinsic sample S2-CVD exhibits a linear increase of the current with increasing laser powers [Figure 4.13 (b)]. The nonlinear dependence is more noticeable when the Fermi level is increased by gating in S1-EXF, as seen in Figure 4.13 (c); whereas gating does not lead to any obvious change on linear dependence of photoresponse for device S2-CVD [Figure 4.13 (d)]. When the gate voltage is lowered down to -40 V, there is a linear dependence of photoresponse with increasing laser power for both samples. This distinction between the photoresponse behaviour of S1-EXF and S2-CVD necessitates temporal measurements.

Figure 4.13 At 4.2 K, drain current vs. drain voltage at dark, and under laser illumination with various powers are shown in (a) for S1-EXF and (b) for S2-CVD. Gate voltage dependence of drain current are shown in (c) at 5 V drain voltage for S1-EXF and (d) at 16 V drain voltage for S2-CVD. The insets plot the drain current due to illumination which is obtained by subtracting drain current data at corresponding illumination power ($I_{\text{ILLUMINATION}}$) from the drain current data at dark (I_{DARK}).

In off state, at -40 V gate voltage, and with highest drain voltage of 5 V (16 V), photoresponse of S1-EXF (S2-CVD) was measured for 3 mW (10 mW) laser power as shown in Figure 4.14 (a) and (b). The ratio of photoresponse with laser on to off, for S1-EXF, is ~ 3.5 ; for S2-CVD ~ 47 times at 16 V drain voltage. The ratio of photoresponse with laser on to off, for S2-CVD, can be estimated as ~ 14 , by taking

an almost linear dependence of drain current–drain voltage dependence [Figure 4.14 (b)] between 5 V and 16 V drain voltage into account. The decay and rise times of the photoresponse upon turning the laser on and off can be resolved by 100 ms which is the limitation of the measurement system. The decay and rise times can be determined by fitting the decaying and rising parts of the data with a single exponential function. The photoresponse of S1-EXF which is two orders of magnitude higher than that of S2-CVD, shows a decay and rise time of 6 s and 3 s, respectively. This is much longer timescale compared to only 100 ms for both the decay and the rise times for S2-CVD. The data for S2-CVD are limited by the system and it could be actually much less than 100 ms.

Figure 4.14 Time-resolved photoresponse data with laser on and off are shown in (a) for S1-EXF with laser power 3 mW and (b) for S2-CVD with laser power 10 mW. Both decay and rise in photoresponse can be fitted by single exponential. For S1-

EXF, the decaying and rising times are 6 s and 3 s, respectively. For S2-CVD, both time scales are 100 ms. Cartoons, in the panels above, describe the simple band diagrams in both samples when laser is on and off. The barrier is shown only for the contact where the drain voltage is applied. Red full (blue open) circles represent electrons (holes). The Fermi level is E_F , the systems are at -40 V gate voltage (V_g) and 5 V drain voltage (V_d) for S1-EXF, 16 V (V_d) for S2-CVD. The overall band of WS_2 FET with respect to electrodes moves slightly down when the laser is on; it moves upward when the laser is off, accompanied by decrease in the photoinduced carriers. There are trapped states due to the defects and related n-type doping at the barrier, in the case of S1-EXF. Charge carriers are mostly in localized states and electrical transport is via photoconduction in S2-CVD, since it is intrinsic.

In fact, the trap states due to the defect centers are the main reason for the slower photoresponse in n-type S1-EXF. The cartoon on the upper (lower) panel of Figure 4.14 (a) describes the movement of charges for laser illumination on (off), for a drain voltage of 5 V and -40 V gate voltage. When the laser is off, some electrons are trapped in S1-EXF [Figure 4.14 (a), lower panel]. Upon turning the laser on, electron-holes are formed and recombined, while the trapped charges are delayed for recombination. Therefore, the decay time of the photoresponse gets longer until the trapped charges are liberated as in the upper panel of Figure 4.14 (a). Once the laser is back on, first the trapped states will be filled before photo-induced carriers contribute to the current. On the other hand, in S2-CVD, defects can be assumed to be negligible, based on the photoresponse results. The upper (lower) panel of Figure

(b) pictures the situation for an intrinsic 2D semiconductor at -40 V gate voltage and 16 V drain voltage, for laser on (off). Charge carriers are mostly in localized states and electrical transport takes place via photoconductive states [182], as described in the upper panel of Figure 4.14 (b). Once the laser is off, the transport will be limited by thermally activated process, as in the lower panel of Figure 4.14 (b).

Based on these results, monolayer CVD grown WS_2 can be confidently announced as a visible range, fast photoactive material and photodetector. Although photoresponsivity is fairly low for this device, there is still room for improvement. Timescales are expected to be much smaller than 5 ms measured for the multilayer WS_2 [109]. Recently, in a new 2D semiconductor multilayer phosphorene, a response time of 1 ms was measured [183]. However, this material is quite unstable and not robust to environment, which makes it not suitable for applications yet. Rather than that, stable and large area CVD WS_2 is more promising for future photoactive devices, such as p-i-n photodiodes and photomultipliers.

4.5 Conclusion

In this part, we have synthesized two types of WS_2 by CVD growth and both are characterized by Raman, PL as well absorption. Due to its high quality, group B WS_2 samples are used to fabricate FET devices, together with mechanically exfoliated flakes. Subsequently, low temperature photoresponse are studied. The monolayer exfoliated WS_2 FET device which exhibits n-type behavior, exhibits large dark current and low tunability in off state by laser illumination while the monolayer CVD WS_2 FET device exhibits intrinsic semiconductor behaviour, small

dark current, and high tunability in off state by laser illumination. Time resolved measurements of illumination reveal that the ratio of photoresponse with laser on to off is about four times better in the CVD device and response times are as short as the measurement limit of 100 ms which is much faster than that of the exfoliated one (few seconds). These results support the earlier measurements claiming that there are relatively low native defects in CVD grown WS_2 [100] and the fast photoresponse makes CVD WS_2 a suitable optoelectronic material for photoactive devices.

Chapter 5

Dichroic Spin-Valley Photocurrent in Monolayer MoS₂

The aim of valleytronics is to exploit confinement of charge carriers in local valleys of the energy bands of semiconductors as an additional degree of freedom in optoelectronic devices. Thanks to strong direct excitonic transitions in spin-coupled K valleys, monolayer molybdenum disulphide is a rapidly emerging valleytronics material, with high valley polarization in photoluminescence. Here we elucidate the excitonic physics of this material by light helicity-dependent photocurrent studies of phototransistors. We demonstrate that large photocurrent dichroism (up to 60%) can also be achieved in high-quality molybdenum disulphide monolayers grown by chemical vapour deposition, due to the circular photogalvanic effect on resonant excitations. This opens new opportunities for valleytronics applications in which selective control of spin-valley-coupled photocurrents can be used to implement polarization-sensitive light-detection schemes or integrated spintronic devices, as well as biochemical sensors operating at visible frequencies.

In this work, we demonstrate spin-coupled valley-dependent dichroic PC of a CVD grown single-layer MoS₂ phototransistor excited by on-resonance and off-resonance photon energies (1.96 and 2.33 eV, respectively). A PC due to the circular photogalvanic effect (CPGE) arises as a result of circularly polarized light incident on monolayer MoS₂ with an oblique angle. The spin-valley coupling, the valley selection rules and the excitation frequencies determine the magnitude of PC for left and right

circularly polarized states. For excitations that are on-resonance with the excitons, there should be a difference between the CPGE PCs due to left and right circularly polarized excitations; while for excitations, which are off-resonance with the excitons, there should be no difference between these CPGE PCs. Our PC measurements evidence this variation and reveal a high-CPGE PC polarization. We remark on further possibilities of making use of this unique opto-valleytronic control for interdisciplinary applications.

