Electronics and optoelectronic applications of Van Der Waals heterostructures

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**ELECTRONIC AND OPTOELECTRONIC APPLICATIONS OF
VAN DER WAALS HETEROSTRUCTURES**

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

2016

ELECTRONIC AND OPTOELECTRONIC APPLICATIONS OF VAN DER WAALS HETEROSTRUCTURES

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

A thesis submitted to the Nanyang Technological University
in partial fulfilment of the requirement for the degree of
Doctor of Philosophy

2016

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research and has not been submitted for a higher degree to any other University or Institution.

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Abstract

Two-dimensional (2D) layered materials are emerging candidates for future high-performance electronics and optoelectronics due to their unconventional mechanical, electronic and optoelectronic properties. Furthermore, they can be assembled into van der Waals heterostructures which display novel properties. The aim of my thesis is to develop a versatile and efficient assembling method to fabricate van der Waals heterostructures with clean interfaces, and to improve the performance of corresponding electronic and optoelectronic devices. To achieve this goal, I have done the following work.

First, I developed an interface energy-mediated transfer method to fabricate van der Waals heterostructures. 2D layered materials remained intact after transfer because no harsh reaction or supporting polymer was involved in this method. Few-layer graphene, h-BN, MoS₂ and WSe₂ were printed on the same PET substrate in a layer-by-layer manner. They acted as gate electrode, dielectric, n-channel and p-channel semiconductors, respectively in the complementary inverter fabricated on flexible substrates.

Second, the influence of interfacial properties to the photocurrent generation in MoS₂ photo-FETs is studied. By comparing the photocurrent of exposed and h-BN-encapsulated MoS₂ photo-FETs, I found that the trapping states from the interfaces between MoS₂ and SiO₂ is the main reason for prolonged photoresponse. I replaced the common SiO₂/Si gating stack with h-BN/FLG and achieved stable and fast photoresponse of MoS₂ photo-FETs. The hysteresis of the transistors was eliminated because of the dangling bond-free interfaces.

Third, a junction gate field-effect transistor was designed and fabricated on high-performance P-N junction of TMDCs. The quality of P-N junction was improved by doping the intrinsic WSe₂ with oxygen plasma. The doping level was high and stable. N-type MoS₂ was contacted with FLG electrodes to improve the on-currents.

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Abbreviations

2D	Two-Dimensional
AFM	Atomic Force Microscopy
Al ₂ O ₃	Aluminum Oxide
ALD	Atomic Layer Deposition
BP	Black Phosphorus
CAFM	Conductive Atomic Force Microscopy
CNT	Carbon Nanotube
CVD	Chemical Vapor Deposition
DI	Deionized
EBL	Electron Beam Lithography
eV	Electron Volt
FET	Field-Effect Transistor
FLG	Few-Layer Graphene
h-BN	Hexagonal-Boron Nitride
HfO ₂	Hafnium Oxide
I _{DS}	Drain-Source Current
IPA	Isopropyl Alcohol
JFET	Junction Gate Field-Effect Transistor
KPFM	Kelvin Probe Force Microscopy
MESFET	Metal-Semiconductor Field-Effect Transistor
MIBK	Methyl Isobutyl Ketone
MOSFET	Metal-Oxide-Semiconductor Field-Effect Transistor
MoS ₂	Molybdenum Disulfide
NADH	Nicotinamide Adenine Dinucleotide
ODTS	octadecyltrichlorosilane
OM	Optical Microscopy
PDMS	Polydimethylsiloxane
PET	Polyethylene Terephthalate
PL	Photoluminescence

SEM	Scanning Electron Microscope
SiNW	Silicon Nanowire
SiO ₂	Silicon Dioxide
TCNQ	Tetracyanoquinodimethane
TMDC	Transition Metal Dichalcogenides
V _{BG}	Back Gate Voltage
V _{DS}	Drain-Source Voltage
V _{GS}	Gate-Source Voltage
WSe ₂	Tungsten Diselenide
WS ₂	Tungsten Disulfide
ZnO	Zinc Oxide

Chapter 1

Introduction

Based on previous efforts to fabricate van der Waals heterostructures, it is anticipated that the different interfacial interactions between substrates and 2D materials could be harnessed to transfer and print 2D layered materials efficiently for high-performance electronics and optoelectronics. Such a hypothesis guides the content of this thesis, which is designed for three objectives. First, electronic circuits are to be fabricated from van der Waals heterostructures. Second, stable photocurrents of MoS₂ photo-FETs should be obtained by introducing van der Waals interfaces. Last, junction field-effect transistors based on high-quality P-N junctions of transition metal dichalcogenides are to be demonstrated. Detailed experiments, results and discussion are presented in this sequence to prove the hypotheses. Future work based on the results of this thesis is suggested.

1.1 Hypothesis/Problem Statement

Two-dimensional (2D) layered materials, including semimetallic graphene, semiconducting transition metal dichalcogenides (TMDCs) and insulating hexagonal boron nitride (h-BN) hold much promise for a new generation of high-performance electronics owing to their outstanding mechanical, electronic and optoelectronic properties. A variety of novel electronic and optoelectronic devices have been designed and realized by assembling these materials with distinctively different properties into heterostructures which are called van der Waals heterostructures. The assembling methods play a vital role in fabricating van der Waals heterostructures with clean interfaces for high performances while the scaling-up abilities and versatility of the assembling methods are the prerequisites for large-area electronics. However, reported assembling methods have been time-consuming, limited to small scale, intense chemical reaction involved and/or contaminating. The hypothesis of this thesis is that the difference of interfacial interactions between substrates and materials could be harnessed to transfer and print 2D layered materials efficiently for high-performance electronics and optoelectronics.

1.2 Objectives and Scope

The objectives of this thesis are described below.

First of all, the surfaces of SiO₂/Si substrates which are most commonly used substrates for 2D layered materials will be modified to show different hydrophilicity. A variety of 2D layered materials will be deposited onto these substrates by mechanical exfoliation. After thoroughly characterized with optical microscopy (OM), atomic force microscopy (AFM), Raman spectroscopy and photoluminescence (PL) spectroscopy, the 2D layered materials are to be detached from the substrates through a polymer-free transfer process with a high yield. They will be printed onto flexible substrates layer by layer and electronic circuits will be fabricated based on these van der Waals heterostructures.

Second, the influence of interfacial properties to the photocurrent generation in photo-field-effect transistors based on layered semiconductors will be studied. By encapsulating the channel materials with h-BN, the detrimental effects brought by trapping states from common SiO₂ surfaces are expected to be alleviated. Faster and more stable photodetectors are to be constructed on van der Waals heterostructures.

Third, a junction gate field-effect transistor will be designed and fabricated on high-performance P-N junctions of TMDCs. Intrinsic tungsten diselenide (WSe₂) nanosheets will be p-doped with oxygen plasma. Unintentionally n-doped molybdenum disulfide nanosheets will be transferred on to p-WSe₂ to form P-N junctions. By replacing the ordinary metal electrodes with graphene electrodes, the on-current and thus the overall performances of JFETs will be improved.

The synthetic methods such as chemical vapor deposition (CVD) for numerous 2D layered materials have evolved dramatically during last decade, opening the way to high-performance and large-area electronics. Numerous protocols about assembly of these materials and fabrication of devices should be developed to facilitate the commercialization of these materials. I believe the works introduced in this thesis would make a contribution to this end.

1.3 Dissertation Overview

The thesis addresses a new method to transfer 2D layered materials such as graphene, MoS₂, WSe₂ and h-BN in order to fabricate van der Waals heterostructures for electronic and optoelectronic applications. Logic circuits, photodetectors and junction gate field-effect transistors are fabricated based on these van der Waals heterostructures and show much potential in high-performance electronics combined with the advances of material synthesis.

Chapter 1 provides a rationale for the research and outlines the goals and scope.

Chapter 2 reviews the literature concerning electronic and optoelectronic properties of 2D layered materials, and electronic devices based on van der Waals heterostructures. The outstanding photoresponsive properties and novel device designs based on these structures are also reviewed. At the end of this chapter, the main challenges against real applications are described.

Chapter 3 discusses the principles underlying the choice and preparation of materials, characterization of 2D layered materials and their heterostructures, fabrication and testing of electronic devices, data analysis and mechanism study.

Chapter 4 elaborates the interface energy-mediated transfer printing of 2D layered materials for electronics on flexible substrates.

Chapter 5 elaborates the influence of van der Waals interfaces on the photodetecting performance of MoS₂ photo-field-effect transistors (photo-FETs). Faster and more stable photocurrents are demonstrated in MoS₂ photo-FETs with van der Waals interfaces than those with common 2D layered materials-SiO₂ interfaces.

Chapter 6 elaborates the design and realization of junction gate field-effect transistors (JFETs) constructed fully from 2D layered materials.

Chapter 7 draws together the threads of this thesis. Reconnaissance studies are introduced to guide future work.

1.4 Findings and Outcomes/Originality

This research led to several novel outcomes by:

1. Demonstrating an easy and efficient method to transfer and print 2D layered materials for electronics on flexible substrates. Few-layer graphene, h-BN, MoS₂ and WSe₂ nanosheets, acting as gate electrodes, dielectric, n-channel and p-channel

semiconductors, respectively are transferred on to flexible polyethylene terephthalate (PET) substrates from SiO_2/Si substrates sequentially. By virtue of clean interfaces between the layered materials, a high-performance complementary inverter is realized.

