Electrical responses of graphene layers to extrinsic charges

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NANYANG
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**ELECTRICAL RESPONSES OF GRAPHENE LAYERS TO
EXTRINSIC CHARGES**

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING
2010

ELECTRICAL RESPONSES OF GRAPHENE LAYERS TO EXTRINSIC CHARGES

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

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TABLE OF CONTENT

ACKNOWLEDGEMENT	1
TABLE OF CONTENT	3
ABSTRACT	9
LIST OF FIGURES.....	11
LIST OF ABBREVIATIONS AND SYMBOLS	19
CHAPTER 1.....	24
INTRODUCTION	24
1.1 Background and Motivation	24
1.2 Objective and Scope of This Research.....	25
CHAPTER 2.....	27
LITERATURE REVIEW	27
2.1 Introduction to Two-dimensional Graphene	27
2.2 Structure of Graphene.....	28
2.2.1 Visualize One-Atom-Thick Crystals	28
2.2.2 Atomic Structure of SLG.....	29
2.3 Electronic Energy Band Structure of Graphene	30

2.3.1 Carbon Bonding	30
2.3.2 Tight-Binding Calculation.....	32
2.4 Graphene Electronics.....	38
2.4.1 Graphene Field Effect Electronics	39
2.4.1.1 Ambipolarity Behavior of Graphene	39
2.4.1.2 Ultra High Carrier Mobility in Graphene	40
2.4.1.3 Band Gap opening of Graphene.....	41
2.4.2 Ultra High sensitivity of Graphene Based Sensor	43
2.4.3 Graphene Transparent Electrodes	44
2.4.4 Recent Research Progress in Graphene Doping.....	45
2.5 Preparation of Graphene.....	47
2.5.1 Mechanical exfoliation	47
2.5.2 Chemical Vapor Deposition	48
2.5.3 Chemically Derived graphene.....	48
CHAPTER 3.....	50
Experimental Details	50
3.1 Raman Spectroscopy	50
3.2 Electrostatic Force Microscopy	51
3.3 Scanning Kelvin Probe Microscopy	52

3.4 Photoelectrical Response Measurement	52
CHAPTER 4.....	54
CHARGE DOPING FROM SUBSTRATES AND ADJACENT GRAPHENE LAYERS	54
4.1 Introduction	55
4.2 Experimental Section.....	56
4.3 Result and Discussion.....	58
4.3.1 Doping Effect From Adjacent FLG.....	58
4.3.2 Doping Effect From SiO ₂ Substrate	60
4.4 Conclusion	66
CHAPTER 5.....	67
DOPING EFFECTS IN SINGLE-LAYER GRAPHENE FROM AMBIENT ENVIRONMENT	67
5.1 Introduction	68
5.2 Experimental Section.....	69
5.3 Results and Discussions	69
5.3.1 Photoelectrical Response in Pristine SLG	69

5.3.2 Oxygen Effect on SLG Transistors	73
5.3.3 Water Molecules Effect on SLG Transistors	74
5.3.4 Photo-Induced Oxygen Desorption in SLG Transistors	76
5.3.5 Photoelectrical Response from SLG Activated by Photosensitive Polymers	81
5.4 Conclusions	84
CHAPTER 6.....	85
WORK FUNCTION ENGINEERING OF GRAPHENE LAYERS BY CHEMICAL DOPING.....	85
6.1 Introduction	86
6.2 Experimental Section.....	87
6.3 Results and Discussion	88
6.3.1 Photovoltaic Devices Based on n-Si/Graphene	88
6.3.2 Doping Effect study by Scanning Kelvin Probe Microscope	91
6.4 Conclusion:	96
CHAPTER 7.....	97
CONCLUSIONS AND RECOMMENDATIONS.....	97
7.1 Conclusions	97

7.2 Recommendations for Future Work	98
7.2.1 Charge Impurities Effect on Transport Properties of Graphene	98
7.2.2 More Accurate Wavelength Selection of Graphene Based Photo Detector	98
7.2.3 Improving the Power Conversion Efficiency of Graphene-based Solar Cells	99
APPENDIXES.....	100
PHOTOELECTRICAL RESPONSE FROM 2D CARBON NANOTUBE NETWORKS ACTIVATED BY PHOTSENSITIVE POLYMERS.....	100
A.1 Introduction:	101
A.2 Experimental Section.....	102
A.3 Results and Discussion	103
A.3.1 Photoelectrical Response from 2D Carbon Nanotube Networks Field Effect Transistors Activated by Photosensitive Polymers.....	103
A.3.2 Electrostatic Force Microscope Study of Charge Trapping Effect on The Interface of Dielectric Layer.....	105

<i>A.3.3 Photoelectrical Response from 2D Carbon Nanotube Networks on Quartz Substrates</i>	<i>110</i>
A.4 Conclusion	110
REFERENCE	112
LIST OF PUBLICATIONS.....	130
1. Peer-Reviewed Journal Papers	130
2. Conference Presentation	132
3. U.S.A. Patent:	133

ABSTRACT

Graphene has attracted great interest due to their unique electronic structures, physical properties and geometries. Graphene thin layers are very sensitive to the environmental perturbations including heat, photons and charges. With a relatively large cross section for readily receiving molecules or interacting with environmental charges, graphene exhibits greater potential for practical applications in biomolecular sensors, nonvolatile memory cells, solar cells, photo detectors and *etc.* Among all of these applications, graphene layers act as a charge sensor or a charge collector. Therefore, better understanding of the charges interaction with this carbon material is crucial.

In this thesis, we investigate electrical responses of graphene layers to the extrinsic charges and utilize the charge doping effects to extend the application of graphene layers in photoelectronics. For graphene electronic devices, graphene layers were typically in direct contact with the dielectric layers. Owing to their high sensitivity to environmental perturbations, it is necessary to consider the contribution of the extrinsic carriers from the underlying substrates. We first studied the charge doping effect of the supporting substrates to single layer graphene (SLG) by electrostatic force microscopy (EFM), Raman spectroscopy and electrical characterizations. It was found that the SLG can be effectively doped by the underlying materials, which results in a modulation of electronic property. Additionally, other charge doping effects from the surrounding environment, for example, the doping effect from the surface adsorbed oxygen species and charge trapping effect from moistures were investigated. A photo-induced oxygen de-doping

phenomenon was also observed. Furthermore, we extended the photosensitivity of graphene layers to a tunable wavelength by functionalizing them with photosensitive polymers. These results suggest the photoelectrical response of SLG transistors is dominated by photogenerated extrinsic charges rather than the direct photocurrent process. Finally, in order to achieve a controllable doping and tailor the electrical properties, we intentionally modified graphene layers with HAuCl_4 . By this method the surface potential of graphene can be controlled within a range of $\sim 0.5\text{eV}$. The graphene layers were further used as transparent electrodes for Si photovoltaic devices, where we demonstrated that chemical doping can effectively improve the performance of graphene based electronic devices.

LIST OF FIGURES

Fig. 1 Allotropes of carbon with different dimensionalities	27
Fig. 2 (A) A single and bilayer sample suspended on a porous membrane. Optical absorbance is measured at 2.3% per layer. The inset shows the sample design with several apertures. ²⁴ (B) Graphene crystallites on 300 nm SiO ₂ imaged with white light ²⁵	28
Fig. 3 (A) Bright-field TEM image of a suspended graphene membrane, Scale bar 500nm; (B) electron diffraction pattern from a graphene monolayer under incidence angles of 0, reproduced from Ref ²⁶ (C) High resolution TEM image, Scale bar: 2 nm reproduced from Ref ²⁷	29
Fig. 4 STM image, reproduced from Ref ²⁹	30
Fig. 5 The formation of sp^2 hybridization	31
Fig. 6 (A) Graphene lattice cell in real space; (B) reciprocal-lattice in the first Brillouin zone	33
Fig. 7 The energy dispersion relations for 2D graphene through the whole region of the Brillouin zone	37
Fig. 8 The energy dispersion relations for 2D graphene through the whole region of the Brillouin zone in the case of $\mathbf{S} = 0$	38
Fig. 9 Schematic illustration of SLG field effect transistor.	39

- Fig. 10 Schematic diagram showing the band structure and resulting ambipolar field effect in graphene. ^{3, 34} V_g is the gate voltage, E_F indicates the Fermi level of graphene, ρ is resistance.40
- Fig. 11. (A) SEM image of a typical suspended graphene device with a Hall-bar structure. (B) Device schematic side view. Degenerately doped silicon gate (blue), partly etched SiO_2 (green), suspended single-layer graphene (pink) and Au/Cr electrodes (orange). ³⁵41
- Fig. 12 (A) SEM image of device set P1 with parallel GNRs of varying width; (B) SEM image of Device D1 containing GNRs in different relative crystallographic directions with uniform width; (C) Band gap vs width of GNR for the parallel type (p1 to p4) and two with varying orientation (D1, D2). ^{13, 36} E_g is the band gap, W is the width of GNRs, θ denotes the relative crystallographic directions.42
- Fig. 13 (A) Changes in resistivity, by graphene's exposure to various gases diluted in concentration to 1 p.p.m; inset figure shows the SEM image of devices (false colours matching the visible optic images); (B) examples of changes in Hall resistivity during the adsorption and desorption of diluted NO_2 , Green curve shows a reference sample exposed to pure He. ¹⁹ t is the measuring time, ρ is the electrical resistance.....44

- Fig. 14 (A) A transparent ultra-large-area graphene film on flexible substrates (PET) ; (B) the assembled graphene/PET touch panel with outstanding flexibility. ⁵¹45
- Fig. 15 Optical microscope image in white light of graphitic films obtained by mechanical cleavage, thinner layer gives a barely visible contrast in optics. ³47
- Fig. 16 Chemical structures of (A) m-aminophenyl trimethoxysilane (APTMS); (B) Phenyltriethoxysilane (PTS); (C) SiOH/SiO₂(100)/Si (111); (D) APTMS/SiO₂(100)/Si (111); (E) PTS/SiO₂(100)/Si(111) 58
- Fig. 17 (A) Schematic illustration of EFM experiments. (B) The typical EFM images for the graphene films on a SiO₂ substrate (left: V_{tip} is -1.5 V, right: V_{tip} is +1.5 V), where A and B represents the SLG connected to FLG films and the isolated SLG. (C) AFM cross-section showing that the SLG films A and B are with the same thickness ~0.9 nm. (D) EFM phases as a function of V_{tip} for the SLG samples A and B. The surface potential V_0 was obtained by fitting to data points using the equation $\Delta\Phi = -\arcsin[S(V_{tip}-V_0)^2] + T$59
- Fig. 18 (A) The surface potential V_0 of few-layer-graphene on SiO₂ substrates plotted as a function of their thickness, where we have examined six substrates with $V_0 = 0.86, 0.50, 0.19, 0.10$ and -0.12 V respectively. (B) The change in the sample surface potential after SLG screening vs. the initial substrate surface potential, where the

positive value of $V_0(\text{SLG}) - V_0$ (sub) indicates that the electron concentration in SLG is increased and the negative one indicates the decrease in electron concentration.....61