5.1 Introduction

Research on two-dimensional materials synthesis and characterization has accelerated since the discovery of graphene [1], for the purpose of utilizing these multifunctional materials in highly efficient nano- and bio-technological platforms [184]. Among 2D materials, particularly transition metal dichalcogenide (TMD) monolayers [2, 3] have shown various interesting properties such as charge density waves [85], unusual strain [95] and thermal energy dependence [96], tunable light emission by chemical control [102] and fast photoresponse [81], which can be used in interdisciplinary device applications.

The general introduction of TMD MoS₂ has been discussed in Chapter 4.2.1 and 4.2.2, including crystal structure and electronic energy dispersion.

5.1.1 Synthesis of MoS₂

There have been extensive studies on growth techniques of TMDs to synthesize high-quality, single-crystal and large-area samples. Among these efforts, high-quality single layer but small area (<10 μm) samples that are mechanically cleaved, have shown strong photoluminescence, fluorescence [87, 94], high-mobility-low-power switching [185], and large photoresponse [80]. Alternatively, samples grown by chemical vapour deposition (CVD) methods [33, 97, 99, 186] also yield quite intense light emission [109],

particularly monolayers of tungsten disulphide (WS₂) have shown stronger photoluminescence than mechanically cleaved monolayers [100]. In terms of electrical transport, both mechanically cleaved and CVD grown WS₂ and MoS₂ have n-type behaviour. In addition, since CVD method allows also growing multiple 2D materials to form hetero- and hybrid structures [3], it offers to tailor functional physical systems and, particularly for optoelectronics and spin-dependent valleytronics. The possibility of synthesizing high-quality samples with much larger size (4500 μm) than mechanically cleaved samples gives CVD growth techniques a major advantage in the development of future technologies based on TMDs.

In Chapter 2.1.2, detailed CVD growth method is introduced.

5.1.2 Valley Physics in Monolayer MoS₂

Most nanodevices today use charge and spin degree of freedom; however, it is also possible to exploit the valley degree of freedom, which is simply the confinement of charge carriers in momentum space of 2D materials.

In monolayer MoS₂, the conduction and valence-band edges are located at the corners (K points) of the 2D hexagonal Brillouin zone [187-189]. Similar to graphene, the two inequivalent valleys constitute a binary index for low energy carriers. Because of the large valley separation in momentum space, the valley index is expected to be robust against scattering by smooth deformations and long wavelength phonons. The use of valley index as a potential information carrier was first suggested in the studies of conventional semiconductors such as AlAs and Si [190]. With the emergence of graphene, the concept of valleytronics based on manipulating the valley index has attracted great interests [191-195].

MoS₂ monolayers have two important distinctions from graphene. First, inversion symmetry is explicitly broken in monolayer MoS₂, which can give rise to the

valley Hall effect where carriers in different valleys flow to opposite transverse edges when an in-plane electric field is applied [192]. Inversion symmetry breaking can also lead to valley dependent optical selection rules for interband transitions at K points [193]. Second, MoS₂ has a strong spin-orbit coupling (SOC) originated from the d orbitals of the heavy metal atoms [189], and can be an interesting platform to explore spin physics and spintronics applications absent in graphene due to its vanishing SOC [196, 197].

Due to the strong SOC, in MoS₂, the valence band (VB) is split by 150 meV [93]. Excitonic transitions are produced because of the direct band gap at low energy K and -K valleys. The upper (lower) VB is associated with the A (B) excitons. The same broken inversion symmetry together with time reversal symmetry is responsible for spin-valley coupling in monolayer MoS₂ and similar TMDs (WS₂, WSe₂ and MoSe₂); that is, the sign of the hole spin in the upper (or lower) VB will oppose in different valleys. The descriptive Hamiltonian [93] can be simply expressed as:

$$\hat{H} = \alpha t (\tau k_x \hat{\sigma}_x + k_y \hat{\sigma}_y) + \frac{\Delta}{2} \hat{\sigma}_z + \frac{2\lambda\tau(\hat{\sigma}_z - 1)}{4} \hat{s}_z \quad (5.1)$$

where α is the lattice constant, t is the effective hopping integral, $\tau (\pm 1)$ is the valley index, $\hat{\sigma}$ is the Pauli matrices, Δ is the energy gap, 2λ is the spin splitting at the VB, and $\hat{s}_z$ is the Pauli matrix for spin; k_x , k_y and k_z are the momentum components in x, y, z coordinates, respectively. The first term is related to the valley related hopping, the second term is purely spin dependent and the last term describes the spin-dependent phenomena as a result of SOC in each valley. The spin-valley coupling in the last term, which leads to the valley polarization, was demonstrated experimentally by light helicity-dependent photoluminescence measurements corresponding to the A and B excitons in monolayer MoS₂ [136, 198]. Recently, in suspended monolayer MoS₂ samples, photocurrent due to the A and B excitons was also revealed [199]. A useful

framework to study light-matter interactions in 2D materials is based on PC experiments performed by circularly polarized excitation [200]. However, helicity-dependent PCs due to excitons with on-resonance and off-resonance excitations in monolayer TMDs are still to be uncovered.

5.1.3 Spin-Valley Coupling and Circular Photogalvanic Effect

The phenomenological expression of light helicity-dependent PC is strictly determined by the crystal symmetry, the angle of incidence, θ , (with respect to the normal to the sample plane), the azimuthal angle, ϕ , (light propagation with respect to the x-direction in the x-y plane) of the excitation beam and the angle of photon polarization, φ , (with respect to the electric field vector direction) [200]. In transverse geometry [Figure 5.8 (a)] in which light is directed in the x-z plane and the PC is measured in the y-direction, ϕ is fixed. If not otherwise specified, in this work, we used $\phi = 90^\circ$ and $\varphi = 45^\circ$, so that by rotating a quarter-wave plate (QWP), polarization of a linearly polarized laser can be varied from 0° linear ($\leftrightarrow$) to 45° left circular ($\sigma -$), back to 90° linear ($\leftrightarrow$) to 135° right circular ($\sigma +$) and then back to 180° linear ($\leftrightarrow$) polarization, and so on.

Monolayer MoS₂ has D_{3h}^1 crystal symmetry [93, 136, 198]. When a Mo atom is in an inversion centre, there is no coinciding atom when a S atom is projected to the 2D plane. When such a symmetry system is subjected to a circularly polarized light field with an oblique angle θ ($\theta \neq 0$), a PC with $\sin 2\varphi$ dependence current due to the CPGE, j_{CPGE} will be the major PC. The angle of incidence θ dependence of j_{CPGE} is $\sin \theta$. At the same time, a PC with $\cos 4\varphi$ dependence, which is due to the transfer of light momentum to electrons, is also present, the so-called linear photon-drag effect (LPDE), j_{LPDE} [200]. In addition, a PC similar to j_{CPGE} in origin, but related to the linear

polarization of light as j_{LPDE} , linear photogalvanic effect (LPGE), j_{LPGE} [200] is also possible, although it should ideally vanish at $\sigma +$ and $\sigma -$ excitations. Based on these three contributions, the total PC can be generally expressed by the phenomenological formula $J = C_1 \sin 2\varphi + L_1 \sin 4\varphi + L_2 \cos 4\varphi + D$. Here C_1 is the coefficient for the CPGE current ($j_{CPGE} = C_1 \sin 2\varphi$); L_1 is for the LPGE current ($j_{LPGE} = L_1 \sin 4\varphi$); L_2 is for the LPDE current ($j_{LPDE} = L_2 \cos 4\varphi$); and D is polarization-independent term.

Figure 5.1 Band diagram of K and -K valleys of MoS₂ and photocurrent generation.