2. Comparing the photocurrent of MoS_2 photo-FETs with van der Waals interfaces and with common $\text{MoS}_2\text{-SiO}_2$ interfaces. MoS_2 nanosheets are interfaced with dangling bond-free h-BN to eliminate the hysteresis brought by trapping states at $\text{MoS}_2\text{-SiO}_2$ interfaces. Transparent few-layer graphene is employed as electrodes in replace of metal electrodes to increase the photon absorption and photocurrent collection. Benefiting from these two modifications, the MoS_2 photo-field-effect transistors with van der Waals interfaces generate stable, fast and sensitive photocurrents.
3. Designing and constructing junction gate field-effect transistors from heterostructures of transition metal dichalcogenides. WSe_2 are p-doped by oxygen plasma treatment and unintentionally n-doped MoS_2 is transferred on to p-doped WSe_2 to form p-n junctions. In this case MoS_2 channels can be turned off by applying a negative gate voltage to p-doped WSe_2 , fulfilling the operation of a junction gate field-effect transistor. Graphene strips are utilized as electrodes for MoS_2 to improve the on-currents as they have shown better carrier injection than metal electrodes.

Chapter 2

Literature Review

This chapter reviews recent study of electronics and optoelectronics of two-dimensional layered materials and their heterostructures. Electronic and optoelectronic properties of two-dimensional layered materials are introduced first. Afterwards layered semiconductors based field-effect transistors and their photoresponse are elaborated. And then special attention is paid to van der Waals heterostructures. The operation mechanism of junction gate field-effect transistors and their nanomaterial counterparts are described as well. Finally, questions needed to answer based on literature and context of this thesis are discussed.

2.1 Overview

Silicon technology has been the driving force for modern electronics and optoelectronics. As the size of silicon metal-oxide-semiconductor field-effect transistor (MOSFETs) approaches the fundamental physical limits, the Moore's Law which projects the increase of electronic components on a single chip will come to an end in the near future.^[1, 2] In addition, the rigidity and high processing temperature of silicon limit its applications in flexible electronics. What's more, the unfavorable indirect band gap sets back the silicon optoelectronics. These limitations of silicon electronics and optoelectronics call for a new generation of materials with superior properties. To this end, semiconducting nanomaterials such as silicon nanowires (SiNWs) and carbon nanotubes (CNTs) have drawn great attention in last two decades.^[3-7]

The last decade has witnessed the rise of 2D layered materials.^[8-12] They comprise of a large family of materials such as graphene, h-BN, TMDCs and black phosphorus (BP), which exhibit rich electronic behaviors ranging from metals, semimetals, semiconductors to insulators. A variety of electronic and optoelectronic applications of 2D layered materials have been investigated. More intriguingly, stacking 2D layered materials or growing their heterostructures brings more unusual electronic and photonic properties.

2.1.1 Electronic and optoelectronic properties of two-dimensional layered materials

The crystal structures, quantum confinement effects and dangling bond-free surfaces of 2D layered materials give rise to unique electronic and optoelectronic properties. The band gaps of these materials span from 0 eV for graphene to 6.0 eV for hexagonal boron nitride, covering an extremely wide electromagnetic spectral range.^[13] The bandstructures, which determines the light-matter interactions, of single-layer h-BN, MoS₂, BP and graphene are shown in Figure 2.1. They are explored for different applications such as transistors, photodetectors and light-emitting devices. In this section, the electronic and optoelectronic properties of 2D layered materials are elaborated with special attention to

graphene and TMDCs, two kinds of 2D layered materials that have been mostly studied.

Figure 2.1 Atomic structures and bandstructures of single-layer h-BN (a), MoS₂ (b), BP (c) and graphene (d).^[13]

Graphene Graphene, a single-layer sheet of carbon atoms packed into a hexagonal honeycomb lattice is known for Dirac electrons.^[14, 15] They behave like massless Dirac fermions and have shown unprecedentedly high mobilities. Ballistic transport over 28 μm in CVD graphene has been observed.^[16] Conduction and valence bands of graphene intersect at the Dirac points as shown in Figure 2.2, which is the origin of its semi-metallic nature. The linear energy dispersion relation and vanishing density of states near the Dirac cones lead to a large tunability of the Fermi level.

Figure 2.2 Energy spectrum (left) and zoom-in of the energy bands at the Dirac point (right).^[15]

The tunable work function of graphene is usually the basis of designing van der Waals heterostructures based on graphene since graphene is frequently used as atomically thin electrodes for carrier injection. Fermi level of graphene shifts with the change of carrier density induced by electrostatic field effect^[17, 18] or charge-transfer doping^[19-21]. Yu et al. applied Kelvin probe force microscopy (KPFM) to monitor the variation of surface potential of a graphene channel induced by electrostatic field effect.^[17] Figure 2.3 (a) is the schematic diagram showing the experiment for measurements. The surface potential of graphene is modulated by applying gate voltage V_g to the degenerately doped Si substrate and measured by using a KPFM with Cr/Au coated probes. A clear change of contrast between graphene and the SiO₂ substrate is observed when the gate voltage is increased. It indicates that the surface potential of graphene responds to the gate voltage. Theoretical and experimental studies relate the Fermi energy to the carrier density by the following equation:

$$E_F = \text{sign}(\Delta V_g) \hbar v_F (\alpha \pi |\Delta V_g|)^{1/2}$$

where α is the dielectric capacitance in electron charge, v_F is the Fermi velocity of single-layer graphene.^[17, 22] For certain applications, the electrostatic doping is replaced by charge transfer doping due to its simplicity.^[19, 20, 23-27]

Figure 2.3 (a) Schematic diagram showing the experiment for measurements. Optical (b), topography (c), SKPM at $V_g = 0$ V (d) and at $V_g = 10$ V (e) images of the device, respectively.^[17]

Graphene features a broadband absorption of photons^[28-30] and ultrafast carrier dynamics^[31-34]. It absorbs constantly 2.293% of light from visible to infrared due to its electronic fine structure. This weak absorption along with high conductivity endows

graphene with a great potential for transparent electrodes. The ultrafast carrier dynamic of graphene is advantageous for developing ultrafast photodetectors.^[35]

Hexagonal boron nitride H-BN is an isomorph of graphene with carbon atoms being replaced by boron and nitrogen atoms. Although the interlayer interaction of h-BN is van der Waals force as that of graphene, the strong in-plane chemical bonding is partially ionic, unlike the pure sp^2 covalent bonding in graphene.^[36] This distinct bonding results in different electronic properties of h-BN. It is an insulator with a large band gap and has been used as a dielectric for graphene transistors.^[37] Unlike traditional SiO_2 and high dielectric oxide dielectrics, h-BN is free of dangling bonds and surface charge traps. In addition, h-BN is atomically flat and uniform even when the thickness is reduced to a single layer. It is an alternative for ultrathin dielectric applications where the properties of oxide are difficult to control.

Conductive atomic force microscopy (CAFM) has been used to study the electronic tunneling through ultrathin h-BN layers.^[38, 39] Figure 2.4 (C) shows the uniform resistance map of h-BN tunneling layer with different thicknesses.^[39] No pinholes or defects which lead to spikes of measured currents on the layer of same thickness are observed. The breakdown electric field is as high as 1GV/m which is comparable to that of SiO_2 . At low biases, the measured current is ascribed to direct tunneling of electrons through the h-BN layers. This mechanism is corroborated by the linear I-V relation at low biases and the exponential decay of low-bias conductance with increased thicknesses. At high bias, Fowler-Nordheim tunneling dominates and the current increases nonlinearly with bias. (Figure 2.4 (D))

Transition metal dichalcogenides The general formula of TMDCs is MX_2 where M is a transition metal and X is a chalcogen. They crystallize predominantly in a layered structure with metal atoms sandwiched between two chalcogen atom layers. A few TMDCs such as MoS_2 , WS_2 , WSe_2 are semiconductors with band gaps of 1.0-2.5 eV when the metal coordination is trigonal prismatic.^[40] The electronic structures of semiconducting TMDCs depend on their thicknesses. For example, bulk MoS_2 has an

indirect band gap of 1.2 eV but gradually change to direct with a value of 1.9 eV for single-layer MoS₂.^[41-43] (Figure 2.5) The crossover of band gap results in distinct light-matter interactions. Photoluminescence from single-layer MoS₂ is much stronger than that from few-layer or bulk MoS₂. The absorption edge redshifts for few-layer MoS₂ compared to single-layer MoS₂, resulting in different photoresponsive range.

Figure 2.4 (A) Schematic diagram of the CAFM measurement setup. H-BN layers are deposited on a graphite substrate. The current is recorded when a conductive AFM probe scans over the surface. (B) Topographic image of the h-BN layers measured by a tapping mode AFM. (C) Resistance map measured at the same position in (B). (D) I-V curves of h-BN with different thicknesses.

There is usually a small density of free charge carriers in pristine TMDCs due to the presence of crystal defects and substrate effects. For example, the unintentionally n-type doping of MoS₂ is usually ascribed to sulfur vacancies.^[44] Conventional substitutional doping has been tried to tune the carrier type and density.^[45] Thanks to their large specific surface area, the electronic properties of semiconducting TMDCs can also be modified drastically by charge transfer doping with proper dopants. Fang et al. reported degenerate n-doping of MoS₂ and WSe₂ by potassium.^[46] However, potassium is air unstable and this experiment needs to be carried out in vacuum. Later, Lin et al. used thermally evaporated cesium carbonate (Cs₂CO₃) to dope MoS₂.^[47] A clear negative shift of threshold voltage of MoS₂ field-effect transistor can be seen after Cs₂CO₃ doping (Figure 2.6 (a)), indicating an efficient n-doping effect. Unexpectedly, an increased photocurrent is also observed as shown in Figure 2.6 (b). This phenomenon suggests that the optoelectronic properties of 2D layered semiconductors can be tuned by using proper doping strategies.

Mouri et al. reported the n- and p-type doping effects of nicotinamide adenine dinucleotide (NADH) and tetracyanoquinodimethane (TCNQ) on single-layer MoS₂, respectively.^[48] The doping effects lead to a drastic change of the photoluminescence intensity because the quantum yield of photon emission is dependent on the density of free carriers. Many other substances such as DNA^[49], benzyl viologen^[50], dichloroethane^[51] and ozone^[52] are verified dopants for TMDCs.