Fig. 19 The transfer characteristics showing ambipolar conduction behaviors for the bottom-gated field-effect transistors based on the SLG films on SiO_2 substrates with surface potential (a) $V_0 = 0.86$ V, (b), $V_0 = 0.50$ V, and (c), $V_0 = -0.12$ V, respectively. The drain voltage was kept at 0.1 V and the gate voltage was swept from 100 V to -100V. Thickness of SiO_2 was 300 nm, same as those used in EFM studies.63

Fig. 20 (A) Typical SLG Raman spectra obtained in ambient (excited with 488 nm laser). (B), (C), (D) Shown are maps of Raman 2D versus G frequencies for the SLG films on the SiO_2 substrates with surface potential (B) $V_0 = 0.86$ V, (C) $V_0 = 0.50$ V, and (D) $V_0 = -0.12$ V respectively. The upward (downward) trend represents that SLG is *p*-doped (*n*-doped).65

Fig. 21 (A) The typical Raman spectrum for a SLG on a SiO_2 substrate, where G and 2D bands are assigned. Inset shows the optical microscopic image for the SLG transistor device, where the dark lines help to indicate the shape of the SLG. (B) Transfer characteristics ($I_d - V_g$) for the SLG transistor in dark and under W-lamp exposure (3 W/cm²). (C) The method of extracting the I_d change (I_d) from I_d vs.

time measurement for a SLG transistor under the illumination cycle of 400 nm of light (20 W/cm^2) at gate voltage ($V_g = -100 \text{ V}$). (D) I_d decrease (at $V_g = -100\text{V}$) for a SLG transistor upon the illumination of various wavelengths. The light intensity for all wavelengths was maintained at $\sim 20 \text{ W/cm}^2$. The UV-VIS absorption spectrum of graphene is shown in the inset of figure (D).	70
Fig. 22 Lowest-energy atomic geometries found for the adsorption of (A) O_2 (B) H_2O molecules onto a graphene sheet. The gray, red and white balls denote the carbon, oxygen and hydrogen atoms, respectively. ¹¹⁰	73
Fig. 23 Transfer characteristics (I_d - V_g) for the SLG transistor in Ar and in oxygen environments.....	74
Fig. 24 Transfer characteristics (I_d - V_g) for a SLG transistor before and after blowing water vapor on its surface. After blowing water vapor the ΔV_{th} is increased from $\sim 4.1 \text{ V}$ to $\sim 10.2 \text{ V}$	75
Fig. 25 Transfer characteristics (I_d - V_g) for a SLG transistor (A) in air, (B) in vacuum, taken respectively in dark and under W-lamp exposure (3 W/cm^2). The curves under W-lamp exposure were collected after the device was exposed to light for 10 min. (The gate-sweep rate was 1 V/sec and the drain voltage was kept at 0.1 V for all measurements).	77

- Fig. 26 Normalized drain current vs. time for a SLG transistor in air and in vacuum, taken under W-lamp exposure (3 W/cm^2). The light was switched on at time $t = 0 \text{ sec}$. $I_d(t)/I_d(0)$ is the normalized drain current as a function of time, $I_d(0)$ is the initial drain current.78
- Fig. 27 (A) The light intensity dependence of the I_d percentage decrease for a SLG transistor exposing to Xe-light measured at various gate voltages ($V_g = -100$ and 0 V) or drain voltage ($V_d=0.1$ and 0.03 V). (B) The light intensity dependency of I_d percentage decrease for a SLG transistor and an aligned SWNT resistor exposing to Xe-light measured at $V_g=0$ ($V_d=0.1\text{V}$). Inset shows an optical microscopic photo for the SLG device and a SEM picture for the aligned SWNT device.....80
- Fig. 28 (A) Transfer curves for a SLG transistor before and after F8T2 polymer coating. (B) The I_d for the F8T2-coated SLG transistor changes with the exposure of light (W-lamp 80 W/cm^2) in ambient when V_g is ranged from -100V to 150V . (C) I_d percentage changes at various V_g ($-100, -50, 0, 50, 100$ and 150 V) respectively. (D) Optical absorption feature of an F8T2 film on quartz substrate and I_d increase of F8T2 SLG transistors at different wavelengths from 400 to 650 nm . The inset of figure (D) shows the chemical structure of F8T2.82
- Fig. 29 Schematic diagram of the transferring and device fabrication process. The graphene films are synthesized by an APCVD method

on a SiO₂/Si wafer (300 nm thermal oxide) with 300 nm Ni film deposited in advance. The PMMA/CVD-G film was finally transferred to an n-type Si substrate for device fabrication89

Fig. 30 (A) Typical electrical measurement of pristine and 20 sec H₂AuCl₄ doped CVD-G/n-Si photovoltaic devices; (B) Current-voltage plots of the devices with different doping time from 5 sec to 20 mins under AM1.5 illumination; (C) comparison of I_{sc}, V_{oc} and PCE for different doping time. I_{sc} is the shor circuit current, V_{oc} is the open circuit voltage, PCE stands for the power coversion efficiency.....90

Fig. 31 AFM images for as grown CVD-G on 300 nm Ni (A) and those doped with H₂AuCl₄ for (B) 5sec (C) 25sec (D) 45sec, (A') to (D') are the corresponding SKPM images. (E) Shows the surface potential CVD-G on Ni substrate as a function of H₂AuCl₄ doping time.92

Fig. 32 schematic illustration of the photovoltaic devices' band energy diagram. (Values obtained from Ref. 132) q is the electrical charge quantity, E_c and E_v is the conducting band and valence band, E_f is the Fermi level, χ is the electorn ionization potential, Φ is the workfunction of graphene electrode, Φ_B is the charge carrier potential barrier.....94

Fig. 33 I_d-V_g curve of the SWNT-FET before and after coating with (A) F8T2, and (B)F8BT. The inset in each Figure shows the chemical structure of each polymer. The photo-responses observed for (C)

F8T2 and (D) F8BT coated SWNTs-FETs to the illumination cycles of the 450 nm wavelength of light.....	104
Fig. 34 EFM phase images upon light switching for (A) F8T2 coated SiO ₂ /Si substrates and (B) a F8T2-SNFET, with a tip bias at -3V and 3V respectively (C) corresponding topography image of sample (A) and (B) respectively.....	106
Fig. 35 (A) The light-induced phase shift for a F8T2-SNFET in EFM measurement ($V_{\text{tip}} = 3\text{V}$), where we indicate that labels “a” and “b” represent the traces with and without SWNT underneath for the EFM image in inset. (B) Schematic illustration for the distribution of photoexcited charges in the F8T2 layers and also the dissociated charges around SWNTs.....	108
Fig. 36: (A) Schematic illustration of SWNT resistor devices on quartz (B) SEM image of SWNT on quartz (C) Photoresponses of both F8T2- and F8BT-coated SWNT networks on quartz (to the 450nm light) (D) Energy band alignment of these polymers with SWNTs.	109

LIST OF ABBREVIATIONS AND SYMBOLS

CNTs	Carbon nanotubes
MWCNTs	Multi-walled carbon nanotubes
SWCNTs	Single-walled carbon nanotubes
HOPG	Highly-oriented pyrolytic graphite
SLG	Single layer graphene
FLG	Few layer graphene
GNR	Graphene nano ribbon
F8T2	Poly[(9,9-dioctyl-fuorenyl-2,7-diyl)-co-(bithiophene)]
F8BT	poly(9,9-dioctylfluorene-alt-benzothiadiazole)
APTMS	m-aminophenyl trimethoxysilane
PTS	phenyltriethoxysilane
PMMA	Polymethylmethacrylate
HNO ₃	Nitric acid
F4-TCNQ	tetrafluoro-tetracyanoquinodimethane
Na-NH ₂	1,5-Naphthalenediamine

List of Abbreviations and Symbols

An-CH ₃	9,10-Dimethylantracene
An-Br	9,10-Dibromo- anthracene
TPA	tetrasodium 1,3,6,8-pyrenetetrasulfonic acid
ITO	Indium tin oxide
FETs	Field-effect transistors
OLEDs	Organic light emitting diodes
CVD	Chemical vapor deposition
APCVD	Ambient pressure chemical vapor deposition
LPCVD	Low pressure chemical vapor deposition
AFM	Atomic force microscopy
EFM	Electrostatic force microscopy
SKPM	Scanning Kelvin probe microscopy
STM	Scanning tunneling microscopy
SEM	Scanning electron microscope
TEM	Transmission electron microscopy
CPD	Contact potential difference
CCD	Charge coupled device

TB	Tight-binding
UV	Ultraviolet
2D	Two-dimensional
a	Lattice constant
$\vec{a}_1, \vec{a}_2$	Unit vectors
$\vec{b}_1, \vec{b}_2$	Reciprocal lattice vectors for 2-dimensional graphite
φ_j	The atomic wavefunctions in state j
$\Psi_{j(k,r)}$	Eigenfunction in a solid
$\Phi_{j(k,r)}$	Tight binding Bloch function in a solid
$\mathcal{H}$	Hamiltonian of the solid
$\mathcal{H}_{jj'}$	Transfer integral matrix
$\mathcal{S}_{jj'}$	Overlap intefral matrix
$E_{\mu(\kappa)}$	Energy dispersion of a 1-D structure
E_{g2D}	Energy dispersion of 2-D graphite
V_{tip}	Voltage applied on EFM tip
V_{sur}	Surface potential
ΔV_{sur}	Surface potential difference between tip and sample

Φ_{sample}	Workfunction of sample
Φ_{tip}	Workfunction of EFM tip
V_d	Bias applied between source and drain electrodes
I_d	Current between source and drain electrodes
V_g	Gate voltage
I_g	leakage current
ΔV_{th}	Difference between the threshold voltage in the forward scan and in the reverse scan
V_{th}^f	Threshold voltage in the forward scan
V_{th}^r	Threshold voltage in the reverse scan
λ	Wavelength of light
$I(2D)$	Raman intensity of graphene 2D band
$I(G)$	Raman intensity of graphene G band
q	Electrical charge quantity
n_h	The number of holes
n_e	The number of electrons
μ_h	Field-dependent hole mobility
μ_e	Field-dependent electron mobility

List of Abbreviations and Symbols

E	Electric field across the channel
V_{oc}	Open circuit voltage
I_{sc}	Short circuit current
A_e	Contact area of p - n junction
A^*	Richardson constant
χ	Ionization potential
Φ	Fermi energy level
Φ_B	Charge carrier potential barrier
κ	Boltzmann constant
h	Planck's constant.
T	Working temperature

CHAPTER 1

INTRODUCTION

1.1 Background and Motivation

Single wall carbon nanotube (SWNT), which is a crystalline carbon sheet rolled up into long cylindrical tube with diameter of 1-2 nm, has attracted much attention in development of novel nanoelectronic sensors owing to its exceptional electrical properties.^{1, 2} The applications of SWNTs, however, are often plagued with several problems. Particularly, it is difficult to separate metallic nanotubes from semiconducting ones. And when single or a few SWNTs are used, it is challenging to manipulate them for device fabrication, the low photo-capture cross section of isolated tubes probably restrict their applications in photodetection.