The $\sigma +$ and $\sigma -$ excitations which are on-resonance with A exciton, a hole in the upper valence band (VB) (black solid (dash) curve in (a) and (b) for K (-K) valley) and an electron in the conduction band (CB) (black solid curves in (a) and (b)) lead to photocurrent generation in K and -K valleys, respectively. Similarly, the $\sigma +$ and $\sigma -$

excitations which are on-resonance with B exciton, a hole in the lower VB (black solid (dash) curve in (a) and (b) for K (-K) valley) and an electron in the CB lead to PC generation. The blue horizontal dashed lines in (a) and (b) are the Fermi level E_F which can be tuned by V_g . The VBs are split by 150 meV, while the splitting in the CB is negligible. The purple vertical solid (orange long dash) arrows show interband transitions associated with the A (B) excitons when illuminated by on-resonance laser; while turquoise vertical dash-dot arrows show possible transitions by off-resonance laser. For on-resonance laser, $\sigma +$ ($\sigma -$) excitation in K (-K) valley is linked with hole spin $\uparrow$ ($\downarrow$) due to the spin-valley coupling for A excitons. Thus, based on theory, the circular photogalvanic current in K valley, $j_{CPGE}(\omega)_K$ due to the $v_{v(i)\uparrow}$ at $\sigma +$ excitation will be larger (shown by thicker purple right arrow in (c) as a result of transitions represented by purple vertical solid arrows in (a)) than the $j_{CPGE}(\omega)_{-K}$ due to the $v_{v(i)\downarrow}$ at $\sigma -$ excitation (shown by thinner purple right arrow in (d) as a result of transitions represented by purple vertical solid arrows in (b)), which is the reason of the pronounced photocurrent polarization. Similar but opposite scenario for $v_{v(ii)\downarrow}$ and $v_{v(ii)\uparrow}$, by exchanging valleys and spins applies for B excitons (orange right arrows). For off-resonance laser, $\sigma +$ and $\sigma -$ excitations yield a negligible photocurrent polarization due to simultaneous populations of both valleys, as shown by equivalent turquoise right arrows in both (c) and (d).

In a recent work on multilayer WSe₂, the j_{CPGE} was observed due to absorption at L valleys-intraband transitions within the conduction band (CB) [201]. In the case of monolayer MoS₂, spin-valley coupling will be at K valleys and the j_{CPGE} should be due to interband transitions from the VB to the CB, for circularly polarized radiation with energies closer to the exciton energies. When spin couples to valley [93], sign of the spin states of A (or B) excitons in one valley oppose to that in the other valley. By a

simple approach, when excited by $\sigma + (\sigma-)$ excitations with energy slightly higher than the formation/dissociation energy of A exciton, an electron in VB makes an interband transition in K ($-K$) valley, with hole spin up ($\uparrow$ (spin down $\downarrow$)). Similarly, when excited by $\sigma + (\sigma-)$ excitations with energy slightly higher than the formation/dissociation energy of B exciton, an electron in VB makes an interband transition in K ($-K$) valley, with hole $\downarrow$ ($\uparrow$) [Figure 5.1]. This coupling can be understood by the PC generated when circularly polarized light-field irradiated on the sample is perpendicular to the electrodes [Figure 5.8 (a)]. In such a case, the velocities v_v of the carriers in the VB, which absorb this light field, will have a contribution additional to the one due to the band dispersion $\delta\varepsilon(k)/\delta k$ for energy $\varepsilon(k)$ in k space. That contribution is the anomalous velocity which appears as the second term in $v_v(k) = \left(\frac{1}{\hbar}\right)\left(\frac{\delta\varepsilon(k)}{\delta k}\right) - (e/\hbar)E \times \Omega$ [83], where $\hbar$ is the Planck constant, E is the electric field vector, and v is the Berry curvature that has the same magnitude but different sign in K and $-K$ valleys, $\Omega_{K(-K)} = +(-) \Omega \hat{z}$. Then, for excitation that is on-resonance with the A excitons, we can write the magnitude of $v_v(k)$ at $K(-K)$, which actually depends on the light helicity, as $v_{v(i)\uparrow(\downarrow)} = |(e/\hbar)E \times \Omega_{K(-K)}|$ and for excitation which is on-resonance with the B excitons, as $v_{v(ii)\downarrow(\uparrow)} = |(e/\hbar)E \times \Omega_{K(-K)}|$. In this case, the PC due to the $v_{v(i)\uparrow}$ ($v_{v(ii)\downarrow}$), at $\sigma +$ excitation will be larger than the PC due to the $v_{v(i)\downarrow}$ ($v_{v(ii)\uparrow}$), at $\sigma +$ excitation. As an example, for the A excitons, the CPGE current $j_{CPGE}(\hbar\omega)$, (ω is the excitation frequency) is given by $j_{CPGE}(\omega)_{\sigma+(\sigma-)}$ or:

$$j_{CPGE}(\omega)_{K(-K)} = \left(\frac{8e\pi}{\hbar}\right) \sum_{v(i) \rightarrow c} \left(v_c \tau(\varepsilon_c) - \left(\frac{\delta\varepsilon_{v(i)}}{\delta k} - v_{v(i)\downarrow(\uparrow)} \tau(\varepsilon_{v(i)}) \right) \right) |M_{v(i) \rightarrow c}|^2 [f(\varepsilon_c) - f(\varepsilon_{v(i)})] \delta(\varepsilon_c - \varepsilon_{v(i)} - \hbar\omega) \quad 5.2$$

$$\text{and } v_c \tau(\varepsilon_c) > \frac{\delta\varepsilon_{v(i)}}{\delta k} - v_{v(i)\downarrow(\uparrow)} \tau(\varepsilon_{v(i)}),$$

where $v(i)$ is the initial VB state on-resonance with the A excitons and c is final CB states, $M_{v \rightarrow c}$ is the transition matrix from the upper VB states to CB states, v_c is the electron velocity in the CB states, $\tau(\varepsilon_v)$ and $\tau(\varepsilon_c)$ are the momentum relaxation times in the VB and CB, respectively. The Fermi-Dirac functions $f(\varepsilon_c)$ and $f(\varepsilon_v)$ are dependent on the gate voltage and to study purely interband transitions, the Fermi level must be lowered by negative gate voltage (off state). Here we remark at the condition $v_c \tau(\varepsilon_c) > \frac{\delta \varepsilon_v}{\delta k} - v_{v \uparrow(\downarrow)} \tau(\varepsilon_v)$, which determines the sign of $j_{CPGE}(\omega)_{K(-K)}$. We can consider the $j_{CPGE}(\omega)_{K(-K)}$ with three components: (1) $\propto v_c \tau(\varepsilon_c)$; (2) $\propto \frac{\delta \varepsilon_{v(i)}}{\delta k}$; and (3) $\propto v_{v(i) \downarrow(\uparrow)} \tau \varepsilon_{v(i)}$. The third part (anomalous part) is the one that differs for on-resonance excitations. Anomalous parts of the electron velocities in the upper VB states for K and $-K$ valleys for excitations on-resonance with the A excitons are $v_{v(i) \uparrow}$ and $v_{v(i) \downarrow}$, respectively, which are equal in magnitude but opposite in sign. For excitations on-resonance with the B excitons, anomalous parts of the electron velocities in the lower VB states for K and $-K$ valleys are $v_{v(ii) \uparrow}$ and $v_{v(ii) \downarrow}$, respectively. Based on valley selection rules, the sign of $v_{v(i) \downarrow(\uparrow)}$ opposes with the sign of $v_{v(ii) \downarrow(\uparrow)}$, leading to a PC with opposite sign. However, the overall PC $j_{CPGE}(\omega)_K$ and $j_{CPGE}(\omega)_{-K}$ should be in the same direction as shown in upper panel of Figure 5.1, because $v_c \tau(\varepsilon_c) > \frac{\delta \varepsilon_v}{\delta k} - v_{v \downarrow(\uparrow)} \tau(\varepsilon_v)$. Hence on $\sigma + (\sigma -)$ excitations on-resonance with these excitons, the PC $j_{CPGE}(\omega)_{\sigma + (\sigma -)}$ will be determined by the contributions due to $u v_{v(i) \downarrow(\uparrow)}$ and $v_{v(ii) \downarrow(\uparrow)}$. This will make the main difference between $j_{CPGE}(\omega)_K$ and $j_{CPGE}(\omega)_{-K}$. Therefore, spin-coupled valley-dependent currents are expected due to excitons formed after light helicity-selective transitions of electrons from the VB to the CB. For off-resonance excitations, the PC expression due to the CPGE is more complicated.