Figure 2.5 Band structures of MoS₂ with different thicknesses calculated by density function theory. The arrows indicate whether the MoS₂ has a direct or indirect band gap. The top of valence band and bottom of conduction band are highlighted by blue and green, respectively.^[43]

Figure 2.6 (a) Transfer characteristics of a MoS₂ transistor under dark and light conditions before and after Cs₂CO₃ doping. (b) Photocurrents of a MoS₂ transistor under the same illumination conditions with and without Cs₂CO₃ doping.^[47]

2.1.2 Photo-field-effect transistors based on two-dimensional layered materials

Field-effect transistors Graphene was considered as a candidate material in the past-Si age due to unapproachable thin body and high mobility. However, the zero-band gap nature makes it difficult to turn off the graphene transistors. In other words, the on-off ratio of graphene transistors is too small for practical logic circuits. The emergence of 2D semiconducting TMDCs provides new opportunities because of their finite band gap and reasonable mobilities.^[10, 53-58] Radisavljevic et al. demonstrate the first single-layer MoS₂ transistor.^[59] Figure 2.7 shows the fabrication of MoS₂ transistors. It is typical for other 2D semiconductors based transistors as well. Single- and few-layer 2D semiconductors are usually prepared by mechanical exfoliation and deposited on SiO₂/Si substrates. This method is known as “scotch tap method” which was firstly used to exfoliate single-layer graphene.^[14] Semiconductor processings enable electrode fabrication and dielectric deposition. As shown in Figure 2.7 (b) and (c), HfO₂ is deposited by atomic layer deposition (ALD) as high-k top dielectric. Each component of the device has been improved significantly during the last few years. CVD has been employed to synthesize a variety of 2D layered semiconductors such as MoS₂^[60-62], WS₂^[63], WSe₂^[64] etc. as channel materials. Ohmic contacts have been explored for these materials to fabricate transistors with low contact resistance and desired polarity.^[65-73]

The roles the dielectric environment in the performance of transistors have been studied.^[74-82]

Figure 2.7 (a) Optical image of single-layer MoS₂ on Si substrates with 270 nm SiO₂. (b) Optical image of the fabricated devices. Scale bars in (a) and (b) are both 10 μ m. (c) Schematic illustration of a transistor with both top and bottom gates.^[59]

Metal-semiconductor-metal photodetectors One of the simplest photodetectors are metal-semiconductor-metal photodetectors which are semiconductors contacted with two metal electrodes. They are called “photoconductors” when the contacts are Ohmic. However, the contacts are usually engineered to be Schottky ones to reduce the dark currents. A semiconducting nanowire contacted with two Schottky contacts is taken as an example to analyze the electronic transport and photoresponse.^[83] As shown in Figure 2.8, two Schottky barriers with the heights of Φ_{b1} and Φ_{b2} form at two ends of the nanowire. The metal-semiconductor-metal device can be modeled by two back-to-back Schottky diodes in series with a resistor. The left Schottky junction is reverse biased while the right Schottky junction is forward biased when a positive voltage is applied to the right electrode. According to Kirchhoff’s voltage law, we have the following equation:

$$V_{DS} = V_1 + V_{NW} + V_2$$

where V_{DS} is the applied voltage, and V_1 , V_{NW} , V_2 are the voltages on the left junction,

the nanowire and the right junction. The electric current flowing through the device is limited by the reverse biased junction at small V_{DS} and by the series resistor at high V_{DS} .

Figure 2.8 (a) Schematic diagram of a metal-semiconductor-metal diode and its equivalent circuit. (b) Band diagram of the diode with applied bias.

The metal-semiconductor-metal photodiode with Schottky contacts have many advantages over photoconductors with Ohmic contacts in the sensitivity and speed for photon detection.^[84] As the dark current is limited by the reverse biased Schottky junction, a high I_{light}/I_{dark} can be obtained, improving the photosensitivity. On the other hand, the response time is reduced since the photosensitive region is limited to the depletion region where photogenerated electrons are quickly collected by the electrode.

Photo-field-effect transistors The photoresponse of metal-semiconductor-metal photodetector fabricated from two-dimensional semiconductors are controllable by a third gating electrode due to their superior semiconducting properties and ultrathin nature.

These photodetectors are called photo-field-effect transistors or phototransistors in short. Yin et al. reported the first photo-FET based on two-dimensional layered semiconductors and demonstrated the gate-tunable photoresponses.^[85] Since then, a variety of 2D layered semiconductors have been explored for photo-FETs.^[86-94]

Photo-FETs have the similar device structure as FETs without top gate electrode (or with a transparent top gate electrode) as shown in Figure 2.7 (c). As in common metal-semiconductor-metal photodiodes, the photogenerated electron-hole pairs are separated by lateral electric fields and collected by source and drain electrodes. However, the potential profile of the channel can be tuned by the back gate. Recent mechanism studies elaborate the effects of back gate on the photoresponses.^[95, 96] The back gate efficiently change the alignment of Fermi level to the band edges, filling and emptying the states in the band gap as shown in Figure 2.9 (b) and (c). This process leads to a shift of threshold voltage of the FET and its effects are known as photogating effects. On the other hand, light illumination generates free carrier in the conduction and valence bands and improves the conductance of the channel. This photoconductivity mechanism can be discriminated from photogating effects as shown in Figure 2.9 (a).

Figure 2.9 (a) Modulation frequency dependent photocurrent. (b) Schematic diagram of the density of states. (c) Band diagram atomically thin MoS₂. (d) Power dependent photoresponsivity. (e) Gate voltage dependent photocurrents.^[95]

2.1.3 Van der Waals heterostructures

Isolated atomically thin materials can be assembled into designed heterostructures.^[97-99] A layer of 2D material is put on another layer and this process continues. Van der Waals force keeps the artificial material together. (Figure 2.10) Unusual phenomena have been observed and desired device performance has been obtained in these so-called van der Waals heterostructures.

Figure 2.10 Construction of van der Waals heterostructures.^[97]

High-performance FETs Unlike standard SiO₂ which is disordered and have many dangling bonds, h-BN is atomically flat and dangling-bond free. Dean et al. demonstrated graphene FETs with h-BN substrates.^[37] These devices show much better mobilities and carrier homogeneities. The intrinsic doping of graphene is also reduced. Inspired by this work, researchers have investigated other 2D materials based transistors with h-BN substrates.^[100-103] Lee et al. compared the performance of MoS₂ transistors with SiO₂ and h-BN substrates.^[100] As shown in Figure 2.11(a, b), they are denoted as MS and MB devices, respectively. The mobility of MB device is an order of magnitude higher than that of the MS device. In addition, the hysteresis of transfer curves of MB device is reduced significantly compared to that of MS device, corroborating the superior interface qualities of MB devices. Thin h-BN can be used as a dielectric layer by itself as shown in Figure 2.11 (c). A graphene strip acts as the gate electrode here. When the h-BN is thin enough, the gate voltage can be scaled down as shown in Figure (d, e).

Figure 2.11 Schematic diagrams of the MS (a), MB (b) and MBG (c) devices. (d) Transfer characteristics of MS and MB devices. Inset: output characteristics of the MB device (e) Transfer characteristics of the MBG devices.^[100]

P-N junctions Van der Waals materials are flexible in making heterostructures because lattice mismatch is tolerant. Built-in potential forms when two semiconducting layers with different work functions and band gaps are brought together. This potential leads to electric rectifying and photovoltaic effects which show much potential in electronic and optoelectronic applications.^[104-111] Heterostructures based on p-type WSe₂ and n-type MoS₂ have been the model pair of layered semiconductors for P-N junctions. As shown in Figure 2.12 (c) and (d), the heterointerface is predicted to be type-II band alignment. Low-work-function metal, Al and high-work-function metal, Pd are used as the contact materials for n-type MoS₂ and p-type WSe₂, respectively. When measured individually, the MoS₂ and WSe₂ transistors show typical n-FET and p-FET characteristics. The gate-tunable properties allow fine tuning of the p-n diode as shown in Figure 2.12 (b). The rectifying effects change along with the gate voltages, which is peculiar for van der Waals p-n junctions.

Figure 2.12 (a) Schematic diagram (bottom left) and optical image (bottom right) of MoS₂-WSe₂ heterojunction device. Enlarged crystal structure of the MoS₂-WSe₂ heterostructure is shown in the top image. (b) I-V curves of the heterojunction device at different gate voltages. Inset: Transfer characteristics of individual MoS₂ and WSe₂ transistors. (c), (d) Band profiles of the MoS₂-WSe₂ heterostructure in the lateral and vertical directions.^[104]

2.1.4 Junction gate field-effect transistors based on nanomaterials

Junction gate field-effect transistors (JFET) are advantageous over metal-semiconductor (MES) and metal-oxide-semiconductor (MOS) field-effect transistors in applications for high-temperature and high-power operation.^[112] The emergence of semiconducting nanomaterials has inspired novel device design by using these nanomaterials. Standard functions as in conventional devices can be achieved in these devices while more functions can be explored.

Figure 2.13 (a) Transfer curves of the BP JFET with ZnO gating. (b) Transfer curves of the ZnO JFET with BP gating. (c) Output curves of the ZnO JFET with BP gating. (d) Transconductance of ZnO JFET with BP gating under different drain-source voltages.^[113]

Jeon et al. reported a black phosphorus (BP)-gated JFET with zinc oxide (ZnO) nanowire as the channel material.^[113] The operation of JFET is based on the high-quality P-N junction. The ZnO channel is depleted by applying a negative voltage to the BP gate as shown Figure 2.13 (b, d). In other words, the transistor is turned off by the negative gate voltage. The on-off ratio reaches 10^3 .

2.2 Questions to answer based on literature

Although great progress has been made in electronics and optoelectronics based on 2D layered materials and their heterostructures, there are still many challenges towards real

applications. According to the literature review, following questions remain to be answered.