The flat relative of SWNTs, single layer graphene (SLG), has been discovered recently.³⁻⁵ In contrast to the one-dimensional structured SWNTs, graphene is one-atom thick, two-dimensional (2D) carbon sheet. Graphene exhibits unique structural and electrical properties including quantum spin Hall effect,⁶ phase coherent transport,⁷ bipolar supercurrent,⁸ suppression of the weak localization,⁹ and deviation from the adiabatic Born-Oppenheimer approximation.¹⁰ The high intrinsic carrier mobility ($\sim 200,000 \text{ cm}^2/\text{V-s}$) makes SLG promising for transistors and high-frequency circuit applications. Although SLG is semi-metallic, the band gap of SLG can be controlled by patterning SLG to graphene nano ribbon (GNR).¹¹⁻¹⁴ Therefore, graphene has been anticipated as a promising alternative to carbon nanotubes in various applications¹⁵⁻¹⁸.

Most importantly, SLG has great potential for the application in sensing area, due to the fact that graphene is an exceptionally low electrical noise material¹⁹ and its unique two-dimensional planar structure, readily receiving molecules or interacting with incident photons that promises it being the ultra-sensitive and ultra-fast electronic sensor. It has been demonstrated that graphene has the ability to sense single molecule in a controlled environment.¹⁹ Although, this is a promising proof for the high sensitivity of graphene, for practical applications the requirement of ultrahigh vacuum greatly limits the practicality of these devices. The graphene based sensor working in ambient condition is demanding. Owing to the high sensitivity of SLG films to environmental perturbations, for developing graphene based devices, we believe it is fundamentally important to study the contribution of the extrinsic charges from their surroundings. Another issue is the selective sensitivity, as any analyte that can donate or withdraw electrons will results in carrier concentration change in graphene. Therefore, the functionalization of graphene's basal plane or its edges is essential for analyte-specific sensing.

1.2 Objective and Scope of This Research

In this thesis we intend to study the electrical responses in graphene layers to extrinsic charges and utilize the charge doping effect in graphene electronics. Graphene being a one atom thick carbon sheet commonly comes in direct contact with substrate, thus interface state plays an important role in its electrical properties. We investigate the environmental charge interactions from the underlying substrates and the doping effect from surface adsorbates such as moisture and oxygen. In Chapter 4, we used electrostatic force microscopy (EFM) to investigate the doping effect of SLG from the underlying SiO₂ substrates. It was found the graphene tends to screen off the

potential of the underlying substrates as a result of the charge exchange at their interface, which leads to the doping in graphene film. The effective doping from the substrates further changes the electric properties of SLG. Besides the interfacing substrates, water molecules and oxygen species are enriched under ambient conditions and it has been demonstrated they can *p*-dope the graphene sheet.¹⁹ In Chapter 5, we studied the effect of water and oxygen, and compared the transfer characters of SLG devices in air and in vacuum. The hysteresis in graphene transistors was attributed to the charge traps at the dielectric interface. A photoinduced oxygen desorption phenomenon in SLG was observed. The photodesorption phenomenon became more obvious when the wavelength of light approached to ultraviolet (UV) region. The photoresponse of SLG devices was further extended to a tunable wavelength of light by covering the graphene sheet with photosensitive polymer. The observations suggest the photoelectrical response of SLG transistors is dominated by extrinsic charge doping mechanisms. The studies on environmental charge sensitivity of SLG make it clear that it is possible to control graphene's doping type and doping level by extrinsic materials. In Chapter 6, we deliberately doped graphene layers with gold nano particles to control the carrier concentration. It was found that the Fermi level of graphene can be adjusted which opened the possibility of work function engineering for graphene electrodes. The advantages of work function engineering were further demonstrated by Si based photovoltaic cells with chemical doped graphene electrodes.

CHAPTER 2

LITERATURE REVIEW

Here, we discuss the chemical bonding, electronic structures and electrical properties of graphene layers. Some of the recent progresses in graphene preparation, including mechanical exfoliation, chemical method and chemical vapor deposition are also reviewed. The fundamental knowledge shall help us to comprehend the experimental results discussed in this thesis.

2.1 Introduction to Two-dimensional Graphene

Two-dimensional (2D) single layer graphene (SLG) can be seen as a sheet formed by sp^2 -hybridized honeycomb carbon network. As shown in Fig 1. SLG is accepted as basic building block for all the other graphitic materials with various dimensionalities, for example, wrapping up to 0D spherical fullerenes, rolling into 1D carbon nanotube (CNTs) and stacking to 3D graphite. Therefore, the SLG plays an important role in understanding the electronic properties in the other allotropes of graphitic materials.

Fig. 1 Allotropes of carbon with different dimensionalities

Although, theoretically, graphene has been studied for more than sixty years,^{20, 21} in the real world, strictly free state 2D crystals were thought not to exist due to their thermodynamically instability at finite temperatures.^{22, 23} Free state mono layer carbon material was believed tend to form curved structures such as soot, fullerenes and carbon nanotubes rather than free-standing graphene.³ Therefore, SLG was only limited to an “academic” material until year 2004, when graphene was experimentally discovered by Geim and co-workers at Manchester University by repeating exfoliation of graphite flakes.³ Right after the discovery, SLG attracts lots of attentions for their unique electronic, mechanical, optical and chemical characteristics, the finding of graphene opened up a whole new avenue for understanding the fundamental physics and searching of potential applications.

2.2 Structure of Graphene

2.2.1 Visualize One-Atom-Thick Crystals

Fig. 2 (A) A single and bilayer sample suspended on a porous membrane. Optical absorbance is measured at 2.3% per layer. The inset shows the sample design with several apertures.²⁴ (B) Graphene crystallites on 300 nm SiO₂ imaged with white light²⁵

Direct visual observation of SLG is impossible, due to the low optical absorbance of SLG which is only 2.3% as shown in Fig.2 (A).²⁴ The researchers at Manchester University introduced a method to enhance the optical contrast of SLG by putting the SLG on SiO₂/Si wafer (see Fig.2 (B)).²⁵ The thickness of SiO₂ layer was specially chosen (300nm). Due to the interference effect between SLG and substrates, the SLG became visible under white-light illumination. This simple method for quick identification of SLG contributes a lot to the progress in the SLG study.

2.2.2 Atomic Structure of SLG

Fig. 3 (A) Bright-field TEM image of a suspended graphene membrane, Scale bar 500nm; (B) electron diffraction pattern from a graphene monolayer under incidence angles of 0, reproduced from Ref²⁶ (C) High resolution TEM image, Scale bar: 2 nm reproduced from Ref²⁷

To look into the atomic structure of isolated SLG, graphene layers was experimentally studied by transmission electron microscopy (TEM)²⁶. Fig.3 (A) displays the graphene sheet, it can be self-supported on metal grids, which allows the method of characterization using TEM. The electron diffraction patterns in Fig.3 (B) and high resolution TEM in Fig.3 (C) show that graphene has a hexagonal lattice feature. The scanning tunneling microscopy (STM) was also used to study the electronic topography of graphene.^{28, 29} From the STM image in Fig.4, it shows the

electron density of the six carbons are completely equivalent which confirmed the honeycomb structure of graphene.

Fig. 4 STM image, reproduced from Ref ²⁹

2.3 Electronic Energy Band Structure of Graphene

2.3.1 Carbon Bonding

Each carbon atom has 6 electrons, and the electronic ground state of carbon electrons has a configuration of $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^0$. The two electrons in $1s^2$ orbital are strongly bonded, which are called core electrons, the other four weakly bonded electrons in $2s$ and $2p$ orbitals are valence electrons. The electronic wave functions for these four electrons can mix up with each other, the mixing of a single $2s$ electron with $n=1,2,3$ $2p$ electrons is called sp^n hybridization. For sp^2 hybridization, one of the $2s$ electron is promoted to $2p_z$ orbitals and the left $2s$ orbital mixes with two of the three

2p orbitals ($n=2$) forming a total of 3 sp^2 orbital with one remaining p -orbital as shown in Fig. 5:

Fig. 5 The formation of sp^2 hybridization

Thus, in graphene, each carbon atom has 3 closest neighbors, between each of the two carbon atoms forming one σ bond by overlapping two sp^2 orbitals and the delocalized orbital of π bond between the carbon atoms perpendicular to the molecular plane is formed by $2p-2p$ overlap. The sp^2 hybridization leads to a trigonal planar structure between each carbon atom that are separated by 1.42 Å. Thus, three of the four valence electrons in each carbon form the σ bond, the fourth electron in $2p$ orbital forms one-third of a π bond with its neighbors. The π electrons are valence electrons which dominate the transport properties of graphene, therefore they play an important role in the electronic properties of graphene. The delocalization stabilizes the in-plane carbon bonding and results in the loosely bound π electrons of high mobility. And the long-range π -conjugation in graphene also yields extraordinary thermal and mechanical properties.