$$j_{CPGE}(\omega)_{\sigma+}(\sigma-) = \left(\frac{8e\pi}{\hbar} \right) \sum_{v \rightarrow c} (v_c \tau(\varepsilon_c) - \left(\frac{\delta \varepsilon_v}{\delta k} - v_{v(\uparrow \text{ or } \downarrow)} \tau(\varepsilon_{v(i)}) \right)) |M_{v \rightarrow c}| |f(\varepsilon_c) - f(\varepsilon_v)| \delta(\varepsilon_c - \varepsilon_v - \hbar\omega) \quad 5.3$$

Here v can be $v_{(i)}$ (upper VB) or $v_{(ii)}$ (lower VB). However, we can simply expect that for off-resonance excitation, $j_{CPGE}(\omega)_{\sigma+}$ and $j_{CPGE}(\omega)_{\sigma-}$ will yield similar current values, since the off-resonance excitation simultaneously populates both K and $-K$ valleys [136]. In the off-resonance excitation, we cannot take advantage of the valley selection rules and spin-valley coupling, which is reflected in the variance between $j_{CPGE}(\omega)_{\sigma+}$ and $j_{CPGE}(\omega)_{\sigma-}$ in on-resonance excitations. This underlines the importance of strong excitonic character that can be obtained in high-quality samples to observe a pronounced difference between $j_{CPGE}(\omega)_{\sigma+}$ and $j_{CPGE}(\omega)_{\sigma-}$.

5.2 Results and Discussions

5.2.1 Device Characterization and Photocurrent

Figure 5.2 Photoluminescence of the sample. The strong excitonic A peak is at 1.84 eV.

The other excitonic B peak is at 2 eV. The respective optical image is shown in the inset. The dash lines in the inset are drawn to make easier to visualize the flakes. The orange bars are Ti/Au contacts. Scale bar is 5 μm .

Figure 5.2 shows the microphotoluminescence of the device prepared by CVD as shown in the inset. The microphotoluminescence measurement is performed by 532-nm laser excitation at room temperature. The strong excitonic peak of A (B) exciton corresponds to pair of an electron in the CB and a hole in the upper (lower) band of the split VB at K valleys. The PL peak for A (B) excitons in these samples is around 1.84 eV (~ 2 eV) and the A excitons are much stronger in intensity. The quality of the flakes was demonstrated by Raman microspectroscopy [Figure 5.3 (a)] and contrast-enhanced fluorescence optical microscope image [Figure 5.3 (b)] respectively. Initial electrical measurements of monolayer MoS₂ field-effect transistors are performed in dark. Drain current versus drain voltage (V_d) characteristics, at zero gate voltage (V_g), are shown in Figure 5.4. For 10 V applied V_d , the field effect transistors characteristics mark an on-state at -30 V [Figure 5.5]. By a linear fit between 30 and 40 V, we can estimate the mobility of these devices from $\mu = (L/W)(dI/dV)(1/CV_d)$. Here L is the device length, W the device width and C is the back-gate capacitance. The mobility is $\sim 0.5 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, as shown in Figure 5.6, which is in agreement with the reported values [80]. Subsequent drain current measurements on illumination by 2.33 eV laser with 20 mWcm^{-2} power density, and comparison with the dark measurements, are illustrated as a function of V_d in Figure 5.7. The drain current as a function of V_g , on illumination ($I_{\text{Illumination}}$) and in dark (I_{Dark}) are compared in Figure 5.5 (a). The ratio of $I_{\text{Illumination}}/I_{\text{Dark}}$ is $\sim 10^4$ in the off state ($V_g = -35 \text{ V}$).

Figure 5.3 (a) Raman spectrum of monolayer MoS₂ grown by chemical vapour deposition. Raman peaks of the monolayer sample grown by chemical vapour deposition (S-CVD) are E_{2g}^1 peak which is at 385 cm^{-1} and A_{1g} peak which is at 403 cm^{-1} . These values are consistent with Ref. [95]. (b) Fluorescence image of monolayer MoS₂ grown by chemical vapour deposition. Solid lines show the Ti/Au contacts. Dash (white) lines show the flake. The scale at the bottom right is $1\text{ }\mu\text{m}$. The fluorescence image of the device grown by chemical vapour deposition is clear.

Figure 5.4 Drain current vs. drain voltage characteristics of monolayer MoS₂ field-effect transistors at zero gate voltage at dark. Black empty circles are the data for the sample grown by chemical vapour deposition (S-CVD). Red empty squares are the data for the sample prepared by mechanical cleaving (S-MC). Both S-CVD and S-MC data are taken at zero gate voltage at dark, and shown in logarithmic scale.

Figure 5.5 Device characterization of the sample. (a) Gate voltage dependence of drain

current, at 10 V drain voltage, in dark (empty squares) and upon 20 mWcm⁻² illumination by 2.33 eV laser (full squares). The ratio of $I_{\text{Illumination}}$ to I_{Dark} is about 10^4 in the off state ($V_g = -35$ V) (b) Photocurrent measured as a function of laser power density at $V_g = -40$ V is shown. The data (full squares) are fit to a straight line and a photoresponsivity (R) of 3.5 AW⁻¹ is obtained.

Figure 5.6 Mobility of monolayer MoS₂ samples and drain current ratios for light ON and OFF. (a) Gate voltage dependence of drain current for the sample grown by chemical vapor deposition (S-CVD) and (b) for the sample prepared by mechanical cleaving (S-MC), at dark and 10 V drain voltage. Mobility of the samples is determined by fitting a straight line to the data between 30 V - 40 V. The mobilities of S-CVD and S-MC are approximately 0.5 and 9 cm²V⁻¹s⁻¹, which are in agreement with the reported values [80]. (c) Gate voltage dependence of the ratio of drain current obtained upon illumination (illuminated by 2.33 eV laser with a power density of 20 mWcm⁻²) to that

obtained in dark for S-CVD and (d) for S-MC are given. Both devices exhibit a ratio of $I_{\text{illumination}} / I_{\text{Dark}} \sim 10^4$ in the off state, while S-MC exhibits large variations in the off state. This may be considered as a consequence of localization and less effective screening of charge carriers [202] or midgap states [203] in S-MC.

Figure 5.7 Drain current vs. drain voltage characteristics of monolayer MoS₂ field-effect transistor grown by chemical vapour deposition, S-CVD, at zero gate voltage, in logarithmic scale. Empty squares show the data at dark, full squares show the data at 20 mWcm^{-2} illumination by 2.33 eV laser excitation.

Laser power density dependence of drain current at -40 V gate voltage and 10 V drain voltage is measured. Figure 5.5 shows PC ($I_{\text{illumination}} - I_{\text{Dark}}$) versus laser power density. Photoresponsivity (R) at the minimum power for the device shown in the inset to Figure 5.2 is about 3.5 AW^{-1} , which is about two orders of magnitude lower than the reported one [80]. The power dependence of the measured drain current (I_d) can be fitted

according to $I_d \propto (\text{Laser Power})^\alpha$, where α is about 0.7 for our samples and the reported MoS₂ [80]. At higher power densities, R drops either due to the trap states in MoS₂ or the interface of MoS₂ and the substrate [204]. Therefore, to elucidate the photoinduced transport effects of monolayer MoS₂, further PC measurements at both high and low laser power densities are performed using conventional amplitude modulation and lock-in detection.