Although a few methods have been reported to transfer two-dimensional layered materials from original substrates on to another substrate, these methods usually rely on supporting polymers which brings many problems. First, 2D layered materials are put under harsh experimental conditions when they are detached from the substrates in some transfer methods. Second, dissolution of the supporting polymer after stacking is not complete and polymer residues remain on the surface. These residues are detrimental for the performance of heterostructure devices. Third, annealing at inert atmosphere after dissolution of polymers removes the residues but this high-temperature process is not compatible with flexible substrates. So is it possible to transfer two-dimensional layered materials without supporting polymer and to fabricate clean van der Waals heterostructures on flexible substrates?

Due to the slow dynamics of trap states at the interfaces, photoresponse of MoS₂ photo-field-effect transistors has been slow and unstable. Photo-induced charge trapping leads to prolonged or even persistent photoconductance, which is unfavorable for applications as optical switches. Previous studies have shown that the interfaces of both MoS₂-air and MoS₂-SiO₂ deteriorate the photoresponse but they seldom look into the interfaces separately. Is the MoS₂-SiO₂ or MoS₂-air interface main reason for the slow and unstable photoresponse? Could photo-field-effect transistors with van der Waals interfaces outperform the conventional ones?

Electronics built totally from two-dimensional layered materials are promising for high-performance applications. Although junction gate field-effect transistors have been demonstrated for black phosphorus-zinc oxide heterostructures, JFET fabricated totally from two-dimensional layered materials have not been reported. Based on the doping strategies and fabrication techniques of p-n junctions, can we fabricate JFET totally from two-dimensional layered materials?

2.3 PhD in context of literature

In this thesis, I address the aforementioned questions by developing an easy method to fabricate clean van der Waals heterostructures and exploring their electronic and optoelectronic applications. My contributions to this research direction are described below.

First, an efficient method is developed to transfer two-dimensional layered materials including graphene, h-BN, MoS₂, and WSe₂ etc. The detachment of the materials is based on the difference of interface energy and supporting polymer is not needed. Electronic devices fabricated totally from two-dimensional layered materials are demonstrated on PET substrates. This study is instructive in fabrication of large-area high-performance electronics with the development of material synthesis.

Second, stable and fast photoresponse is realized in MoS₂ photo-field-effect transistors with van der Waals interfaces. This strategy can be extended to other two-dimensional layered semiconductors based photoresponsive devices. The intrinsic optoelectronic properties of 2D layered semiconductors can be studied and high-performance photodetectors can be fabricated in this device structure.

Third, a junction gate field-effect transistor fabricated from heterostructures of semiconducting TMDCs is demonstrated for the first time. Few-layer graphene acts as Ohmic contacts to MoS₂ while oxygen plasma is used to dope WSe₂. The techniques of contact engineering and doping can be applied to other semiconducting layer materials, thus improving the electronic and optoelectronic performance of van der Waals heterostructures.

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Chapter 3

Experimental Methodology

The principles underlying the selection of materials and techniques are discussed in this chapter. All of the 2D materials were prepared by mechanical exfoliation of layered crystals because this method provides high-quality materials with good repeatability. High-quality van der Waals heterostructures were prepared from these 2D materials by stacking. Electronic devices were fabricated via standard semiconductor processes. Electronic and optoelectronic performances of the devices were tested with standard and home-made setups to achieve both accuracy and flexibility.

3.1 Rationale for selection

Mechanical exfoliation from synthesized or natural crystals is utilized to prepare layered nanosheets on SiO₂/Si substrates, although CVD has been advancing rapidly in the last few years. The rationale underlying the selection of the preparation method is the good repeatability and high quality of mechanically exfoliated layered materials. After preparation of the nanosheets and van der Waals heterostructures, conventional semiconductor processing is employed to fabricate the devices as it provides both good flexibility and precision. Based on these materials and techniques, the study presented in this thesis becomes feasible.

3.2 Preparation of layered materials and heterostructures

3.2.1 Substrate treatments

The SiO₂/Si wafers are sonicated in a mixture of acetone and deionized (DI) water in a beaker for 5 min and then rinsed thoroughly with DI water. They are boiled in a piranha solution (97% sulfuric acid:30% hydrogen peroxide = 3:1) at 120 °C for 30 min. The resulting SiO₂ surface is highly hydrophilic due to the hydroxylation reaction. Alternatively, oxygen plasma (Harrick PDC-32 Plasma Cleaner) is used to treat the SiO₂/Si wafers or PET substrates to clean the surface and make it hydrophilic. In order to make the surface of some wafers to be hydrophobic, they are stored in a petri dish in a vacuum oven overnight. A drop of octadecyltrichlorosilane (ODTS) is added close to the wafer before setting the temperature of the vacuum oven to 50 °C.

3.2.2 Mechanical exfoliation of layered materials

Graphite (NGS Naturgraphit GmbH, Germany), hexagonal-boron nitride (HQ Graphene, Netherlands), molybdenum disulfide (SPI supplies, USA), and tungsten diselenide (2DSemiconductors) crystals are used to prepare nanosheets on SiO₂/Si substrates. A thin piece is cleaved from the crystal by using a strip of adhesive tape. Another strip of

adhesive tape is covered on the thin piece and peeled away. This process is repeated for several times until there are many small flakes on the tape. The tape is then put on to a SiO_2/Si chip and rubbed gently with a marker pen. Finally the tape is peeled away slowly, leaving some nanosheets on the substrates for further inspection. Figure 3.1 shows the photograph of mechanical exfoliation.

Figure 3.1 Photograph of mechanical exfoliation.

3.2.3 Stacking of layered materials

The fabrication of van der Waals heterostructures is based on precise stacking of layered materials. The stacking is accomplished on a microscope (Nikon Eclipse LV100D) with a telephoto lens as shown in Figure 3.2. The bottom material (denoted as B) on the substrate is fixed while the top material (denoted as T) on polydimethylsiloxane (PDMS) is controlled by micromanipulators. The top material is aligned to the bottom material through the microscope and brought to contact with the bottom material.

Figure 3.2 Schematic diagram showing the setup for stacking of layered materials.

3.3 Characterization

3.3.1 Optical microscopy

It has been reported that 2D nanosheets, such as graphene and MoS_2 , show notable contrast to substrate when they are deposited onto Si capped with a layer of SiO_2 with proper thicknesses due to the weak absorption of 2D nanosheets and the interference at the interfaces.^[1] When the bright-field optical images are captured at a proper exposure time using white light source, this contrast can even be used to estimate the layer number of these 2D materials, although the step heights of a monolayer is less than 1 nm.^[2] Figure 3.3(A-F) are the bright-field optical micrographs of MoS_2 with a layer number of 1-6, respectively. Quantitative data can be obtained by analyzing the gray value of the blue, green or red channel.^[2, 3] The quality and thickness of other layered materials such as graphene, WSe_2 can also be roughly assessed by using optical microscopy as shown in Figure 3.4.

Figure 3.3 (A-F) Optical microscope images of one- to six-layer MoS₂ nanosheets deposited on Si substrate capped with 300 nm SiO₂ (scale bars: 10 μm). “1L”, “2L”, “3L”, “4L”, “5L” and “6L” indicate monolayer, bilayer, trilayer, quadrilayer, pentalayer and hexalayer, respectively. (G-L) AFM topography images of the MoS₂ nanosheets in (A-F), respectively (scale bars: 5 μm). (M-R) AFM height profiles of MoS₂ nanosheets indicated by the dark dashed lines in (G-H), respectively.

Figure 3.4 (A, B) Optical images of single- and double-layer graphene on 90 nm SiO₂, respectively. (C, D) Optical images of single- and double-layer WSe₂ on 285 nm SiO₂, respectively.

3.3.2 Atomic force microscopy

The thicknesses of layered two-dimensional materials were measured directly by using AFM (Dimension ICON with NanoScope V controller, Bruker, USA). AFM analysis further confirmed the layer numbers because step heights of 0.6-0.7 nm were unambiguously observed as shown in Figure 3.3 (G-R). This step height correlates to the 0.65 nm interlayer spacing of S-Mo-S single layers of MoS₂ crystals. This characterization is quite straightforward but the interpretation of the results needs special care because the apparent thicknesses measured by AFM are easily interfered by the large chemical contrast between 2D materials and the surrounding substrates, confined water layer beneath the materials and adsorbed contaminants on the surfaces.^[4-6]

3.3.3 Raman spectroscopy

Raman spectra were obtained on a WITec CRM200 confocal Raman microscopy system with excitation lines of 488nm and 633nm and an air-cooled charge coupled device (CCD) as the detector (WITec Instruments Corp, Germany). The Raman band of Si at 520 cm⁻¹ was used to calibrate the spectrometer. The power is kept at the lowest value to avoid heating effects. Monolayer, bilayer and few-layer graphene were distinguished from the G and 2D peaks. The intensity ratio of 2D to G peak for monolayer graphene is over 2 while the ratio is about 1 for bilayer graphene, as shown in Figure 3.5. The ratio is less than 1 for few-layer graphene and bulk graphite.

Figure 3.5 Raman spectra of single- and double-layer graphene.

Raman spectroscopy acts as a rapid, nondestructive and complementary characterization method for MoS₂. It has been reported that the positions of E_{2g}¹ and A_{1g} peaks vary monotonously with the layer numbers of MoS₂ nanosheets when excited off resonance.^[7, 8] The E_{2g}¹ mode arises from in-plane vibration of two sulfur atoms relative to the molybdenum atom while the A_{1g} mode is related to the out-of-plane vibration of sulfur atoms in the opposite direction. As shown in Figure 3.6, the frequency of E_{2g}¹ peak decreases while the frequency of A_{1g} peak increases with increasing thickness. This frequency shifts can be explained by Coulombic interactions and possible stacking-induced changes of the intralayer bonding.^[7] These thickness-dependent Raman spectra provide accurate identification of layer numbers for all of our MoS₂ samples.