2.3.2 Tight-Binding Calculation

To reveal the unique transport behavior, tight-binding (TB) method was used to study the electronic properties of graphene. In 1947, P. R. Wallace gave the first TB description of graphene by considering the nearest and next-nearest-neighbor interaction for graphene p_z orbital and neglecting the overlap between wave functions centered at different atoms.²⁰ The band structure of graphene shown an unusual semi-metallic behavior. The more widely known TB calculation for the π electrons in 2D graphene was described by Saito and Dresselhaus³⁰, their discussion provides a simple and good prediction for graphene's solid state properties by considering the nonfinite overlap between the basis functions, but includes only interactions between nearest neighbors. Here we briefly go through the TB calculation and reach the summary of the unique electronic properties of 2D graphene. The following discussions on simple TB models are mainly drawn from Saito and Dresselhaus's pervious work.

As shown within the dotted rhombus in Fig. 6 (A) the unit cell of 2D graphene lattice consists of two carbon atoms (A and B). Three high symmetry points: center, corner and the center of the edge in the first Brillouin zone are defined in Fig.6 (B) as Γ , K and M . The lattice basis vectors in real space are $\vec{a}_1$ and $\vec{a}_2$ while $\vec{b}_1$ and $\vec{b}_2$ are the corresponding reciprocal-lattice basis vectors in the Brillouin zone, $a=2.46 \text{ \AA}$, which is the lattice constant of graphene. Then the unit vectors:

$$\vec{a}_1 = (\sqrt{3}a/2, a/2), \quad \vec{a}_2 = (\sqrt{3}a/2, -a/2) \quad (1)$$

$$\vec{b}_1 = b(1/2, \sqrt{3}/2), \quad \vec{b}_2 = b(1/2, -\sqrt{3}/2) \quad (2)$$

where $b = 4\pi/a\sqrt{3}$, which is the lattice constant in reciprocal space.

Fig. 6 (A) Graphene lattice cell in real space; (B) reciprocal-lattice in the first Brillouin zone

A tight binding Bloch function is given by:

$$\phi_j(\kappa, r) = \frac{1}{\sqrt{N}} \sum_R^N e^{i\kappa R} \varphi_j(r - R), (j = 1, \dots, n) \quad (3)$$

κ is the wave vector, R is the position of the atom, n denotes the number of atomic wavefunctions in the unit cell and φ_j denoted the atomic wavefunctions in state j . We have n Bloch functions in the solid for a given κ . To form $\phi_j(\kappa, r)$, the φ_j in the N unit cells are weighted by the phase factor $e^{i\kappa R}$ and summed over the lattice vector R of the whole crystal. The eigenfunctions in the solid $\psi_j(\kappa, r)$ ($j=1, \dots, n$), where n is the number of Bloch wavefunctions, are expressed by a linear combination of Bloch functions $\phi_{j'}(\kappa, r)$ as follows:

$$\psi_j(\kappa, r) = \sum_{j'=1}^n C_{jj'}(\kappa) \phi_{j'}(\kappa, r) \quad (4)$$

$C_{jj'}$ are coefficients to be determined. Then the i -th eigenvalue $E_i(\kappa)$ can be expressed as:

$$E_i(\kappa) = \frac{\langle \psi_j | \mathcal{H} | \psi_j \rangle}{\langle \psi_j | \psi_j \rangle} = \frac{\int \psi_j^* \mathcal{H} \psi_j dr}{\int \psi_j^* \psi_j dr} \quad (5)$$

where $\mathcal{H}$ is the Hamiltonian of the solid. By substituting eigenfunctions $\psi_j(\kappa, r)$ into $E_i(\kappa)$ and making a change of subscripts:

$$E_i(\kappa) = \frac{\sum_{jj'=1}^n C_{jj'}^* C_{jj'} \langle \phi_j | \mathcal{H} | \phi_{j'} \rangle}{\sum_{jj'=1}^n \langle \phi_j | \phi_{j'} \rangle} = \frac{\sum_{jj'=1}^n \mathcal{H}_{jj'}(\kappa) C_{jj'}^* C_{jj'}}{\sum_{jj'=1}^n \mathcal{S}_{jj'}(\kappa) C_{jj'}^* C_{jj'}} \quad (6)$$

Here, $\mathcal{H}_{jj'}(\kappa)$ and $\mathcal{S}_{jj'}$ are called transfer integral and overlap integral matrices.

They can be defined by:

$$\mathcal{H}_{jj'}(\kappa) = \langle \phi_j | \mathcal{H} | \phi_{j'} \rangle ; \quad \mathcal{S}_{jj'} = \langle \phi_j | \phi_{j'} \rangle \quad (j, j' = 1, \dots, n) \quad (7)$$

In the tight binding method, the eigenvalues $E_i(\vec{k})$ and coefficients $C_{jj'}$ can be obtained by solving the secular equation:

$$\text{Det}[\mathcal{H} - E\mathcal{S}] = 0 \quad (8)$$

Therefore, we need to know the transfer integral $\mathcal{H}_{jj'}(\kappa)$ and overlap integral matrices and $\mathcal{S}_{jj'}$ for the selected $\mathcal{K}$ points. As the 2D graphene lattice consists two inequivalent carbon atoms A and B, two Bloch functions are constructed from the carbon atomic orbital. If only the nearest-neighbor interactions are considered, this

become the case for one-dimensional carbon chain, then by substituting Eq.(3) into Eq.(7) and let $j=j'=A$ there is only an integration over a single atom in $\mathcal{H}_{AA}$ and $\mathcal{H}_{BB}$:

$$\begin{aligned}
 \mathcal{H}_{AA} &= \frac{1}{N} \sum_{R,R'} e^{iK(R-R')} \langle \varphi_A(r-R') | \mathcal{H} | \varphi_A(r-R) \rangle \\
 &= \frac{1}{N} \sum_{R=R'} \epsilon_{2p} + \frac{1}{N} \sum_{R=R' \pm a} e^{iKa} \langle \varphi_A(r-R') | \mathcal{H} | \varphi_A(r-R) \rangle \\
 &\quad + (\text{terms more distant than } R = R' \pm a) \\
 &= \epsilon_{2p} + (\text{terms more distant than } R = R') \quad (9)
 \end{aligned}$$

Therefore, the largest contribution to the matrix element comes from $R=R'$ and ϵ_{2p} is the orbital energy of the $2p$ level.

For the $\mathcal{H}_{AB}$ the maximum contribution is from the nearest neighbors of A and B when $R' = R \pm a/2$:

$$\begin{aligned}
 \mathcal{H}_{AB} &= \frac{1}{N} \sum_R e^{iKa/2} \langle \varphi_A(r-R) | \mathcal{H} | \varphi_B(r-R-a/2) \rangle \\
 &\quad + e^{-iKa/2} \langle \varphi_A(r-R) | \mathcal{H} | \varphi_B(r-R+a/2) \rangle \\
 &= 2t \cos(\kappa a/2) \quad (10)
 \end{aligned}$$

Where $t = e^{-iKa/2} \langle \varphi_A(r-R) | \mathcal{H} | \varphi_B(r-R+a/2) \rangle$. The overlap matrix $\mathcal{S}_{jj}$ can be calculated with that the overlap integral yields unity for the case of $\mathcal{S}_{jj}$ with

$\mathcal{S}_{AA} = \mathcal{S}_{BB} = 1$ and $\mathcal{S}_{AB} = \mathcal{S}_{BA} = 2\mathcal{S} \cos(\frac{\kappa a}{2})$ where $\mathcal{S}$ is the overlap integral between the nearest atoms A and B.

Now we extend to 2D graphene. The relations $\mathcal{H}_{AA} = \mathcal{H}_{BB} = \epsilon_{2p}$ from 1D carbon chain can still be used, while for the 2D graphene, each carbon atom A has three nearest-neighbor B atoms denoted by $\vec{R}_1$, $\vec{R}_2$ and $\vec{R}_3$ the total contribution from all the nearest-neighbors to $\mathcal{H}_{AB}$ can be expressed as:

$$\mathcal{H}_{AB} = t(e^{-iKR_1} + e^{-iKR_2} + e^{-iKR_3}) = tf(\kappa) \quad (11)$$

Here, $f(\kappa) = e^{i\kappa_x a/\sqrt{3}} + 2e^{-i\kappa_x a/2\sqrt{3}} \cos(\kappa_y a/2)$ and use the equation $\mathcal{S}_{AB} = \mathcal{S}_{BA}^* = \mathcal{S}f(\kappa)$ and $\mathcal{H}_{AB} = \mathcal{H}_{BA}^*$ we can solve the secular equation and the eigenvalues $E(\kappa)$ are obtained as a function $\omega(\kappa)$, κ_x , κ_y

$$E_{g2D}(\kappa) = \frac{\epsilon_{2p} \pm 2t\omega(\kappa)}{1 \pm \mathcal{S}\omega(\kappa)} \quad (12)$$

Where the + signs in the numerator and denominator go together giving the bonding π energy band, and the – signs give the anti-bonding π^* band as shown in Fig. 7. And the lower π band is fully occupied by the two $2p_z$ electrons in graphene unit cell.

Where the function

$$\omega(\kappa) = \sqrt{|f(\kappa)|^2} = \sqrt{1 + 4 \cos\left(\frac{\sqrt{3}\kappa_x a}{2}\right) \cos \frac{\kappa_y a}{2} + 4 \cos^2\left(\frac{\kappa_y a}{2}\right)} \quad (13)$$

Fig. 7 The energy dispersion relations for 2D graphene through the whole region of the Brillouin zone.

From Eq. (12), when $S=0$ the bonding π energy band, and the anti-bonding π^* band become symmetrical around $E=\epsilon_{2p}$. This gives the simple approximation for the electronic structure of graphene layer:

$$E_{g2D} = \pm t \sqrt{1 + 4 \cos\left(\frac{3}{2} k_y a\right) \cos\left(\frac{\sqrt{3}}{2} k_x a\right) + 4 \cos^2\left(\frac{\sqrt{3}}{2} k_x a\right)} \quad (14)$$

This is the band structure of graphene as function of K_x and K_y as illustrated in Fig.8. The valence and conduction bands connect at six corners of the Brillouin zone, resulting that graphene is a semi-metal with zero-gap. The existence of a zero gap at the K points gives raise to quantum effects in the electronic structure of graphene.