Figure 5.8 Experimental configuration and photocurrent. (a) Description of photocurrent setup using the lock-in technique to collect the PC amplitude and phase is given. Using a linearly polarized laser with a quarter-wave plate (QWP), circularly polarized light obtained and directed on the sample with an oblique angle θ . By rotating QWP, it is possible to change the angle of photon polarization φ . (b) PC of the sample illuminated by 2.33 eV laser, for $\varphi = 0^\circ$ and $\theta = 45^\circ$. Spheres are the data for 10 V drain voltage and 9.78 Wcm⁻² laser power density. Up triangles are the data for 10 V drain voltage and 60 mWcm⁻². Pentagons are the data for 0.7 V drain voltage and 60 mWcm⁻². Helicity-dependent PC is measured in this regime (off state), in which there are only photogalvanic and photon-drag effects.

In Figure 5.8 (b), gate dependence of PC signal for different V_d and laser power

density with 2.33 eV excitation is presented for $\varphi=0^\circ$ and $\theta=45^\circ$ configuration as described in the experimental setup of Figure 5.8 (a). Both PC signal amplitude and phase are measured. Phase is around 0° while the V_g , V_d and laser power are varied; no sign change of PC is observed as shown in Figure 5.9. At high V_d of 10 V, both high-power-density data (9.78 Wcm^{-2}) and low-power-density data (60 mWcm^{-2}) are being affected by bolometric effects as in the AB-stacked bilayer graphene [35], which are due to the high channel doping. The PC amplitude increases almost linearly from 100 to 200 nA from -40 V to 40 V for high power density; from 3 to 20 nA for low power density. At low V_d of 0.7 V and low power density (60 mWcm^{-2}), the measured PC is dominated by photogalvanic effect, photon-drag effect and low channel doping. The PC amplitude increases logarithmically from 0.1 to 8 nA, in accordance with the gate dependence of drain current data in Figure 5.8 (b). Low V_d also prevents artificial PC such as photogating effects [42] and photothermal effects [205]. Therefore, intrinsic photogalvanic effects are expected to appear at low V_d and low illumination intensity. Here we focus on this regime to address subtle effects of light helicity on spin-valley PCs, which has been a subject of fundamental opto-spintronic applications [206-208].

Figure 5.9 Photocurrent measurements of monolayer MoS₂ grown by chemical vapour deposition. (a) Photocurrent amplitude and (b) phase for the sample grown by chemical vapor deposition, S-CVD, illuminated by 2.33 eV laser, for $\varphi=0^\circ$ and $\theta=45^\circ$ are given. In (a), spheres are the data for 10 V drain voltage and 9.78 Wcm^{-2} laser power density. Up triangles are the data for 10 V drain voltage and 60 mWcm^{-2} . Pentagons are the data for 0.7 V drain voltage and 60 mWcm^{-2} . All the phase data in (b) (open spheres, open up triangles, and pentagons data correspond to the data in (a)) are close to be 0° .

5.2.2 Helicity-Dependent PC by 2.33 and 1.96 eV Excitations

Figure 5.10 Spin-coupled valley-dependent dichroic photocurrent in monolayer MoS₂.

(a) Photocurrent as a function of angle of photon polarization φ when illuminated by 2.33 eV (off-resonance with the excitons) laser is shown. The PC data are collected by rotating a quarter-wave plate which changes polarization of a linearly polarized laser from 0° linear ($\leftrightarrow$) to 45° left circular ($\sigma -$), back to 90° linear ($\leftrightarrow$) to 135° right circular ($\sigma +$), and then back to 180° linear ($\leftrightarrow$) polarization, and so on. The cyan curve is the fitting function based on the phenomenological PC formula for monolayer MoS₂, yielding negligible polarization between $\sigma +$ and $\sigma -$ excitations. (b) PC as a function of φ when illuminated by 1.96 eV (on-resonance) laser. The magenta curve is the fitting function based on the phenomenological PC formula for monolayer MoS₂, yielding a polarization of ~60% between $\sigma +$ and $\sigma -$ excitations, which controls the valley currents in K (linked with hole spin up) and $-K$ (linked with hole spin down) valleys, respectively.

Figure 5.10 shows the light helicity-dependent PC results by varying the angle of photon polarization (φ) for off-resonance (2.33 eV photon energy, 0.7 V drain voltage and 60 mWcm⁻² illumination intensity) and for on-resonance excitation (1.96 eV photon energy, 2 V drain voltage and 100 mWcm⁻² illumination intensity) at $V_g = -40$ V. As expected, for off-resonance excitation [Figure 5.10 (a)], the PC exhibits no clear dependence on angle of photon polarization (that is, $\sigma +$ and $\sigma -$ excitation). Indeed, there is no preferential optical transition (due to electron-photon interaction and scattering events) from the upper or lower VBs to the CB, in terms of valleys, on absorption of photon energies off-resonance with the excitonic transition. The data are fitted to the phenomenological formula $J = C_1 \sin 2\varphi + L_1 \sin 4\varphi + L_2 \cos 4\varphi + D$ and the fitting parameters are tabulated in Table 5.1. The component of PC response related to circularly polarized light is the j_{CPGE} . But for this excitation, j_{LPDE} is the dominant

contribution. Thus, by subtracting j_{LPDE} and polarization independent term from the measured PC, $PC(\sigma \pm)$, one can obtain $j_{CPGE}(\sigma \pm) = PC(\sigma \pm) - (-L_2 + D)$. Then PC polarization can be defined as:

$$P = \frac{|j_{CPGE}(\sigma+) - |j_{CPGE}(\sigma-)|}{|j_{CPGE}(\sigma+) + |j_{CPGE}(\sigma-)|} \quad 5.4$$

By using the parameters in Table 5.1, P is $0.8 \pm 0.4\%$. Based on microscopic description of the CPGE valley current, $v_{v(i)}$ - and $v_{v(ii)}$ -dependent terms cancel each other and eventually results in a negligible PC polarization.

Table 5.1 Photocurrent components of the sample excited by circularly polarized light.

	C₁	L₁	L₂	D
1.96 eV	-3.5	-1.5	1.8	145.1
2.33 eV	-0.2	-0.7	3.2	99.5

Parameters are determined from the phenomenological photocurrent (PC) formula fittings for the monolayer MoS₂ grown by chemical vapor deposition. The PC components are obtained by 1.96 and 2.33 eV circularly polarized excitations.

The picture changes remarkably in the case of PC observed for excitation with photon energy at 1.96 eV, which is on-resonance with the excitonic transitions. This photon energy is on-resonance mainly with A excitons. When pumped at 1.96 eV, the energy jumps just above the A exciton but below the B exciton. This excitation is on resonance with either A or B excitons. However, it can populate mainly K valleys for $\sigma +$ excitations and $-K$ valleys for $\sigma -$ excitations related to the A excitons [97]. Since A excitons are much stronger in intensity than the B excitons and 1.96 eV is an energy below the B excitons, populations in K ($-K$) valleys due to $\sigma +$ ($\sigma -$) excitations related to the B excitons are negligible.