Figure 3.6 (A) Raman spectra of 1-6L and bulk MoS₂. The vertical lines indicate the positions of E_{2g}¹ and A_{1g} peaks of bulk MoS₂. The dashed lines show the thickness-dependent peak position evolution of 1-6L MoS₂. (Excitation line: 488nm) (B) Peak analysis of MoS₂ nanosheets.

3.3.4 Scanning electron microscopy

Scanning electron microscopy images were taken on a JOEL JSM-7600 field-emission scanning electron microscope. In some experiments, a thin layer of gold is sputtered on the specimen to increase its conductivity.

3.3.5 Photoluminescence spectroscopy

Photoluminescence spectra are obtained on a WITec CRM200 confocal Raman microscopy system with excitation lines of 488nm and an air-cooled charge coupled device (CCD) as the detector (WITec Instruments Corp, Germany). The transition from indirect band gap to direct band gap when the thickness of some transition metal dichalcogenides such as MoS₂ is reduced to single layer leads to a dramatic increase of the quantum yield of photoluminescence.^[9] The PL peaks at ~630 nm and ~670 nm correspond to the direct transitions with the energy difference originating from the spin-orbital splitting of valence band.^[9] The PL intensity of single-layer MoS₂ is much stronger than that of few-layer and bulk MoS₂, indicating much higher PL quantum efficiency regardless of that single-layer MoS₂ have reduced amount of material.

Figure 3.7 Photoluminescence spectra of 1-6L and bulk MoS₂. (Excitation line: 488nm)

3.4 Device fabrication and testing

3.4.1 Electron beam lithography

Although electron beam lithography (EBL) is expensive and its throughput is low, it is an essential technique for nanodevices as it provides both design flexibility and location precision. EBL was used to pattern electrodes for devices of two-dimensional layered materials and their heterostructures in this thesis. The process flow of device fabrication is illustrated in Figure 3.8. A thin layer of polymethyl methacrylate (PMMA, Microchem, USA) is spin-coated on the substrates with 2D layered materials or heterostructures. Electron beam is used to pattern the electrodes by exposing specific areas with a proper dose. The electron beam breaks the chemical bonds of the polymer, making them soluble in developer solutions (MIBK:IPA=1:3) while other areas remain insoluble. In fact, two-time EBL was used to pattern the electrode in my study because the precise alignment of electrodes to the materials or heterostructures requires marking using EBL. After metallization, the entire polymer layer was peeled away in acetone.

Figure 3.8 Schematic diagram of process flow of electron beam lithography and metallization. (A) Spin coating of PMMA on the substrate with 2D materials. (B) Patterning using electron beam. (C) Develop. (D) Thermal evaporation of metal. (E) Lift-off.

3.4.2 Thermal evaporation

Metal was deposited on the developed samples in high vacuum ($\sim 5 \times 10^{-7}$ mbar). The gold source (TED PELLA, USA) was loaded in a tungsten boat (TED PELLA, USA) and evaporated by joule heating. Sometimes a thin layer (1-5 nm) of chromium (Cr) was used as the adhesive layer before gold deposition. It is deposited in the same chamber from a Cr coated tungsten rod (TED PELLA, USA). Vacuum was never broken during the entire process of evaporation. The deposition rate was monitored and kept lower than 0.5 angstrom/s.

3.4.3 Thermal annealing

Thermal annealing in a tube furnace was employed to improve the contact between the metal electrode and the 2D layered materials, and to clean the surface after dissolution of the polymers.^[10] The setup for thermal annealing is shown in Figure 3.9. A mixture of hydrogen (20 sccm) and argon gas (200 sccm) is used to protect the samples. The annealing normally took 30 min at 200 °C.

Figure 3.9 Photograph of the setup for thermal annealing.

3.4.4 Electronics testing

The electric performances of the devices were tested on a probe station (Miromanipulator, USA) under ambient conditions. Voltages and currents were applied and measured by using a Keithley 4200 SCS semiconductor parameter analyzer (Keithley Instruments, USA). The setup for electronics testing is shown in Figure 3.10.

Figure 3.10 Photograph of the setup for electronics testing. Left: Micromanipulator probe station. Right: Keithley 4200 SCS semiconductor parameter analyzer.

3.4.5 Photoresponse testing

The photoresponse was tested by irradiation the devices with white light from a xenon lamp. The light is directed onto the device through a fiber coupled with a collimator as shown in Figure 3.11. The incident power is tuned by the neutral filter.

Figure 3.11 Schematic diagram of the illumination for photoresponse testing.

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Chapter 4

Transfer Printing of 2D Layered Materials

This chapter introduces a novel transfer method for 2D layered materials including graphene, h-BN, MoS₂ and WSe₂. The surface properties of the substrates are proven to be vital for high-yield transfer and printing. As a proof of concept, a complementary inverter is fabricated on a flexible substrate via layer-by-layer transfer printing of 2D layered materials. A voltage gain of about 30 is obtained at a drive voltage of 5 V.

4.1 Introduction

Graphene and other 2D layered materials have drawn great attention in the last decade due to their unconventional mechanical, electronic and optoelectronic properties.^[1-4] High strength and atomic thickness make them ideal for flexible applications.^[5-8] Reasonable mobility and sizable band gap of some TMDCs and BP promise a new generation of nanomaterials for high-performance transistors.^[4, 9] In addition, the strong and unique light-matter interaction paves a way for novel optoelectronics.^[10, 11] Moreover, assembly of different 2D layered materials into van der Waals heterostructures allows researchers to explore and design new functions. To this end, a few methods have been developed to transfer and assemble 2D layered materials. In the most common transfer process, a supporting polymer layer is spin-coated on the substrates with 2D layered materials. The 2D layered materials are released from the substrates by etching away the substrates,^[12] water intercalation,^[13] or direct peeling-off^[14]. The supporting polymer is dissolved in specific solvents after it is stacked on to another substrate. However, the dissolution is usually not complete and leaves polymer residues on the surface of 2D layered materials, deteriorating the performance of van der Waals heterostructure devices. This problem is more severe when multiple transfer steps are needed. Here, a clean transfer printing method for 2D layered materials is presented. The release from the donor substrate and printing to the acceptor substrate of 2D layered materials are both mediated by difference of surface energy. Therefore, a supporting polymer is not needed. As a proof of concept, a complementary inverter fabricated totally from 2D layered materials is demonstrated on a flexible substrate.

4.2 Results and Discussion

Graphene, h-BN, MoS₂ and WSe₂ nanosheets were prepared on hydroxylated SiO₂/Si substrates by mechanical exfoliation and characterized as introduced in Chapter 3. A piece of thin PDMS film was put on the 2D layered materials and a drop of DI water was added to the perimeter of the PDMS film. The water penetrated under the PDMS film and float PDMS film with the 2D layered materials. Then the PDMS film with the 2D layered

materials on top is picked up slowly by a pair of tweezers and put on a filter paper for subsequent printing process. The acceptor substrate was treated with oxygen plasma for several minutes to increase its surface energy. When put on the acceptor substrate and peeled away slowly, the PDMS film left the 2D layered materials on the acceptor substrate, accomplishing the transfer printing process. Figure 4.1 summarize the process of transfer printing of 2D layered materials.

Figure 4.1 Schematic flow diagram of transfer printing. (a) 2D layered materials on a donor substrate. (b) 2D layered materials covered with a piece of PDMS film. (c) PDMS with 2D layered materials floated by DI water. (d) PDMS with 2D layered materials transferred onto the acceptor substrate. (e) 2D layered materials left on the acceptor substrate after PDMS is peeled away.

To assess the effectiveness of this transfer method, low-magnification optical images were taken to compare the nanoflakes on the donor substrate and the nanoflakes transferred on to PDMS film. As can be seen in Figure 4.2, every MoS_2 nanoflake from the donor substrate was transferred on to PDMS, making the image (a) and (b) have mirror symmetry. It indicates that the transfer yield approaches 100%. Similar results were obtained on other 2D layered materials such as graphene, h-BN and WSe_2 .

Figure 4.2 (a) Optical image of MoS_2 nanoflakes on SiO_2/Si substrates prepared by mechanical exfoliation. (b) Optical image of the same nanoflakes in (a) transferred on PDMS film.

The quality of the transferred and printed 2D layered materials was evaluated with topographic and spectral characteristics. Figure 4.3(a) is an optical image of a MoS₂ nanosheet with clearly distinguishable sing-, double- and tri-layer regions which have been confirmed by AFM (Figure 4.3 (d)). After transferred onto PDMS, the contrast of the nanosheet is weakened due to the lack of light interference (Figure 4.3 (b)). It is hard to observe thin layers of 2D layered materials, especially for graphene and h-BN which have weak absorption of light. Moreover, due to the large roughness of PDMS and strong chemical contrast between the inorganic materials and PDMS, AFM can no longer measure the correct thickness of 2D layered materials. As seen in Figure 4.3 (e), the steps among regions with different layer numbers disappear. Therefore, mechanical exfoliation of layered crystals directly on PDMS stamp for fabrication of van der Waals heterostructures is disadvantageous compared with the method introduced here.^[15-17] The advantage of the method introduced here over the conventional polymer supporting method is that it is contaminant free. The same nanosheet printed on 300 nm SiO₂ is clean and intact without annealing. (Figure 4.3 (c, f))

Figure 4.3 Optical and AFM images of a MoS₂ nanosheet on 90 nm SiO₂, PDMS and 285 nm SiO₂, respectively. Scale bars in (d-f): 5 μm.

The lossless transfer printing process is further corroborated by PL characterizations. PL spectra of single-layer MoS₂ on SiO₂/Si substrate and on PDMS film are plotted in Figure

4.4 (a). Several changes of the PL spectrum can be observed when single-layer MoS₂ is transferred onto PDMS film. First, the absolute intensity of the PL peak is lower for single-layer MoS₂ on PDMS film. Second, the peak position blue-shifts to 1.89 eV from 1.82 eV. Third, the Raman peaks are rather weak for single-layer MoS₂ on PDMS film. These changes can be ascribed to substrate related doping and interference effects.^[18-20] However, the normalized photoluminescence by the Raman intensity is much stronger on PDMS film because the quantum yield of exciton emission is higher than that of trion emission.^[21] Although PL spectra are not identical, the PL imaging in Figure 4.4 (c) is similar to (b). The mapping of integrated PL intensity is uniform over the entire region with the same thickness, indicating that the transfer process brings little contaminant.