Fig. 8 The energy dispersion relations for 2D graphene through the whole region of the Brillouin zone in the case of $S = 0$

2.4 Graphene Electronics

One of the most unique features of the graphene band structure is: the first two bands of graphene neither have a gap nor overlap with each other. Instead they intersect at two inequivalent points, which are known as Dirac points in the first Brillouin zone and the vicinity of the Dirac points is conical. This linear band dispersion near the high-symmetry vertices of its Brillouin zone makes the low-energy excitations in graphene be massless, chiral, Dirac fermions. In graphene the Dirac fermions show many unusual behaviors, for example, the anomalous integer quantum Hall effect can be observed in graphene even at room temperature.⁴ And the Dirac fermions are not sensitive to external electrostatic potentials, which make the electrons propagate without scattering over several micrometers in graphene.³ The charge carriers also show a constant speed at $\sim 10^6$ m/s which is independent of energy,⁴ even when the

number of charge carrier falls to zero, graphene still have a non-zero minimal conductivity.^{31, 32} The unique properties of graphene led to an explosion of interest in the application of graphene in electronic devices.

2.4.1 Graphene Field Effect Electronics

2.4.1.1 Ambipolarity Behavior of Graphene

Fig. 9 Schematic illustration of SLG field effect transistor.

The ambipolar charge transport in graphene originates from the electron energy dispersion in SLG as discussed by tight binding calculation. In graphene the conduction and valence bands meet at the Dirac point, and the Fermi level lies right on the Dirac point, when there is no external charge doping. Fig.9 shows the device structure of a typical SLG field effect transistor. Si is used as the back gate to modulate the Fermi level of graphene. As shown in Fig. 10, with a positive gate voltage there are electrically induced negative charges in graphene, the Fermi level shift to the upper part of the Dirac point which introduces a significant number of electrons as free carriers. It is the similar case for holes, when there is a negative gate voltage applied the Fermi level shift down below the Dirac point, resulting in extra

holes in the valence band. The truly ambipolar behavior of graphene suggests that there could be novel devices structures by controlling the doping level locally or dynamically.³³ The ambipolarity of graphene also benefit the applications of SLG in the field of charge detection. The electrical responses of graphene to molecular adsorption are significant, as either electron withdrawing or donating groups can lead to a chemical gating of SLG which results in a conductance change.¹⁹

Fig. 10 Schematic diagram showing the band structure and resulting ambipolar field effect in graphene.^{3,34} V_g is the gate voltage, E_F indicates the Fermi level of graphene, ρ is resistance.

2.4.1.2 Ultra High Carrier Mobility in Graphene

The extremely high carrier mobility of graphene had been predicted by theoretical study long time ago.²⁰ The prediction motivated the first experiments of SLG devices right after its discovery.^{3,4} For these studies, the SLG was obtained by mechanical exfoliation method on SiO_2 substrates, it was found that the carrier motilities for both

electrons and holes were as high as $15,000 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, but the mobility shows an independent of temperature between 10 and 100 K, which suggested the mobility was still limited by the defects of SLG or due to the impurities. In 2008, Kim and his coworkers at Columbia University achieved a tenfold improvement in mobility by suspending graphene sheet over trench to minimize the extrinsic scattering (shown in Fig.11).³⁵ The obtained carrier mobility is in excess of $200,000 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. The extremely high carrier mobility indicated that the charge transport is ballistic on micrometer-scale even at room temperature which makes graphene have great potential in the field of high speed semiconductor industry.

Fig. 11. (A) SEM image of a typical suspended graphene device with a Hall-bar structure. (B) Device schematic side view. Degenerately doped silicon gate (blue), partly etched SiO_2 (green), suspended single-layer graphene (pink) and Au/Cr electrodes (orange).³⁵

2.4.1.3 Band Gap opening of Graphene

It was expected that SLG could even replace the state-of-the-art silicon in semiconducting electronics. However, the lack of band gap of SLG hinders the implication for logic devices, as the SLG based transistors cannot be completely turned off. In order to overcome this problem, one of the solutions is to pattern the

graphene sheet into narrow ribbons. Owing to the quantum mechanical construction of electronic wave functions in the direction perpendicular to the axis of the ribbon, a confinement-induced gap can be opened.^{11, 14}

In 2007, Kim's group in Columbia University and Phaedon's group in IBM experimentally showed the band gap opening of graphene independently. They lithographically patterned the mechanical exfoliated SLG into graphene nano ribbon (GNR) structure.^{13, 36} The energy gap of GNR scales with the ribbon width. As displayed in Fig.12.

Fig. 12 (A) SEM image of device set P1 with parallel GNRs of varying width; (B) SEM image of Device D1 containing GNRs in different relative crystallographic directions with uniform width; (C) Band gap vs width of GNR for the parallel type (p1 to p4) and two with varying orientation (D1, D2).^{13, 36} E_g is the band gap, W is the width of GNRs, θ denotes the relative crystallographic directions.

Other methods for forming GNR such as scanning tunneling microscope (STM) lithography,³⁷ catalytic crystallographic etching,^{38, 39} chemically deriving from expandable graphite,¹² unzipping SWNT^{40, 41} have also been demonstrated. As previously discussed by the tight binding calculation, the zero-band gap of graphene

originates from the symmetric location of carbon atom A and B in the lattice cell. Therefore, an alternative way to engineer the band gap can be achieved by breaking the lattice symmetry of graphene. Researchers in University of California at Berkeley, achieved a tunable graphene bandgap of 250 meV, by using bi-layer graphene structure with external electric field.⁴² Their results demonstrate the potential applications of graphene in nanoelectronics and nanophotonics.

2.4.2 Ultra High sensitivity of Graphene Based Sensor

The SLG has a unique 2D nano-structure, all of its atoms are exposed to the adjacent environment providing the greatest sensor area per unit volume, readily receiving molecules or interacting with environmental charges. In addition, SLG has inherently low electrical noise property due to the quality of its crystal lattice and the 2D feature enables SLG to screen more charge fluctuation. Therefore, the SLG has very high charge sensitivity,¹⁹ with these advantages, it is hardly surprising that SLG has great potential for various applications in bio-molecular sensors, nonvolatile memory cells, solar cells, photo detectors and *etc.*

In 2007, it was shown that graphene has the capability to detect single-electron at room temperature.¹⁹ The resistivity of graphene either increase or decrease when it is exposed to various gases. This resistance change was attributed to the chemical doping effect from the analytes. Opposite sign of carriers generated by different analytes was observed. For example, with graphene's exposure to NO₂ the electrons were withdrawn and resulted in an increased number of hole carriers. While NH₃ can donate electrons to graphene which lead to an increase of conduction by electrons (see Fig.13(A)). The changes of Hall resistivity in a three-layer graphene device occurred in a step-like manner, which was caused by the adsorption and desorption of

individual molecules, as shown in Fig.13(B). The high sensitivity of graphene sensor is mainly due to that graphene is an exceptionally low-noise material electronically. Besides the charge sensitivity, an equally important property is the chemical doping ability of graphene by both electrons and holes in high concentrations. This makes it is possible to control graphene's doping type and form p - n junctions within a single graphene layer. Also, by controlling the carrier concentration, the Fermi level of graphene can be adjusted which opened the possibility of work function and sheet resistant tailoring of graphene electrodes.

Fig. 13 (A) Changes in resistivity, by graphene's exposure to various gases diluted in concentration to 1 p.p.m; inset figure shows the SEM iage of devices (false colours matching the visible optic images); (B) examples of changes in Hall resistivity during the adsorption and desorption of diluted NO_2 , Green curve shows a reference sample exposed to pure He. ¹⁹ t is the measuring time, ρ is the electrical resistance.

2.4.3 Graphene Transparent Electrodes

Graphene layer has very low opacity which is around 2.3 %. ²⁴ and it can be further chemically doped to decrease the sheet resistance, these advantages make graphene promising for high performance transparent conducting films. The solution processing of chemically derived graphite oxide for transparent conductor film has

been developed by Mullen and co-workers.⁴³ However, the conductivity of these films is limited⁴⁴ and high enough electrical conductivity is required for good electrodes. Recently, there are tremendous progresses in the synthesis of graphene film by chemical vapor deposition (APCVD).⁴⁵⁻⁵⁰ The most recent achievement is the continuous large area graphene thin films with surface area up to 30 inch can be obtained by CVD method (see Fig.14).⁵¹ Additionally, the electrical properties of graphene films can be further improved by multiple roll-to-roll transfer and chemical doping with nitric acid (HNO_3).

Fig. 14 (A) A transparent ultra-large-area graphene film on flexible substrates (PET) ; (B) the assembled graphene/PET touch panel with outstanding flexibility.⁵¹

2.4.4 Recent Research Progress in Graphene Doping

Doping in graphene-related materials has been attracting lots of research activity in the past few years, as controlling the type and the concentration of charge carriers is essentially import for graphene electronics.⁵²⁻⁵⁷ An atomically thin layer of graphene is sensitive to the adsorption of atoms and simple molecules. The principle of chemical doping has been demonstrated by simply exposing graphene to various gases such as NH_3 , H_2O and NO_2 in vacuum condition.¹⁹ The Hall effect measurement shows that

charge carrier can be induced in graphene¹⁹ and the NH₃ adsorbate induces electrons. By contrast, water and NO₂ result in holes as charge carriers in graphene. A more practical and robust approach to dope graphene was reported by Coletti et al.⁵² Angle-resolved photoemission spectroscopy was used to show the hole doping effect of graphene after adsorbing tetrafluoro-tetracyanoquinodimethane (F4-TCNQ) onto the graphene surface. And it was found that the doping effect of F4-TCNQ can be preserved in air and the temperature resistant can be up to 200 °C. Other organic molecules such as 1,5-Naphthalenediamine (Na-NH₂), 9,10-Dimethylantracene (An-CH₃), 9,10-Dibromo-anthracene (An-Br) and tetrasodium 1,3,6,8-pyrenetetrasulfonic acid (TPA) have also been documented as electron-donors or acceptors for graphene.⁵⁴ These molecules can stably bind to graphene surfaces via strong π - π interaction between their aromatic rings and the graphene. Electrical measurements on the graphene based field-effect transistors (FETs) suggest that the aromatic molecules with electron-donating groups (Na-NH₂, An-CH₃) cause *n*-doping while those with electron-withdrawing groups (TPA, An-Br) impose *p*-doping on graphene. Another approach of chemical doping is by oxidizing agents or metal salts. Nitric acid (HNO₃) was found to be an effective reagent to dope large area graphene films with *p*-carriers.⁵¹ The sheet resistance of graphene films can also be reduced by doping with AuCl₃ in nitromethane.⁵⁶ Au nano-particles can be formed on the surface of graphene after doping with AuCl₃, which induce holes in graphene layers. The sheet resistance of graphene can be further reduced to 54Ω/□ at 85% transmittance by layer-by-layer doping method using the same chemical.⁵⁸

Fig. 15 Optical microscope image in white light of graphitic films obtained by mechanical cleavage, thinner layer gives a barely visible contrast in optics.³

2.5 Preparation of Graphene

Generally speaking, there are two different approaches for obtaining SLG. One is the top down method; graphene sheet can be fabricated from the bulk graphite material by physical or chemical exfoliation technique. The other way is by the bottom up approach, graphene sheet can be growth by chemical vapor deposition (CVD) or the carbon segregate from SiC substrate. Among those methods, mechanical exfoliation and CVD yield better crystalline qualities.