In this case, the angle of photon polarization dependence of PC exhibits a clear difference between $\sigma +$ and $\sigma -$ excitations in Figure 5.10 (b), as expected for spin-coupled valley currents with resonant excitation. As shown in Table 5.1, the parameter C_1 is much larger compared with the 2.33 eV excitation, although L_1 is still small and L_2 gets relatively smaller. The coefficients C_1 and L_2 stand as the most prominent ones in determining polarization-dependent PC ($\sigma \pm$). The parameter C_1 becomes negligible for the on-resonance excitation once the angle of incidence $\theta = 0^\circ$, as shown in Figure 5.11 and Table 5.2. The figure of merit for PC polarization can be taken as the ratio of $|C_1|/|L_2|$, which is 0.06 for off-resonance (2.33 eV) excitation and 1.94 for on-resonance (1.96 eV) excitation. In terms of microscopic origin, the PC polarization for the excitation on resonance with the A excitons can be qualitatively given as $\sim |v_{v(i)}\tau(\varepsilon_v)|/|v_c\tau(\varepsilon_c)|$ based on the j_{CPGE} defined earlier in Figure 5.1. In other words, j_{CPGE} dominates and the concomitant P has high values of $60 \pm 30\%$ when excited by 1.96 eV. This value is larger when compared with PL polarization at zero V_g presented in Figure 5.12. This could be due to loss of polarization during the process of circularly polarized excitation and collection in PL measurements. Also, in PC measurements, we are able to identify purely the CPGE-dependent valley current and additional effects in PL are suppressed. The large error in P can be explained by the fluctuations in the data. One straightforward reason could be due to the device fabrication, which can be enhanced, and it is an ongoing work. If this is an intrinsic property, it could be due the fact that the density of excitons [Figure 5.1] in S-CVD is much lower than that in mechanically cleaved (S-MC) samples. Indeed, well-defined helicity dependent PC response can be seen in S-MC in Figure 5.13. Another note is about the nature of the intrinsic strain in S-CVD. The relatively smaller compressive strain may lead to a pronounced valley polarization⁶ in S-CVD sample. The large fluctuations in S-CVD

can be alternatively explained in terms of non-uniform emission-absorption processes in CVD samples. As a result, valley currents in different valleys can be affected by these non-uniformities, leading to a largely varying PC polarization, when excited by 1.96 eV on-resonance laser. On the other hand, when samples are excited by 2.33 eV laser, which is off-resonance for both A and B excitons, there are no fluctuations in valley current. The latter also implies the role of on-resonant excitation with excitons and its relation to the j_{CPGE} and PC polarization

It is possible to obtain a better signal by further improvement of device fabrication. As a control experiment, we use the same experimental setup at $\theta = 45^\circ$ with on-resonance laser, only by replacing circularly polarized light by linearly polarized light (use half-wave plate instead of QWP); the data at 45° , 135° , 225° and 315° yield similar values, unlike circularly polarized excitation. We also give a comparison of our results of the CVD grown monolayer MoS₂ sample with the results of a mechanically cleaved monolayer MoS₂ sample shown in Figure 5.14. Electrical measurements are presented in Figure 5.6, Figure 5.7 and Figure 5.15. Circularly polarized PL is shown in Figure 5.16 and light helicity-dependent spin-valley current is shown Figure 5.13 together with Table 5.2. In mechanically cleaved sample, the PC polarization that reflects the spin-valley coupling is relatively smaller than the CVD sample as explained before, which makes CVD grown MoS₂ devices promising for spin-dependent opto-valleytronic applications.

Figure 5.11 Light helicity dependent photocurrent in monolayer MoS₂ grown by chemical vapor deposition for normal incidence. (a) Photocurrent as a function of angle of photon polarization ϕ is shown for the monolayer MoS₂ grown by chemical vapor deposition (S-CVD) when illuminated by 2.33 eV (off-resonance with excitons) laser at $\theta = 0^\circ$. The green curve is the fitting function based on the phenomenological PC formula for monolayer MoS₂, yielding negligible PC polarization. (b) PC as a function of angle of incidence of polarization ϕ is shown for S-CVD when illuminated by 1.96 eV (on-resonance with A exciton) laser. The red curve is the fitting function based on the phenomenological PC formula for monolayer MoS₂, yielding a similarly negligible PC polarization. These data provide evidence for spin-valley PC due to the differences of the CPGE observed for σ^+ and σ^- excitation only for $\theta \neq 0^\circ$, and for laser on-resonance with A exciton.

	C_1	L_1	L_2	D
1.96 eV	-0.2	-1.1	5.4	146.7
2.33 eV	-0.3	0.3	4.1	107.0

Table 5.2 Photocurrent components of the monolayer MoS₂ grown by chemical vapor deposition, excited at normal incidence. Parameters are determined from the phenomenological photocurrent fittings. The PC components obtained by 1.96 and 2.33

eV circularly polarized excitations at $\theta = 0^\circ$. For both on-resonance (1.96 eV) and off-resonance excitations, C_1 is negligibly small. As expected, the circular photogalvanic effect not observed for no oblique incidence ($\theta = 0^\circ$, normal incidence). The linear photogalvanic and linear photon-drag terms are the only observed polarization dependent components.

Figure 5.12 Circularly polarized photoluminescence of monolayer MoS₂ grown by chemical vapour deposition. The peak photoluminescence (PL) of the sample grown by chemical vapour deposition (S-CVD) is at 1.865 eV. The PL intensity of S-CVD for both left (black solid curve) and right (red dash dot curve) circularly polarized PL upon excitation with left circularly polarized light is shown on the right axis. On the left axis degree of circular polarization (blue solid curve) yields a PL polarization of $\sim 10\%$.

Figure 5.13 Spin coupled valley dependent dichroic photocurrent in monolayer MoS₂ prepared by mechanical cleaving. (a) Photocurrent as a function of angle of photon polarization ϕ when illuminated by 2.33 eV (off-resonance with excitons) laser, for the monolayer MoS₂ sample prepared by mechanical exfoliation (S-MC). The cyan curve is the fitting function based on the phenomenological PC formula for monolayer MoS₂, yielding negligible polarization. (b) PC amplitude as a function of angle of incidence of polarization when illuminated by 1.96 eV (on-resonance with A exciton) laser, for S-MC. The magenta curve is the fitting function based on the phenomenological PC formula for monolayer MoS₂, yielding a polarization of $\sim 40 \pm 8 \%$. The data at 1.96 eV excitation show large PC variation and much clear helicity dependent PC which may be due to larger exciton density in S-MC.

Figure 5.14 (a) Raman peaks of the mechanically cleaved sample (S-MC) are E_{2g}^1 peak which is at 385 cm^{-1} and A_{1g} peak which is at 403 cm^{-1} . The spectrum is similar to that of the sample grown by chemical vapour deposition, S-CVD. (b) Photoluminescence of S-MC is shown. The strong direct excitonic A peak is at 1.89 eV for S-MC. The peak intensity is doubled in S-MC and a blueshift of $\sim 50\text{ meV}$ observed, compared to S-CVD. This could be due to modulated n-type doping for S-MC sample [80]. The other direct excitonic B peak is at 1.98 eV for both S-MC and S-CVD. The respective optical image

is shown in the inset. The dash lines in the inset are drawn to make easier to visualize the flakes. The orange bars are the Ti/Au contacts. The scale bar is 2 μm . (c) Fluorescence image of the sample prepared by mechanical cleaving (S-MC). Solid lines show the Ti/Au contacts. Dash lines show the flake. The scale bar is 1 μm . The fluorescence image is relatively weaker than the sample grown by chemical vapour deposition (S-CVD).

Figure 5.15 (a) Drain current vs. drain voltage characteristics of mechanically cleaved monolayer MoS₂ field-effect transistor S-MC, at zero gate voltage, in logarithmic scale. Empty circles denote the data at dark, full circle show the data at 20 mWcm⁻² illumination by 2.33 eV laser excitation. (b) Drain current vs. gate voltage characteristics of mechanically cleaved monolayer MoS₂ field-effect transistor S-MC, at 10 V drain voltage, in logarithmic scale. Empty circles show the data at dark, full circles show the data at 20 mWcm⁻² illumination by 2.33 eV laser excitation.

Figure 5.16 The peak photoluminescence (PL) of monolayer MoS₂ prepared by mechanical cleaving (S-MC) is at 1.865 eV. The PL intensity of S-MC for both left (black solid curve) and right (red dash dot curve) circularly polarized PL upon excitation with left circularly polarized light is shown on the right axis. On the left axis degree of circular polarization (blue solid curve) yields a PL polarization of $\sim 10\%$.