Figure 4.4 (a) Photoluminescence spectra of single-layer MoS₂ on SiO₂/Si substrate and on PDMS film. PL imaging of a MoS₂ nanosheet with single-, double- and tri-layer regions on SiO₂/Si substrate (b) and on PDMS film (c). Same color scales are used in (b) and (c).

The 2D layered materials transferred on PDMS were used to prepare van der Waals heterostructures by using a deterministic transfer method.^[15] This step is denoted as printing in accordance with the inking step introduced above. A MoS₂-WSe₂ heterostructure was fabricated and characterized as shown in Figure 4.5. A single-layer MoS₂ nanosheet was stacked onto a WSe₂ nanosheet with single- and double-layer regions. The layer numbers were confirmed by AFM (Figure 4.5(b)), photoluminescence (Figure 4.5(c)) and Raman spectroscopy (Figure 4.5(d)). The position of Raman peaks show little change after stacking but a slight change of photoluminescence spectra is observed as shown in Figure 4.5 (e, f). Neither the PL of MoS₂ nor WSe₂ is significantly suppressed, indicating that the coupling between MoS₂ and WSe₂ is weak.^[22] The photoluminescence imaging with the integrated peak intensity in the range of 1.5-1.75 eV (WSe₂) and 1.75-2.25 eV (MoS₂) is shown in Figure 4.5(g) and (h), respectively. The

uniform distribution of the integrated intensity indicates the high quality of the van der Waals heterostructures.

Figure 4.5 (a) Optical and (b) AFM topographic images of the MoS₂-WSe₂ heterostructures. (c) PL spectra of individual materials. (d) Raman spectra of individual materials and their heterostructures. (e, f) PL spectra of the heterostructures in comparison with those of individual materials. Photoluminescence imaging of the heterostructure shown in (a) with MoS₂ (g) and WSe₂ (h) peaks.

The influence of the surface properties on the transfer printing is studied to reveal the mechanism of this method. Figure 4.6 sketches the dynamics of 2D materials with (a) and without (b) DI water when the PDMS is peeled from the SiO₂ substrates. 2D materials adhere to PDMS film when DI water is added while they remain on SiO₂ without DI water. Two additional interfaces are created in either case. The competition of interface energy leads to the different behaviors of 2D materials as indicated by arrows. This mechanism is further confirmed with orthogonal experiments. If the SiO₂ substrates are modified to be hydrophobic or the PDMS is modified to be hydrophilic, the transfer process is unsuccessful.

Figure 4.6 Schematic illustration of the mechanism of transfer printing.

As a proof-of-concept, a complementary inverter is fabricated totally from 2D layered materials. Few-layer MoS₂ and WSe₂ are used as the n- and p-channel, respectively. Few-layer graphene acts as the bottom gate electrode and h-BN acts as the dielectric materials. The inset of Figure 4.7 (a) shows the layout of the circuits. Transfer characteristics of the n-channel and p-channel field effect transistors are plotted in Figure 4.7 (b). Both transistors have an on-off ratio over 10⁶ and the threshold voltage matches each other. These characteristics result in a high performance inverter as shown in Figure 4.7 (c). A voltage gain of about 30 is obtained at a drive voltage of 5 V.

Figure 4.7 Complementary inverter on a flexible PET substrate. (a) Optical image of the inverter and the inset shows the scheme of the circuits. (b) Transfer characteristics of the MoS₂ and WSe₂ transistors both at $V_{DS}=1V$. (c) Voltage transfer characteristics of the inverter at supply voltages of 1V, 2V and 5V.

4.3 Conclusions

Surface energy-mediated transfer printing method is simple but highly efficient in fabrication of van der Waals heterostructures. The material characterizations reveal that it is a clean method that leads to little contamination of 2D materials. High-performance electronic devices based on van der Waals heterostructures further confirm the usefulness of this method.

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Chapter 5

Stable Photocurrent Generation in MoS₂ Photo-FETs

The photodetecting performances of 2D layered semiconductors are usually deteriorated by the trap states at the interfaces. The intrinsic photoresponse is obscured, impeding rational design of photo-FETs based on 2D layered semiconductors. In this chapter, MoS₂ photo-FETs with van der Waals interfaces are fabricated. The transfer characteristics of these transistors show little hysteresis in the dark and under light illumination, indicating stable operation of these photo-FETs.

5.1 Introduction

Photodetectors underpin a variety of applications ranging from X-ray imaging to night vision.^[1] New materials and structures have been explored to shorten the response time, improve the sensitivity and expand the spectral range. Nanomaterials are appealing for these purposes because they exhibit intriguing optoelectronic properties, ease of processing and compatibility with conventional semiconductor electronics.^[2] Recently, two-dimensional layered semiconductors, such as MoS₂ and BP have drawn much attention for photodetecting applications.^[3-6]

2D layered semiconductors based photodetectors are frequently configured into a lateral metal-semiconductor-metal structure.^[7-9] Photogenerated electron-hole pairs are separated by lateral electric field and collected by corresponding electrodes. The change of channel conductance is reflected in the photocurrent, which is similar to the operation of conventional photoconductors or photoresistors. However, the electric contacts to 2D layered semiconductors are usually not Ohmic. Besides, they can be gated by another electrode to change the band profile of the photodetector. In addition, the ultrathin body of 2D layered semiconductors makes them extremely sensitive to the surroundings such as substrates and atmosphere.^[10-12] These variations result in distinctively different performances of photo-field-effect transistors even from the same kind of 2D layered semiconductors.^[13] This inconsistency impedes the commercialization of 2D layered semiconductors based photo-FETs.

The stable operation of photo-FETs is also very important to study the mechanisms of photoconductance.^[14, 15] To eliminate the effects of gas adsorption and desorption, the photo-FETs are measured in vacuum or encapsulated with a transparent material. The encapsulating layer can be polymer or oxide. However, it introduces surface states which may facilitate the recombination of electrons and holes. In other words, the intrinsic photoresponse is obscured. Furthermore, the interface between 2D layered semiconductors and the substrates are not affected by the encapsulation. The interface states are still detrimental for the stable photocurrent generation in photo-FETs. In this

chapter, a MoS₂ photo-FET with van der Waals interfaces is demonstrated. It shows stable photoresponse and is a model structure which can be applied to other 2D layered semiconductors.

5.2 Results and Discussion

All the 2D layered nanosheets were prepared on SiO₂/Si substrate by mechanical exfoliation. They were subsequently characterized by using OM, AFM and Raman spectroscopy. Few-layer MoS₂ transistors were fabricated and tested as control experiments. Figure 5.1 (a) shows a typical set of MoS₂ transistors with 285 nm thick SiO₂ as the dielectric material. Au/Cr stack is used as the contact metal. The output curves are shown in Figure 5.1 (b). Drain-source current (I_{DS}) increases significantly as the back gate voltages (V_{BG}) are increased from -20 V to 80 V with steps of 10 V, displaying characteristics of a typical n-type FET. I_{DS} increases linearly with source drain bias (V_{DS}), indicating quasi-Ohmic contact properties. The transfer characteristics are studied by sweeping V_{BG} at a fixed V_{DS} as shown in Figure 5.1 (c). The field-effect mobility (μ_{FE}) is extracted by using the following equation:

$$\mu_{FE} = \frac{L}{WC_i V_{DS}} \times \frac{dI_{DS}}{dV_{BG}}$$

where $W=7.2 \mu\text{m}$ is the channel width, $L=3.0 \mu\text{m}$ is the channel length, and $C_i=1.23 \times 10^{-4} \text{ Fm}^{-2}$ is the capacitance per unit area of back gate dielectric. The extracted value of μ_{FE} ($8.2 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) is within the range of field-effect mobilities of few-layer MoS₂ on SiO₂ substrates.^[12, 16, 17] The on-off ratio of the transistor is $\sim 10^5$, a value acceptable for digital electronics applications. A noticeable hysteresis is also observed in the transfer curve. The difference of onset voltages where subthreshold region begins is 22 V and it is used as a measurement of hysteresis in following discussions.

Figure 5.1 (a) Optical image of a set of transistors based on a single MoS₂ flake. (b) Output curves of a MoS₂ transistor at different back gate voltages from -20 V to 80 V with steps of 10 V. (c) Transfer characteristics of a MoS₂ transistor with a bias of 0.1 V.

The photoresponse of few-layer MoS₂ transistors are studied by illuminating the devices

with a xenon lamp through a microscope lens. Figure 5.2 shows the performance of MoS₂ photo-FETs on SiO₂/Si substrates. I_{DS} - V_{BG} curves (Figure 5.2 (a)) were measured in the dark and under illumination. Source-drain current under illumination (I_{Light}) is significantly larger than the current in the dark (I_{Dark}) when the V_{BG} is swept from negative to positive or the other way around, indicating a noticeable photoconductivity of photo-FET. The semilogarithmic plot of the same data in Figure 5.2(a) is shown in Figure 5.2 (b). It reveals the photoconductivity when the transistor is turned off by V_{BG} . Photocurrent is obtained by subtracting I_{Dark} from I_{Light} , i.e. $I_{Ph}=I_{Light}-I_{Dark}$. I_{Ph} and I_{Light}/I_{Dark} which represents the sensitivity of the photo-FET are plotted in Figure 5.2 (c). When the transistor is turned on, it acts like a conventional photoconductor. I_{Ph} saturates at around 1.4 μ A when the V_{BG} increases but I_{Light}/I_{Dark} is approaching 1. In other words, I_{Ph} is large but the sensitivity of the MoS₂ photo-FET is low when the transistor is in the on-state. However, when the transistor is in the off-state, I_{Ph} decreases rapidly when the negative V_{BG} is increased. But I_{Light}/I_{Dark} ratio increases dramatically. I_{Light}/I_{Dark} is over 10^4 when V_{BG} is -70 V. The tunability of photocurrent and I_{Light}/I_{Dark} makes MoS₂ photo-FET more flexible in photodetecting applications. Nevertheless, the hysteresis introduces prolonged photoconductance, limiting the responding speed of MoS₂ photo-FETs. After being stressed at $V_{BG}=-20$ V for 5 s under light illumination, I_{DS} - V_{DS} is measured. The conductance of the MoS₂ channel increases for 4 orders of magnitude as shown in Figure 5.2 (d). The persistent photoconductance leads to extremely slow photo-switching performance as shown in Figure 5.3.