2.5.1 Mechanical exfoliation

Graphene was first discovered by the method which is called micro mechanical exfoliation³ This method is a common and fast technique for obtaining SLG. The starting material is highly-oriented pyrolytic graphite (HOPG) or natural graphite. The

scotch tape is used to repeatedly peel flakes of graphite off from the bulk material until the flakes on the scotch tape is thin enough. This is followed by pressing the tape with thin graphite flakes against a Si wafer with a 300 nm SiO₂ layer on top and gently scratching the tape on the backside with tweezers. After peeling the tap off from the substrate, thin layer of graphite flakes can be left on the substrate. Among these flakes one could find SLG under optical microscope by observing the light color contrast between SLG and Si wafer.

2.5.2 Chemical Vapor Deposition

Although the Scotch tape method for SLG preparation gives high quality SLG, it normally resulted in a haphazard layout and the SLG can only be randomly pick up which limits further applications. Recently, there are tremendous progresses in the synthesis of graphene film by CVD.^{45-50, 59} By exposing carbon source to metal surface (such as Ni and Cu) at high temperature, after cooling down to room temperature graphene layers can precipitate on the metal surface. The graphene sheet obtained by the CVD method has outstanding optical, electrical and mechanical properties which enable numerous applications, including the use in large-scale flexible, stretchable, foldable transparent electronics. The scaling up can be readily achieved as the size of graphene sheet is only limited by the metal substrate.

2.5.3 Chemically Derived graphene

Other ways for preparation graphene sheet have also been developed. For example, graphene sheet can be fabricated by reduction of the chemical derived graphene oxide from bulk graphite.⁶⁰⁻⁶² With the self-assembly technique large size graphene film can be obtained, however, these graphene films show relatively poor electrical

conductivity owing to the interlayer junctions and structural defects induced during the chemical processing.

CHAPTER 3

EXPERIMENTAL DETAILS

Several key experimental set-ups for this thesis are briefly introduced, including Confocal Raman spectroscopy, Kelvin probe, Scanning Kelvin Probe and photoelectrical measurement. Other specific experimental details shall be discussed in each chapter.

3.1 Raman Spectroscopy

Raman spectroscopy is a sensitive tool to probe the nature of graphene including the structural and electronic characteristics.⁶³⁻⁶⁵ Raman spectroscopy provides information on the defects (D-band), in-plane vibration (G-band) and stacking orders (2D-band) of graphene layers.⁶⁶ The D-band is due to the TO phonon branches around the K point of the Brillouin zone and requires a defect for its activation. The D-band intensity is related to the amount of disorder.⁶⁷ The 2D peak is the second order of the D-band.⁶⁴ SLG can be determined by the symmetric and sharp features of 2D-band. G-band corresponds to the E_{2g} phonon vibration at the Brillouin zone center. The stiffening and sharpening of G-band reflects the electron or hole doping effects.⁶³

In our experiments, the Raman spectra were recorded using a WITEC confocal spectrometer with X 100 objective lens the grating used is 600 lines/mm, and an air cooling charge coupled device (CCD) as the detector. 488nm excitation and low power level (~1mW) in order to avoid any heating effect. The Raman spectra were then fitted to a Lorentzian profile to extract the peak position. In order to obtain the raman images,

the sample was carried by a piezo stage for Raman image scan, at each point of moving step the Raman spectrum was recorded for a integration time of 0.3 second. The characteristic Raman peak at 520 cm^{-1} in a silicon wafer was used as a reference to calibrate the spectrometer.

3.2 Electrostatic Force Microscopy

Electrostatic force microscopy has been used to study electrical properties on a nanometer scale.⁶⁸⁻⁷⁰ We perform electrostatic force microscope (EFM) study using the phase measurement mode. It is a dual-pass technique. Two scans are conducted in tapping mode, where the tip is mechanically driven around its resonance frequency. During the first scan, topography information is acquired. The tip is then lifted and the line scan is repeated at a constant distance from the surface based on the recorded profile. During the second scan (interleave scan), a DC voltage is applied to the tip. The long range electrostatic force between the tip and the sample surface alters the tip resonance frequency, inducing a change in both the phase and amplitude signals. Attractive and repulsive forces will give rise to opposite phase shift. Recording the phase shift reveals information about charge/potential distribution on the sample surface. An Asylum Research MFP-3D system with Olympus (OMCL-AC240TM) Pt coated cantilevers is used for the experiments. The tip curvature radius is $\sim 15\text{nm}$, quality factor 190, spring constant 2 N/m , resonance frequency $\sim 70\text{ kHz}$ and cantilever length $240\text{ }\mu\text{m}$.

3.3 Scanning Kelvin Probe Microscopy

The surface potential was measured by a dual-pass technique in tapping mode using scanning Kelvin probe method (SKPM) based on an atomic force microscopy (AFM) system Dimension 3000 from Veeco Metrology Group with NanoScope™ Signal Access Module. The measurement was conducted in air with Olympus (OMCL-AC240TM) Pt coated cantilevers. The tip curvature radius is ~15 nm, quality factor ~190, spring constant 2 N/m, resonance frequency ~70 kHz and cantilever length 240 μm . The contact potential difference (CPD) value between tip and sample surface was taken as the averaged value over an area of 1 μm by 1 μm . The standard deviation of the experiment was 10 mV. For details of the surface potential study, the dual-pass mode means topography information was acquired in the first scan; the second scan was then performed while the tip was maintained at a constant distance (10 nm above the sample surface). Both a DC single and an AC signal at the resonant frequency of the cantilever are applied to the metal coated AFM probe while the tip is lift up. If a potential difference (ΔV_{sur}) exists between the tip and the sample surface, the signal creates a varying electrostatic force causing an oscillating motion in the cantilever. The ΔV_{sur} is measured by adjusting the DC voltage till there is no DC potential difference. The DC voltage is recorded as the CPD value.

3.4 Photoelectrical Response Measurement

Photoelectrical measurements for SWNTs and SLG transistors were performed using a Keithley semiconductor parameter analyzer, model 4200-SCS. Broad-band light sources (250W W-lamp or 450 W short arc Xe-lamp) and band-pass filters ($\pm 10\text{nm}$) were used to select desired band of light. The intensity of light was estimated

by a photometer with a photo-detector (International Light Corp.) without further calibration.

The n -Si/Graphene photovoltaic devices were irradiated under a solar simulator at AM 1.5 with a light intensity of 100 mW. Electrical testing was performed by Agilent 4156C precision semiconductor parameter analyzer.

CHAPTER 4

CHARGE DOPING FROM SUBSTRATES AND ADJACENT GRAPHENE LAYERS

Owing to the high sensitivity of single layer graphene (SLG) films to environmental perturbations, for the SLG electronic devices it is necessary to consider the contribution of the extrinsic carriers from their surroundings. In this Chapter we discuss the doping effect in SLG from the underlying substrates. When SLG is on SiO₂ substrates, the charge exchange at their interface results in a dipole, which direction strongly depends on the contact potential difference between the SLG and the substrates. Electrostatic force microscopy (EFM) reveals that the surface potential of graphene either increases or decreases, depending on the initial surface potential of substrates, to a "bulk" value with their thickness. The experimental charge screening length of SLG is longer than its thickness. The consequence of screening is the effective doping of graphene, where the substrate-dependent *p*- or *n*-doping of graphene is further corroborated by Raman spectroscopy and electrical measurements for the transistor devices. Also, the unique electronic structures of SLG films make them sensitive to the doping rather than effective gating from the SiO₂ substrates. Our results promise a practical strategy to tailor the electronic properties of graphene for nanoelectronics.

4.1 Introduction

Graphene-derived nanomaterials are promising for applications such as atomically thin transistors, sensors and other nanoelectronic devices. Both theoretical and experimental results have demonstrated that the Fermi energy shift of SLG has been achieved by deliberate doping from metal,⁵³ gas molecules¹⁹ or electrical gating,^{71,72} showing that the electronic structure of SLG films is very sensitive to the environmental perturbations. Moreover, the effect of SiO₂ substrate has been ignored for a long time until a recent discovery that the surface SiO⁻ bonds efficiently gated the organic thin-film transistors.⁷³ Perhaps unexpected from its perfect two-dimensional structure, the carrier density inhomogeneity in the SLG films deposited on SiO₂ substrates has been identified and attributed to either the intrinsic mechanical ripples in the SLG sheet⁷⁴ or the charged impurities in the insulating dielectrics.⁷⁵⁻⁷⁸ Although the screening of substrate charge impurity by graphene layers has been investigated by theoretical⁷⁹⁻⁸¹ and experimental works,^{82, 83} the impacts of the insulating substrate SiO₂ to graphene films are not fully elucidated. Herein, we scrutinized this issue using EFM, Raman spectroscopy and electrical characterization. Our results suggest that the effective doping from the underlying substrate⁷³ is predominant rather than the effective gating from substrates. It is concluded that the contact potential difference between SiO₂ substrates and SLG films controls the direction of the dipole formed at the interface. The substrate-induced electron injection (depletion) in SLG films actually imposes effective *n*- (*p*-) doping to the SLG films.