5.3 Summary and Conclusions

Our results of exciton-related spin-coupled valley-dependent PC are consistent with helicity-dependent PL measurements¹¹ and recent observation of the valley Hall effect in monolayer MoS₂ [209]. These results may have a number of applications in nanoelectronics and photonics, such as polarization sensitive light-detection schemes or integrated spintronic devices. Furthermore, more examples can be developed based on magnetoelectric effects of bilayer TMDs [210] and spin-orbit interaction in graphene/TMD hybrid systems [211], since CVD grown TMD devices are promising in

terms of electrical transport [212]. Thanks to room-temperature operation, the control over spin-dependent valley PC is more application oriented than the recently discovered helicity-dependent PC of topological insulators [44]. Moreover, special attention should be paid to biological environments, which are sensitive to light handedness and color. Examples can be given in the areas of light-harvesting chlorophyll (LHC) research [213] and biomolecule-nanoparticle interaction [214]. For instance, light helicity dependence has been demonstrated for the chiral LHC, which functions around red color (633 nm - 1.96 eV) wavelength but insensitive to green colour [215]. This realizes the possibility of integrating chiral LHC with ultrasensitive spin-valley-coupled MoS₂ phototransistors. Also, the biophysical community has been investigating the protein binding to nanomaterials for vision-related nanomedical purposes [216]. On the basis of our observations, we believe it is viable to utilize the unique optoelectronic features of MoS₂ in the exploration of light sensitive bio-nano systems.

We emphasize that high-quality monolayer MoS₂, which is a spin-valley coupling system grown by chemical vapour deposition fabricated as phototransistor exhibits helicity dependent PC behaviour, based on its unique symmetry conditions. Spin-dependent valley currents can be generated by circularly polarized laser, and can be manipulated by laser excitation and electrical gating. We were able to demonstrate that in K or $-K$ valleys with given spin (up or down, respectively) exciton-related electron conduction can take place, and PC polarization as high as 60% was obtained by choosing a suitable visible laser with a known circular polarization ($\sigma +$ or $\sigma -$). The observed PC polarization degree is even higher than the PL polarization since we can resolve purely the CPGE-dependent valley current. The findings in this work shed light into the intrinsic photogalvanic effects and helicity-selective transitions in monolayer transition metal dichalcogenides. Beside their fundamental importance, we believe these

results may pave the way for application of opto-valleytronic device concepts in interdisciplinary research spanning from nanoelectronics and photonics to biotechnologies.

Chapter 6

Conclusions and Future Perspectives

6.1 Conclusions

This thesis contains three parts. Firstly, we present the preliminary results on the helicity dependent photocurrent in biased bilayer graphene. Secondly, low temperature photoresponse of monolayer WS_2 with fast response time is studied. Thirdly, we demonstrate the observation of dichroic spin-valley photocurrent in monolayer MoS_2 .

6.1.1 Helicity dependent PC in biased bilayer graphene

In this part, we report the experimental determination of the PC response of bilayer graphene as a function of light intensity and state of polarization, as well as carrier density and polarity. The data shows qualitative features in common with the PC that is expected to arise from the photon-drag and the circular photogalvanic effects, as seen in monolayer graphene. In addition, we identify a non-negligible contribution to the PC of different nature, with anomalous dependence on light polarization. These results highlight the richness of bilayer graphene photoresponse, providing an opportunity to establish light helicity as an approach to manipulate the photoconductive behavior of future optoelectronic graphene devices.

6.1.2 Low temperature photoresponse of monolayer WS_2

High photoresponse can be achieved in monolayers of transition metal dichalcogenides. However, the response times are inconveniently limited by defects. Here, we report low temperature photoresponse of monolayer WS_2 prepared by

exfoliation and CVD method. The exfoliated device exhibits n-type behaviour; while the CVD device exhibits intrinsic behaviour. In off state, the CVD device has four times larger ratio of photoresponse for laser on/off and photoresponse decay-rise times are 0.1s (limited by our setup), while the exfoliated device has few seconds. These findings are discussed in terms of charge trapping and localization.

6.1.3 Dichroic spin-valley PC in monolayer MoS₂

In this part, we elucidate the excitonic physics of monolayer MoS₂ by light helicity-dependent PC studies of phototransistors. We demonstrate that large PC dichroism (up to 60%) can also be achieved in high-quality MoS₂ monolayers grown by CVD, due to the circular photogalvanic effect on resonant excitations. This opens up new opportunities for valleytronics applications in which selective control of spin-valley-coupled PCs can be used to implement polarization-sensitive light-detection schemes or integrated spintronic devices, as well as biochemical sensors operating at visible frequencies.

6.2 Future Perspectives

6.2.1 Photocurrent in ABA stacked Tri-layer Graphene

We would like to carry on our study on graphene based photocurrent to thicker layers. As a start, we performed helicity dependent measurement on ABA (Bernal) stacked tri-layer graphene. Figure 6.1 shows our results, indicating that the tri-layer graphene also exhibits similar helicity dependent photoresponse. Further experiments and theoretical explanation are need for this work.

Figure 6.1 Helicity dependent photocurrent in ABA tri-layer graphene.

6.2.2 Magneto-Photoconductivity of Three-Dimensional Topological Insulator

6.2.2.1 Introduction

Topological insulator (TI) is an exotic phase of quantum matter with an insulating bulk state as well as time-reversal symmetry-protected Dirac-like surface states. The materials having TI phase belong to a large family of material systems ranging from 2D to 3D and from HgTe quantum wells to bismuth, selenium, tellurium, and antimony based alloys [217]. Well-known examples of bismuth based TI materials are bismuth selenide (Bi_2Se_3) and bismuth telluride (Bi_2Te_3) which are 3D TI for thickness above 5 nm (5 quintuples) [218]. One of the intriguing differences between these two similar tetradymite type structure 3D TI systems, is the unconventional hexagonal warping of the surface states in Bi_2Te_3 [219] which is the reason behind the observations of snowflake shape of the Fermi surface in angle resolved photoemission spectroscopy [220] and surface band oscillations in scanning tunneling microscopy

[221]. A rich spin texture is a natural expectation of the warping of the surface states. In order to make use of the spin properties of TI systems, as a first step, the conduction of surface states shouldn't be masked by bulk conduction. Although Bi_2Te_3 is usually rather metallic and the Fermi energy is way above the Dirac point, it is possible to make Bi_2Te_3 non-metallic and Shubnikov-de Haas (SdH) oscillations can be observed; which is a clear sign of the surface state conduction as shown at low temperature transport studies [222]. Another transport feature of TI materials is the weak-antilocalization (WAL) observed as a negative magneto-conductance in Bi_2Te_3 thin films [223] due to the absence of backscattering by nonmagnetic impurities [224]. At high magnetic fields, the WAL is suppressed. In magneto-transport of 3D Bi_2Te_3 , a detailed and careful analysis is required to extract information about surface state conduction. In these two transport signatures, the SdH oscillations and the WAL, distinguishing bulk conduction from surface state conduction remains as a challenge.

On the other hand, opto-electronic response of the surface states can be obtained from helicity-dependent photocurrents by using circularly polarized light [75]. As demonstrated in 250 nm thick 3D TI Bi_2Se_3 , the sign of spin-dependent photocurrent changes based on light helicity as a result of circular photogalvanic effect (CPGE) acting on the helical Dirac surface states [44]. This shows the importance of photocurrent studies in TI to identify the surface state conduction. The CPGE can also be observed at normal incidence if a magnetic field is applied [75]. Therefore, it is possible to observe surface state conduction by photocurrent at non-zero magnetic field. The photo-excited carriers in the surface states can couple with the magnetic field and there will be a net photocurrent which has magnetic field dependence. In this work, we present low temperature magneto-photoconductance (MPC) of two 3D Bi_2Te_3 samples, with different thickness, excited by polarized light with a normal incidence on to the sample

plane and the magnetic field applied in the illumination direction. We show that even at zero-degree angle of photon polarization it is possible to distinguish surface states from bulk states by MPC and provide a discussion in terms of localization effects. Then we further elaborate the temperature dependence of MPC in the thicker sample which shows unexpected localization behaviour. We interpret this observation in terms of separation of surface state conduction from bulk conduction.