Adsorption and desorption of gas molecules and trapping states on the surface of SiO₂ are considered as two reasons for the hysteresis of 2D layered materials based transistors.^[18-21] To investigate these two factors individually, we fabricate transistors on a MoS₂ nanosheet partially covered by an h-BN strip as shown in Figure 5.4 (a). The h-BN isolates MoS₂ from the atmosphere, so the electronic property of MoS₂ is solely affected by the SiO₂ substrates. The I_{DS} - V_{BG} transfer curves of the uncovered transistor (measured between electrode 1 and 2) are similar to the ones in Figure 5.1 (b), displaying a hysteresis of about 14 V. Surprisingly, the I_{DS} - V_{BG} curves of the h-BN-covered device (measured between electrode 2 and 3) do not show much difference. The hysteresis of the

h-BN-covered transistor is 15 V, close to that of the uncovered transistor. The similar hysteresis values imply that atmosphere plays a minor role in the charge trapping. The trapping states of the SiO₂ substrate are the main source of the hysteresis.

Figure 5.2 (a) Transfer characteristics of a MoS₂ transistor with (red line) and without (black line) light illumination. (b) The same data as in (a) plotted in a semilogarithmic scale. (c) V_{BG} dependent photocurrent (dark) and $I_{\text{light}}/I_{\text{dark}}$ (blue) when the V_{BG} is swept from -80 V to 80V. (d) I_{DS} - V_{DS} curve before (dark) and after (red) gate stressing at -20 V for 5 s under light illumination.

Figure 5.3 Photo-switching of a MoS₂ photo-FET at $V_{DS}=0.5$ V, $V_{BG}=0$ V.

Figure 5.4 (a) Optical image of a few-layer MoS₂ nanosheet partially covered by an h-BN strip with EBL patterning. (b) I_{DS} - V_{BG} transfer characteristics of the uncovered MoS₂ transistor. (c) I_{DS} - V_{BG} transfer characteristics of the h-BN-covered MoS₂ transistor.

Next, the MoS₂ photo-FETs with dangling bond-free h-BN as the dielectric are

characterized. Few-layer h-BN and MoS₂ are stacked onto few-layer graphene on SiO₂/Si substrates by using the transfer printing method introduced in Chapter 4. Few-layer graphene and h-BN act as the gate electrode and dielectric, respectively. H-BN is superior to SiO₂ when used as gate dielectric because its atomically smooth and dangling bond-free surface.^[22-24] Figure 5.5 (a) shows two MoS₂ transistors contacted with Au/Cr and few-layer graphene. Electrode 3 and 4 are the source drain electrodes while the gate voltage is applied through electrode 2. Figure 5.5 (b) is the semilogarithmic plot of transfer characteristics. In the dark or under light illumination, the hysteresis is negligible when the gate voltage is swept from -1 V to 1 V, and back to -1V, in contrast to the large hysteresis observed in MoS₂ transistors on SiO₂ substrates. Benefiting from the hysteresis-free transfer characteristics of the MoS₂ transistors on h-BN, we obtained stable operation of photo-FETs as shown in Figure 5.5 (c). At a given V_{DS} and V_{BG} , the I_{Ph} and I_{Light}/I_{Dark} is specific and stable. They are not affected by the history of applied voltage or light illumination.

5.3 Conclusions

By comparing the optoelectronic properties of exposed and h-BN-encapsulated MoS₂ photo-FETs, the source of persistent photoconductivity is addressed. Trapping states at the interface between semiconducting materials and the oxide substrates play a vital role in the prolonged photoresponse. By replacing conventional SiO₂/Si gating stack with h-BN/FLG, we demonstrate stable operation of MoS₂ photo-FETs, which can be used as a model structure to investigate the intrinsic photoresponse of 2D layered semiconductors.

Figure 5.5 (a) Optical image of MoS₂ transistors with h-BN as the dielectric and few-layer graphene as the gate electrode. (b) Transfer characteristics of the Au/Cr contacted MoS₂ transistor in the dark (black) and under light illumination (red). (c) Gate voltage-dependent photocurrent and $I_{\text{Light}}/I_{\text{Dark}}$.

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Chapter 6

Junction Gate Field-Effect Transistors (JFETs) Fabricated from Transition Metal Dichalcogenides (TMDCs)

In contrast to MOSFETs, JFETs do not require dielectric layers between the channel material and the gate. Thus they have simpler device structures and are more flexible. In this chapter, JFETs fabricated from TMDCs are demonstrated for the first time. At drive voltages of 2 V, the on-off ratio reaches 10^4 , a value good enough for logic electronics.

6.1 Introduction

High-quality dielectric materials are indispensable in MOSFET-based electronic applications. SiO₂ has been the optimal choice for Si electronics thanks to its reasonable dielectric constant and stability. Recently, high-k dielectric materials such as Al₂O₃ and HfO₂ draw great attention because they facilitate further scaling of Si electronics.^[1, 2] High-k dielectric materials are usually deposited by atomic layer deposition (ALD). It is an expensive process and has not been applied to large-area applications although proof-of-concept devices based on high-k dielectrics have been demonstrated on flexible substrates.^[3, 4] Large-area electronics appeals for solution-processed dielectric materials among which polymer dielectric^[5] and boron nitride^[6] are two candidates.

Besides synthesizing solution-processed dielectric materials, constructing FETs without gate dielectric materials is another solution for large-area flexible electronics. Metal-semiconductor field-effect transistors (MESFETs) and junction-gate field-effect transistors (JFETs) are two complementary kinds of transistors to the universal MOSFETs. They are usually used for high-speed and microwave circuits. However, they may be competitive against MOSFETs in a variety of applications if their corresponding performances could be improved. Nanomaterials based MESFETs and JFETs are thus fabricated and tested. MESFETs rely on high-quality Schottky junctions between a moderately doped semiconductor and a metal gate and thus called Schottky gate transistors. CdS-Au^[7, 8], MoS₂-Pd^[9], MoS₂-NiO^[10], Rubrene-Au^[11] and ZnO-Au^[12] Schottky junctions have been utilized for MESFET applications. Similarly, JFETs are based on P-N junctions and CdSe:In-Si^[13] and ZnO-BP^[14] have been proved to be reasonable pairs of materials for this application.

2D layered semiconducting materials can be explored for JFET applications. Recently, MoS₂-WSe₂ heterostructures have been studied and shown P-N junction like transport properties.^[15-18] However, the transport properties are not ideal for JFET applications. Herein, we demonstrate that few-layer WSe₂ nanosheets are efficiently p-doped by oxygen plasma treatment. The heterostructures fabricated by transferring MoS₂ onto p-

doped WSe₂ show improved properties P-N diodes. The conductance of MoS₂ is increased by replacing Au/Cr electrodes with few-layer graphene. Based on these engineering approaches, we fabricated high-performance JFETs from TMDC heterostructures for the first time.

6.2 Results and Discussion

WSe₂ is a layered semiconductor with low unintentional doping density and has a relatively weak Fermi-level pinning effect. Therefore, p-type and n-type MOSFETs can be fabricated by contacting them with high and low-work-function metals, respectively.^[19-21] Besides, WSe₂ FETs usually work in enhancement mode without charge-transfer doping because of its low conductivity without electrostatic doping.^[22, 23] The low intrinsic doping level is bad for the performance of MoS₂-WSe₂ P-N junctions. It results in a large series resistance and a large ideal factor. On the other hand, the reserve current is large because the potential difference between n-MoS₂ and p-WSe₂ is not large enough.^[17, 24] These characteristics need to be improved to realize high-performance JFETs and this can be done by p-doping WSe₂. Here we demonstrate that oxygen plasma treatment efficiently p-dopes WSe₂.

Few-layer graphene and h-BN are utilized as gate electrode and dielectric material, respectively. This gating stack provides excellent electrostatic control. As shown in Figure 6.1 (a), the WSe₂ nanosheet is contacted with Au/Cr electrodes. The current is in the picoampere range with the gate electrode floated, which is in agreement with the low unintentional doping level of WSe₂. After oxygen plasma treatment for 30 s the conductivity increases dramatically as shown in Figure 6.1 (b). The I-V curve is not linear after oxygen plasma treatment because Cr forms Schottky contacts to WSe₂. Nevertheless, the ambipolar transfer characteristics turn to unipolar p-type transfer characteristics as compared in Figure 6.1 (c) and (d). At a sufficiently high source-drain bias ($V_{DS}=1.0$ V), the on-off ratio decreases to less than 10^3 after oxygen plasma treatment because of barrier lowering due to image charges, indicating the doping level in WSe₂ is approaching degenerate.

Figure 6.1 P-doping of WSe₂ by oxygen plasma treatment. (a) Optical image of WSe₂ transistors with an h-BN/FLG gating stack. (b) I_{DS} - V_{DS} curves with gate electrode floated before (black) and after (red) oxygen plasma treatment. I_{DS} - V_{GS} transfer characteristics of a WSe₂ transistor before (c) and after (d) oxygen plasma treatment.