4.2 Experimental Section

SLG films were obtained using the micro-mechanical exfoliation technique.³ In brief, natural graphite flakes (from NGS) were repeatedly cleaved with adhesive tapes and then transferred to various SiO₂ substrates. We verified the SLG films using Raman spectroscopy and atomic force microscopy (AFM), as previously described.^{64,}⁸⁴ Details of EFM measurement are as described in Chapter 3. EFM can map out the phase shift of the cantilever, a lag between the drive frequency and the cantilever oscillation. The $\Delta\Phi$ is related to electrical force gradient dF/dz by the equation: $\tan(\Delta\Phi) \sim (k/Q)(dF/dz)$,⁸⁵ where Q and k represent the quality factor and the elastic constant of the cantilever and z is the distance between the tip and the sample surface. Fig. 16(A) schematically shows the tip-sample system in our EFM setup. When the capacitive force dominates, the electrostatic force F can be normally described as:⁸⁵

$$F \approx \frac{1}{2} \frac{\partial C}{\partial z} \Delta V^2 \quad (15)$$

where Z is the distance between tip and sample surface, C is the capacitance of the tip-sample system and ΔV is the potential difference between the tip and the sample $\Delta V = V_{tip} - V_0$, V_{tip} is the voltage applied to the tip and V_0 is a z -dependent potential on the sample surface. The phase shift can then be derived as:⁸⁶

$$\Delta\Phi = -\arcsin \left[\frac{Q}{2k} \frac{d^2 C}{dz^2} (\Delta V)^2 \right] \quad (16)$$

Q is the quality factor of tip, k equals to the tip spring constant. As seen from equation (16), the minimum phase shift occurs when $V_{tip} = V_0$. Therefore, V_0 is obtained by fitting the phase shift data at different V_{tip} to the following equation:⁸⁶

$$\Delta\Phi = -\arcsin[S(V_{tip}-V_0)^2] + T \quad (17)$$

where S is related to the parameter $(Q/2k)(d^2C/dz^2)$ and T is the experimental offset.

The value of V_0 can be determined from the valley point of the fitted curve. It is noted that V_0 is actually the contact potential difference between the sample and the tip, $V_0 = \Phi_{sample} - \Phi_{tip}$, where Φ represents the Fermi level of the materials.)

The SiO₂ substrates [300 nm thermal oxide on As-doped Si (0.001-0.005 Ω cm)] with various values of V_0 (0.86, 0.50, 0.19 and 0.10 V) were selected. It is noted that the values vary with the method of growing SiO₂ and the cleaning process of SiO₂ surface. It is believed that the impurities or surface chemical bonds may cause the difference in V_0 . We have also intentionally modified the surface of SiO₂ substrates with m-aminophenyl trimethoxysilane (APTMS) and phenyltriethoxysilane (PTS), where the V_0 for the modified substrates can be extended to -0.12 V and 0.89 V, respectively. The chemical structures of APTMS, PTS, Si wafer with and without surface modification are shown in Fig.16. The SiO₂ surface is basically hydrophilic and can attract atmospheric moisture, which is due to the fact that the SiO₂ surface possesses hydrolyzable Si-OH groups (as shown in Fig.21 (C)). And due to the formation of Si-OH groups, electrons can be electrochemically trapped as immobile surface Si-O⁻ ions.⁷³ PTS and APTMS can react with the Si-OH group and form a monolayer on the surface of SiO₂ which blocks the free SiO⁻ groups. Fig.21 (D) shows the AMPTS modified SiO₂ surface. The amine group of APTMS is an electron donating group which contributes to the negative surface potential value (-0.12 V). By contrast, the surface potential of SiO₂ slightly increases from 0.86 V to 0.89 V after

surface modification reaction using PTS, indicating that fewer electrons were trapped by SiO^- group at the surface.

Fig. 16 Chemical structures of (A) m-aminophenyl trimethoxysilane (APTMS); (B) Phenyltriethoxysilane (PTS); (geometry not optimized) (C) SiOH/SiO₂(100)/Si (111); (D) APTMS/SiO₂(100)/Si (111); (E) PTS/SiO₂(100)/Si(111)

4.3 Result and Discussion

4.3.1 Doping Effect From Adjacent FLG

SLG films obtained from mechanical exfoliation sometimes are in junction with the few-layer-graphene (FLG) films. We first show that the surface potential of the isolated SLG is different from that of the SLG connected to FLG films. Fig. 17 (B) demonstrates the typical EFM images (left: V_{tip} is -1.5 V, right: V_{tip} is +1.5 V) for the graphene films on a SiO₂ substrate, where A indicates a SLG connected to FLG films and B is an isolated SLG. The AFM cross-section profile Fig. 17(C) shows that the SLG films A and B are with the same thickness ~ 0.9 nm. It is worthy pointing out that

this measured thickness falls into the range of reported SLG thickness which varies from 0.4 to 1.2 nm. And the variation has been attributed to the AFM instrumental offset.⁸⁴ The isolated graphene B gives a brighter contrast than A at negative tip

Fig. 17 (A) Schematic illustration of EFM experiments. (B) The typical EFM images for the graphene films on a SiO₂ substrate (left: V_{tip} is -1.5 V, right: V_{tip} is +1.5 V), where A and B represents the SLG connected to FLG films and the isolated SLG. (C) AFM cross-section showing that the SLG films A and B are with the same thickness ~0.9 nm. (D) EFM phases as a function of V_{tip} for the SLG samples A and B. The surface potential V₀ was obtained by fitting to data points using the equation $\Delta\Phi = -\arcsin[S(V_{tip} - V_0)^2] + T$.

voltage while a darker contrast is obtained if the tip voltage is positive. The nice fitting of the EFM results to the Eq.(3) indicates that the capacitive force dominates under our EFM measurement conditions Fig. 17(D). And it allows us to extract the surface potential V₀ for both samples. The surface potential of the isolated graphene B is ~0.74 V, which is higher than that of SLG A (0.65 V). Since both A and B are on the same

substrates (with a surface potential 0.89 V), the observed lower surface potential of SLG A must be attributed to the influence from the jointed FLG films which exchange carriers with the SLG A. Datta et al.⁸³ studied the screening effect of FLG films by EFM measurement, they suggest the charge impurities accumulate close to the interface of graphene and substrate and the variation in surface potential of FLG is determined by the spatial distribution of doped charges that are transferred to the graphene. For FLG films less than five layers thick, the electrostatic potential measured at the exterior graphite surface substantially reduces as the number of layers decreases demonstrate the screening effect of FLG to the charge impurities of underneath substrate. The results of Datta et al. also suggested that the SLG was not able to completely screen off the substrate potential, likely owing to its intrinsically low carrier concentration. Similarly, our experiment demonstrates that the isolated SLG B can only partially screen off the substrate potential (0.89 V), giving a measured surface potential of 0.74 V. The better screening observed for SLG A (0.65 V) therefore suggests that the connected FLG films can provide carriers to the SLG for enhancing the screening effect.

4.3.2 Doping Effect From SiO₂ Substrate

It is likely that the screening effect is originated from charge exchange (as a result of dipole formation⁸⁷) between the graphene and the substrates. In principle, it is possible to control the polarity of the dipole, hence the type of the charge added into the graphene layers, by selecting the substrates with suitable surface potential. To demonstrate the possibility, we examined the effect of various SiO₂ substrates on graphene surface potential. Fig. 18(A) shows that the measured surface potential either

Fig. 18 (A) The surface potential V_0 of few-layer-graphene on SiO_2 substrates plotted as a function of their thickness, where we have examined six substrates with $V_0 = 0.86, 0.50, 0.19, 0.10$ and -0.12 V respectively. **(B)** The change in the sample surface potential after SLG screening vs. the initial substrate surface potential, where the positive value of $V_0(\text{SLG}) - V_0(\text{sub.})$ indicates that the electron concentration in SLG is increased and the negative one indicates the decrease in electron concentration.

increases or decreases with the graphene thickness, depending on the initial surface potential V_0 of bare substrates (shown as the points at 0 nm of thickness). In this experiment, we carefully selected the isolated SLG films or the ones connected to relatively small size of FLG films to reduce the unwanted doping effect from jointed

FLG films. When the surface potential of bare SiO₂ substrate is above 0.19 V, the surface potential of graphene on SiO₂ decreases with their thickness. Opposite trend was observed for the graphene layers on the substrates with surface potential < 0.19 V. These results can be reasoned by the screening of various substrate potentials. Interestingly, when the substrate has a surface potential around 0.19 V, the measured surface potential of SLG or FLG films does not significantly vary with graphene thickness. We speculate that, in this case, the substrate exhibits a contact potential (or Fermi energy) similar to the graphene layer and therefore no significant charge exchange occurs between the graphene and the substrates. These results clearly demonstrate that the Fermi energy difference between the substrate and graphene layers drives the carrier redistribution at the substrate-graphene interface.

If a SLG or very a thin FLG is used, the direct consequence of the incomplete potential screening (or charge exchange) is the electron injection or depletion in graphene. In a general sense, electron injection (depletion) is referred to the effective *n*-(*p*-) doping from substrates to FLG or SLG films. Fig. 18(B) plots the change in the sample surface potential after SLG screening vs. the initial substrate surface potential, showing the substrate-dependent doping effect to SLG films. The positive value of $V_0(\text{SLG}) - V_0(\text{sub})$ indicates that the electron concentration in SLG is increased and the negative one represents the decrease in electron concentration. And the effect of substrates demonstrated in Fig. 18(B) only refers to the change of carrier concentration (or shift of Fermi energy), for example, *n*-doping occurs when $V_0(\text{SLG}) - V_0(\text{sub})$ is > 0. The eventual doping state of the SLG, however, also depends on its initial carrier concentration (contributed from the possible *p*-doping in ambient⁵). Nevertheless, the

results postulate the possibility of tuning electronic property of graphene devices by substrates.

Fig. 19 The transfer characteristics showing ambipolar conduction behaviors for the bottom-gated field-effect transistors based on the SLG films on SiO_2 substrates with surface potential (a) $V_0=0.86$ V, (b), $V_0=0.50$ V, and (c), $V_0= - 0.12$ V, respectively. The drain voltage was kept at 0.1 V and the gate voltage was swept from 100 V to -100V. Thickness of SiO_2 was 300 nm, same as those used in EFM studies.