6.2.2.2 Experimental

Exfoliated flakes of Bi_2Te_3 were fabricated into four terminal devices. Two samples were picked for MPC measurements, with thickness 68 nm (S1) and 110 nm (S2) as determined by AFM measurements. The current voltage (IV) characteristics and the laser power dependence of photocurrent of the two samples are similar and comparable to the previously reported ones [225]. Figure 6.2 (a) and (b) shows the IV at room and 4 K, and photocurrent at various laser powers at 4 K, respectively, for S1.

Measurements are performed in a cryostat with a micrometer precision stage. After locating the devices, IV is performed by four-probe technique. The measured linear IV indicates the contacts are ohmic. Then, a beam spot of 1 μm is focused at the center of the two electrodes separated by 2 μm . A linearly polarized solid-state laser with wavelength 532 nm chopped by 137 Hz frequency and the magnitude and phase of photocurrent signal are collected by a low noise current pre-amplifier connected to a lock-in amplifier. A quarter waveplate is set initially to zero-degree photon polarization. Photocurrent is measured for laser powers lying in the linear response regime. The magnetic field is applied perpendicular to the sample plane.

Figure 6.2 (a) IV characteristics of sample 1 (S1) and (b) photocurrent as a function of incident laser power for S1. The photocurrent response is linear with laser power.

6.2.2.3 Preliminary Results and Discussion

6.2.2.3.1 Laser power and thickness dependence of the MPC

In Figure 6.3 (a), the laser power dependence of the MPC of the thinner sample, S1 for 80 and 120 μW laser powers at 4 K is given. The MPC behaviors at two different laser powers are similar and based on the linear dependence of photocurrent of Figure 6.2 (b), it seems to be proportional at all fields. There is a negative MPC up to 4 T, which turns to a positive MPC at higher fields. The negative MPC is qualitatively similar to the previously observed WAL in transport [223]. As the field increases, the negative MPC is suppressed by spin-dependent transport term due to the surface states since there are no magnetic impurities in the system. But also, as the 3D quantum limit is exceeded at high fields [226] and two surface states can be coupled as the thickness get smaller [227], it is possible to observe a positive MPC. This turnover from negative MPC to positive MPC at 4 T agrees well with the previous transport in low carrier density Bi_2Se_3 [226].

Figure 6.3 (a) Photocurrent of thinner sample S1 shown at two different laser power. (b) Normalized photocurrent at 120 μW of two samples are compared. The MPC of the thinner sample dramatically changes sign around 4 T, while thicker sample becomes constant.

While S1 exhibits a turnover as a function of field and several photocurrent contributions take place; the thicker sample, S2, exhibits a simple negative MPC behavior. In Figure 6.3 (b), the photocurrent values of S1 and S2 at 4 K and 120 μW laser power are compared. The photocurrent value of S1 at zero field (4 T) is taken as 1 (0) and the photocurrent value of S2 at zero field (5.5 T) is taken as 1 (0). The negative MPC in S2 seems to saturate around 5.5 T. But at higher fields, it looks like constant rather than a positive MPC. This could be due to the increase in the ratio of bulk state conduction to surface state conduction as the thickness of TI increases. Since there is no positive MPC at higher fields, one can think that there is only one surface state at play and the analysis of the thicker sample S2 can be simpler. Similar to magneto-transport, this effect can be taken as WAL effect and useful parameters can be extracted.

6.2.2.3.2 Temperature Dependence of MPC

The magnitude of negative MPC of S2 drops as temperature increases as seen in Figure 6.4. There are some fluctuations of MPC, which may remind the Aharanov-Bohm

oscillations observed in topological insulator nanoribbons for in-plane magnetic fields [228]. On the other hand, S1 doesn't seem to have these fluctuations. As S2 is twice as thick, there could be contribution from the side surface states coupling with magnetic field. Although there is no clear trend in the fluctuations in S2, they are up to 10 pA. Given the fact that the change in photocurrent as a function of time at zero field within half an hour is not more than 1 pA, these fluctuations are not only noise. This need to be further studied in a different setup in which the applied field can be varied from perpendicular to the sample plane to in-plane.

Figure 6.4 Temperature dependence of MPC at several temperatures shown.

The temperature dependent MPC data can be fit to localization formula [229] for photocurrent as follows:

$$\Delta PC = -\frac{\alpha e^2}{2\pi^2 \hbar} \left[\ln \frac{\hbar}{4B e l_\phi^2} - \psi \left(\frac{1}{2} + \frac{\hbar}{4B e l_\phi^2} \right) \right] \quad (6.1)$$

where e is the electronic charge, $\hbar$ is the Planck's constant, l_ϕ is the phase coherent length, and ψ is the digamma function. α should be equal to 1 and -1/2 for the orthogonal

and symplectic cases, respectively. The fitting in Figure 6.5 (a) yields that, $\alpha = -0.65$, -0.56 , -0.32 , and 0.26 at 4 K, 10 K, 20 K, and 30 K, respectively. If α is $-1/2$ there should be one surface state, if it is equal to -1 there should be two surface states involved in the conduction of this strong spin-orbit coupling system. At temperatures below 20 K, there seems to be one surface state contributing to the conduction, which also explains why there is no positive MPC at higher fields. As temperature increases α drops because the surface state conduction becomes smaller. Eventually, at 30 K, there is a sign change of α which indicates, bulk states completely mask the surface states conduction.

Figure 6.5 (a) The difference between the photocurrent PC at a field and the PC at zero field, ΔPC , as a function of magnetic field at several temperatures is given, the curves are repositioned for a better presentation, the red solid lines are the localization fittings (b) phase coherence lengths plotted against temperature and fitted to $T^{-\frac{p}{2}}$ for $p = 0.75$ (dot), 1 (solid), 1.5 (dash dot), and 3 (dash).

In Figure 6.5 (b), the phase coherence lengths l_ϕ that are extracted from the localization fitting are plotted. The temperature dependence of $l_\phi \sim T^{-\frac{p}{2}}$ can provide information about the carrier-carrier ($p = 3/2$) or carrier-phonon interactions ($p=3$) [230]. Several possible fittings are shown: $p=3$ (dash) seems to be worse; while $p=0.75$ (dot)

and 1 (solid) are better ones (which have no physical meaning), $p=1.5$ (dash dot) is a better fit than $p=3$. This may indicate the electron-electron interaction, which is due to the bulk carriers may also play a role at low temperatures. This means in addition to weak-antilocalization due to the surface states, bulk state conduction can be identified by carrier-carrier interaction [231]. However, there is only one data point under 10 K and this data point deviates from the expectation of $p=1.5$ curve. Therefore, there is a need for more data points less than 10 K to have a better understanding of this MPC feature.

6.2.2.4 Summary and conclusion

Briefly, we present the difference in magneto-photoconductivity behavior of two metallic 3D Bi_2Te_3 samples with different thickness for 2.33 eV linearly polarized excitation with zero photon polarization. A negative MPC for both samples at fields lower than 4 T can be understood as WAL similar to transport. At higher fields, 68 nm thick sample shows positive MPC due to the coupling of surface states. The 110 nm thick sample shows photocurrent due to one surface state and as shown by the localization fitting analysis of MPC data at several temperatures, bulk conduction can be identified separately.

These preliminary results demonstrate another way to identify surface states, in addition to the photocurrent at zero magnetic field and oblique incidence. Similarly, the control over surface states by MPC can be studied by right and left circularly polarized excitations, as well as wavelength dependence of MPC. To further understand the physical mechanism of these phenomena, additional experiments and theoretical calculation are required.

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