The mechanism behind the p-doping is ascribed to the transfer of holes from the surface oxide layer induced by oxygen plasma to the underlying WSe₂ layers as reported by Yamamoto et al.^[25] The stability of this doping strategy is monitored by exposing the device under ambient conditions for 10 days. In contrast to p-doping by ozone treatment, oxygen plasma-treated WSe₂ retains its p-doping properties as shown in Figure 6.2. At a sufficiently high gate voltage ($V_{GS}=1.0$ V), the WSe₂ transistor is still degenerately doped, indicating the high stability of p-doping of oxygen plasma treatment.

Figure 6.2 I_{DS} - V_{GS} transfer characteristics of a WSe₂ transistor after oxygen plasma treatment and exposure to ambient conditions for 10 days.

The conductance of a JFET is controlled by the voltage applied to the gate electrode which depletes the carriers in the channel. Although the carrier concentration in the channel can be tuned by the back gate voltages for 2D layered semiconductors, it is usually fixed to retain the simple operation and device structure, especially for JFETs on flexible substrates. In this case, the conductance of the intrinsic channel material is the upper limit of the total conductance of the JFETs. Therefore, when MoS₂ is used as the channel material for JFETs, the contact resistance should be minimized to increase the on current. Here, we prove that few-layer graphene (FLG) is a superior contact material to MoS₂ compared to conventional Au/Cr metal stack. A single MoS₂ strip is used to compare the contact properties as shown in Figure 6.3 (a). When the back gate is floated, the conductance increases over 35-fold if FLG is used as the contacts. The on-currents of the FLG-contacted MoS₂ transistor are more than twice as large as those of the Au/Cr-contacted transistors at any back gate voltages. (Figure 6.3 (c, d)) Transfer characteristics shown in Figure 6.3 (e, f) reveal that the Au/Cr-contacted MoS₂ transistor operates in enhancement mode while FLG-contacted MoS₂ transistor operates in depletion mode. All these advantages of FLG contacts make them suitable for JFETs.

Figure 6.3 Comparison of Gr- and Au/Cr-contacted MoS₂ transistors. (a) Optical image of a few-layer MoS₂ strip contacted by both few-layer graphene and Au/Cr electrodes. (b) I_{DS} - V_{DS} curves of Au/Cr-contacted (black) and FLG-contacted (red) devices with back gate floated. Back gate-dependent I_{DS} - V_{DS} curves of Au/Cr-contacted (c) and FLG-contacted (d) MoS₂ transistors. I_{DS} - V_{BG} transfer characteristics of Au/Cr-contacted (e) and FLG-contacted (f) MoS₂ transistors.

Based on the strategies mentioned above, JFETs from MoS₂-WSe₂ JFETs can be fabricated. Few-layer MoS₂ and graphene strips are transferred onto oxygen plasma-doped WSe₂ sequentially. Au/Cr electrodes are used to contact both FLG and p-doped WSe₂ as shown in Figure 6.4 (a). P-doped WSe₂ acts as the gate while MoS₂ acts as the channel material. MoS₂ is depleted of electrons when contacted with p-doped WSe₂.

However, when a positive voltage is applied to the p-WSe₂ gate, the depletion width shrinks and the bottom MoS₂ layers become conductive. Thus the I_{DS} increases abruptly as shown in Figure 6.4 (b). The on-off ratio is larger than 10^4 , which is good enough for digital logic applications. Furthermore, the working voltages are below 2 V and the gate leakage currents are less than 10 nA, rendering these JFETs excellent candidates for low-power electronics. To further emphasize the importance of oxygen plasma-doping of WSe₂, the I-V curves of the P-N junctions are compared in Figure 6.4 (c, d). The reverse current of the P-N junction based on oxygen plasma-doped WSe₂ is at least one order of magnitude smaller than that of the P-N junction based on intrinsic WSe₂. This leads to a smaller gate leakage current.

Figure 6.4 JFET fabricated from TMDC heterostructures. (a) Optical image of the JFET. (b) I_{DS} - V_{GS} transfer curves of the JFET. (c) I-V curves of the P-N junction with oxygen plasma-doped WSe₂. (d) I-V curves of the P-N junction with intrinsic WSe₂ and MoS₂.

6.3 Conclusions

Oxygen plasma treatment is a feasible method to p-dope WSe₂. The doping level is high and stable. FLG is a superior contact material for MoS₂ FETs compared to conventional

Au/Cr electrodes. Based on the p-doping of WSe₂ and contact engineering of MoS₂, a high-performance JFET is demonstrated on TMDC heterostructures for the first time.

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Chapter 7

Discussion and Future Work

This chapter draws the threads of my thesis together. A simple and efficient transfer printing method is developed to fabricate clean van der Waals heterostructures. Based on this method, I demonstrate the stable photodetecting characteristics of MoS₂ photo-FETs with van der Waals interfaces. Furthermore, we fabricate JFETs from TMDC heterostructures by using this transfer method. The results introduced in this thesis advance the fabrication of van der Waals heterostructures and their applications in electronics and optoelectronics. The testification of the hypothesis is also discussed. However, the experiments in this thesis are concerned with mechanically exfoliated materials only. The effectiveness of the methods should be tested on large-area synthesized materials as well. Future work based on the results introduced in my thesis is suggested.

7.1 General Discussion

Van der Waals heterostructures are promising for a variety of electronic and optoelectronic applications.^[1-3] The technologies for fabrication of van der Waals heterostructures need to be improved to simplify the processes and improve the performances. On the other hand, novel device structures are to be designed and tested based on these heterostructures. Furthermore, the performance of conventional device is to be improved by replicating the functions with these heterostures. These hypotheses have been proven as discussed in Chapter 4, 5 and 6.

First, a simple and universal transfer printing method is developed. It is based on the difference of interface energy and no harsh reaction is involved. AFM results confirm the cleanness of the surface after transfer. Raman and PL spectra confirm that the crystalline and photonic properties are retained. The compatibility of this method to electronic applications is proved by demonstration of an inverter which is based on n-type MoS₂ and p-type WSe₂ transistors.

Second, the source of unstable photocurrent of MoS₂ photo-FETs is identified. By comparing the photoresponse of exposed and h-BN-covered MoS₂, the persistent photocurrent is ascribed to the trapping states at the MoS₂-SiO₂ interface. When conventional SiO₂/Si gating stack is replaced by h-BN/Gr, the dangling bond-free surface of h-BN results in stable photocurrent.

Last, a JFET based on TMDC heterostructures is demonstrated for the first time. WSe₂ is p-doped by oxygen plasma treatment to improve the quality of MoS₂-WSe₂ P-N junction. MoS₂ is contacted with FLG to minimize the contact resistance. P-doped WSe₂ acts as the gate to deplete or accumulate electrons in the MoS₂ channel.

7.2 Reconnaissance Work and Future Work

7.2.1 Large-area electronics based on van der Waals heterostructures

The commercialization of 2D layered materials for electronic and optoelectronic applications rely on large-area synthesis with high throughput. Recently, great progress has been made in synthesis of semimetallic graphene^[4-6], insulating h-BN^[7, 8] and semiconducting TMDCs^[9-12] by CVD. A few research groups have developed feasible method to transfer these materials from their original substrates.^[13-17] However, most of these studies only demonstrate proof-of-concept device applications and large-area device arrays have emerged only recently.^[18] The reports about electronic devices totally from 2D layered materials are even rarer.^[19]

The transfer printing method introduced in Chapter 4 might be suitable for large-area electronic applications based on van der Waals heterostructures. MoS₂ grown on SiO₂/Si substrates can be transferred to PDMS by using this method according to my reconnaissance work. Although graphene and h-BN are usually grown on metal substrates, they should be placed on flat and contrasting substrates, e.g. SiO₂/Si to get patterned before being transferred to the final substrates for devices. Therefore, they can be transferred to PDMS for printing just like the mechanical exfoliated samples. A major obstacle to the fabrication of large-area electronics based on van der Waals heterostructures is the alignment of the patterned 2D materials when they are stacked layer by layer. The conventional semiconductor technologies could provide solutions for this problem. Marks made from 2D materials could be used under optical microscope for the alignment as in photolithography.

7.2.2 Scanning Photocurrent Microscopic (SPCM) Study on Gr-contacted Stable Photo-FETs

The photoresponse of photodetectors is commonly studied with global illumination, which means the entire device is illuminated and the contribution to photoconductivity

from all components is detected. Such results provide a direct measurement of the performance of photodetectors but the mechanism behind the photoconductivity remains obscure. SPCM has been used to study the spatially resolved photoresponse of nanomaterials such as carbon nanotubes (CNTs)^[20], Si nanowires (SiNWs)^[21], graphene^[22] and MoS₂^[23]. A diffraction-limited focused light is directed on to the device as shown in Figure 7.1. The spatial distribution of electric field is revealed because only the regions where an electric field exists contribute to the photocurrent.

Figure 7.1 (a) Optical image of a graphene device. Scale bar: 2 μm . (b) Gate voltage dependent four-probe resistance. (c) Photocurrent image overlapped on image of light reflection. (d) Schematic diagram of the SPCM setup.^[24]

In Chapter 5, stable photocurrent generation has been realized by replacing the SiO₂/Si gating stack with trapping-free h-BN/FLG combination. Furthermore, the reconnaissance work show that photocurrent of FLG-contact MoS₂ photo-FETs is larger than that of Au/Cr-contact MoS₂ photo-FETs. The transparency of FLG may be the reason of

improved photodetecting performance and the FLG-MoS₂ junction regions may be the main contributor to photocurrents. These hypotheses can be testified by future SPCM studies.

7.2.3 Van der Waals Photo-JFETs

The electronic transport properties of JFETs based on TMD heterostructures are described in Chapter 6. They are also promising candidates for photodetecting applications. The conductivity of the channel is reduced because it is depleted of free carriers, which minimizes the dark current. However, the light absorption is enhanced because the thickness of absorbing materials is increased. These two factors should be beneficial to the photodetecting performances of van der Waals photo-JFETs.

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