To examine the doping from substrates electrically, we prepared graphene field-effect transistors by evaporating source and drain electrodes (Au with a channel length ~ 15 μm) directly on top of the graphene films without using any photo-lithography process. The photoresist or other chemicals involved in photo-lithography or impurities resulting from these processes may give uncertain doping effects. Fig. 19 shows the transfer characteristics (drain current vs. gate voltage) for three transistor devices based on the selected SLG films on various substrates (with $V_0= 0.86$, 0.50 and -0.12 V, respectively). The shape and the size of mechanically

exfoliated graphene films are difficult to control. Consequently, the quantitative comparison between devices cannot be based on obtained absolute conductance. Fortunately, the gate voltage corresponding to the valley point in the transfer curves, which indicates the transition point between electron and hole conduction, allows us to characterize the relative Fermi level (or doping behaviors). The transfer curves clearly demonstrate that the ambipolar curve moves towards negative gate voltage with the decreasing V_0 of substrates, suggesting the increase of electron concentration. This result corroborates well with the conclusions drawn from Fig. 18(B). SLG on the substrate with a V_0 value of -0.12 V manifests *n*-doping characteristics as evidenced by the negative gate voltage at the valley point. This data postulate a simple strategy to make air-stable *n*-type graphene transistors via surface modification of substrates. It is worthy pointing out that we have also modified the SiO_2 surface ($V_0=0.86$ V) with phenyltriethoxysilane (PTS) which is normally used to block the free SiO^- group on SiO_2 . The obtained V_0 is around 0.89 V and the SLG devices exhibit highly *p*-doped characteristics. If the effective gating⁷³ from SiO^- groups is pronounced, the SLG on PTS-modified substrates should exhibit less *p*-doped characteristics. Our results suggest that the effective gating from the substrates is not as pronounced as the direct doping. This could be attributed to the unique semi-metallic characteristics of SLG films which make them less sensitive to the effective gating from the SiO^- groups. The *p*-doping behaviors from PTS modified substrates could be due to the fact that PTS only forms a monolayer on SiO_2 surface and cannot totally shield the surface potential of the underneath SiO_2 layer. The contact potential difference between graphene and PTS modified SiO_2 induces surface dipole, therefore the graphene can be effectively doped and show *p*-type transfer characters.

Raman spectroscopy is a powerful tool to reveal intrinsic optical properties and structures of various carbon materials. Fig. 20(A) shows typical Raman spectra for a SLG obtained at room temperature with 488 nm laser excitation. The characteristic G ($\sim 1582 \text{ cm}^{-1}$) and 2D ($\sim 2690 \text{ cm}^{-1}$) Raman bands are sensitive to the presence of dopants.^{63, 64, 72} Electron and hole doping not only imposes shifts of the ambipolar transfer curves for the SLG based devices but also has distinct effects on the phonon modes for SLG films.

Fig. 20 (A) Typical SLG Raman spectra obtained in ambient (excited with 488 nm laser). (B), (C), (D) Shown are maps of Raman 2D versus G frequencies for the SLG films on the SiO_2 substrates with surface potential (B) $V_0=0.86 \text{ V}$, (C) $V_0=0.50 \text{ V}$, and (D) $V_0= -0.12 \text{ V}$ respectively. The upward (downward) trend represents that SLG is *p*-doped (*n*-doped).

It has been reported that *p*-doping caused up-shifting for both G and 2D Raman frequencies, while *n*-doping resulted in opposite shifting in G and 2D frequencies.^{63, 64,}
⁷² Based on these observations, the Raman 2D vs. G frequency map has been used to distinguish the *n*- or *p*-doping to SLG films.²³ Fig. 20(B)-20(D) map the 2D- and G-band frequencies measured at different locations of the SLG film on three substrates with $V_0 = 0.86, 0.50$ and -0.12 V respectively. And the data points in each graph can be fitted by a downward (or upward) line, showing that variation in 2D frequency inversely (or proportionally) correlates with variation in G frequency, where the downward (upward) line indicates that the SLG is *n*- (*p*-) doped. The Raman results for these SLG films are consistent with the electrical characterizations, confirming that *n* or *p* doping can be controlled by the substrates with various values of V_0 .

4.4 Conclusion

In summary, we studied the surface potential of SLG on insulating substrates using EFM. It was found that graphene tend to screen off the potential of the underlying the substrates as a result of charge exchange (dipole formation) at their interface. And charge exchange leads to the doping in graphene films, which, in turns, modulates the electronic properties of thin graphene layers. The doping effect (*p*- or *n*-doping) is controlled by the original surface potential of the substrates. Such substrate-dependent doping was confirmed by electrical measurements for the graphene transistors made on various substrates. This contribution promises a simple strategy to tailor the electronic properties of graphene via surface modification.

CHAPTER 5

DOPING EFFECTS IN SINGLE-LAYER GRAPHENE FROM AMBIENT ENVIRONMENT

In Chapter 4 we revealed that the *n*- or *p*-doping in single-layer-graphene (SLG) is related to the surface properties of SiO₂ dielectrics which suggests that the electrical properties of SLG films are sensitive to local perturbations, therefore it is also crucial to consider charge doping effects from the environment especially for the devices working in ambient condition. In this chapter we discuss the charge doping effect from ambient environment including oxygen and moisture. A photoelectrical response in pristine SLG transistors was also observed. The illumination of visible light on SLG transistors causes a negative shift in their transfer curves, which is attributable to the desorption of oxygen. However, their hysteresis is not affected by illumination of light, suggesting that charge traps are not affected by the visible light exposure. When SLG are covered with a layer of photoactive polymers, the photo desorption induced current change becomes less significant compared with the effects caused by the surrounding photoactive polymers. These observations suggest that the photoelectrical response is dominated by extrinsic mechanisms rather than the direct photocurrent process. Our results suggest a new strategy for achieving light detection. The photoelectrical properties of SLG extend their potential applications for optoelectronics.

5.1 Introduction

Although the observation of photoconductivity in SWNT has opened many avenues of research in photon-detection and photonic applications,⁸⁸⁻⁹¹ the low photon-capture cross section of isolated tubes restricts their applications. By contrast to isolated SWNTs, SLG films provide relatively larger cross section to receive photons and therefore the photoelectrical responses of SLG transistors are worth investigations. Recently Lee et al. used scanning photocurrent microscopy to study the local electrostatic potential of graphene devices, where it was assumed that photocurrent originated from the photogenerated carriers in graphene.⁹² Owing to the high sensitivity of SLG films to environmental perturbations, it is also necessary to consider the contribution of the extrinsic carriers from their surroundings. It has been demonstrated that the Fermi energy shift of SLG can be achieved by deliberate doping from gas molecules,¹⁶ aromatic molecules,^{54, 93} or electrical gating.^{3, 94} For the SLG films deposited on SiO₂ substrates, the carrier density inhomogeneity has been attributed to either the intrinsic mechanical ripples in the SLG sheet⁷⁴ or the charged impurities in the insulating dielectrics.^{77, 78, 95, 96} Recent reports have also suggested that the *n*- or *p*-doping in SLG is related to the surface properties of SiO₂ dielectrics.^{55, 97} Moreover, the observed *p*-doping of SLG from water molecules^{16, 9} has also attracted lots of discussions.^{57, 98} On the other hand, Liu et al. used Raman spectroscopy to demonstrate that the *p*-doping in reduced graphene oxide was mainly caused by oxygen species bound to graphene at room temperature.⁵⁷

Since the electrical properties of SLG films are very sensitive to local perturbations, it is crucial to consider the effects caused by water and oxygen molecules. We performed the electrical measurements for large size (>10 μm) SLG

transistors with the illumination of light. Results of photoelectrical responses for SLG transistors, including transfer characteristics, light intensity and wavelength dependencies, suggest that their photoresponses are mainly contributed from the photodesorption of oxygen, rather than from the direct excitation of carriers in SLG. The effects of water molecules on electrical characteristics of SLG transistors are also discussed.

5.2 Experimental Section

SLG films were obtained using the conventional micro-mechanical exfoliation technique.⁹ Natural graphite flakes (from NGS Naturgraphit GmbH, Germany) were repeatedly cleaved with adhesive tapes and then transferred on to silicon wafers with 300 nm silicon oxide layer. We verified the SLG films using Raman spectroscopy and atomic force microscopy (AFM)⁵⁵ as described in Chapter 3. The SLG transistor is fabricated by evaporating Au electrodes directly on top of selected, large-size and mechanically-exfoliated SLG films using hard-masks, where no photoresist was used to ensure the electrical characteristics were not affected by the photoresist or other wet-chemicals necessary for the electrode patterning. The typical channel length between source and drain electrodes is around 15~20 μm .

5.3 Results and Discussions

5.3.1 Photoelectrical Response in Pristine SLG

Fig. 21(A) displays a typical Raman spectrum taken on the graphene of a SLG transistor, where inset shows its optical microscopic image. Pronounced G band (at 1585 cm^{-1}) and 2D band (at 2696 cm^{-1}) are observed for the SLG films, consistent with

Fig. 21 (A) The typical Raman spectrum for a SLG on a SiO₂ substrate, where G and 2D bands are assigned. Inset shows the optical microscopic image for the SLG transistor device, where the dark lines help to indicate the shape of the SLG. (B) Transfer characteristics (I_d - V_g) for the SLG transistor in dark and under W-lamp exposure (3 W/cm²). (C) The method of extracting the I_d change (ΔI_d) from I_d vs. time measurement for a SLG transistor under the illumination cycle of 400 nm of light (20 W/cm²) at gate voltage (V_g) = -100 V. (D) I_d decrease (at $V_g = -100$ V) for a SLG transistor upon the illumination of various wavelengths. The light intensity for all wavelengths was maintained at ~20 W/cm². The UV-VIS absorption spectrum of graphene is shown in the inset of figure (D).

those obtained for previously reported SLG films.^{84, 99} AFM is used to measure the thickness of the SLG (~0.85 nm) and it is worthy pointing out that this measured thickness falls into the range of reported SLG thickness which varies from 0.4 to 1.2 nm and the variation has been attributed to the AFM instrumental offset.²⁰ Fig. 21(B) demonstrates the ambient transfer characteristics (Drain current I_d versus gate voltage

V_g) for the SLG transistor in dark and under the exposure of W-lamp (a broadband visible light source; power density: 3 W/cm^2). The valley point of the I_d - V_g curve (forward scan) is initially at 84 V in dark, corresponding to a typical p -doped behavior of graphene layers in ambient. Upon exposure to W-lamp, it is negatively shifted by $\sim 4\text{V}$, demonstrating that broadband white light slightly de-dopes the SLG films. It has been reported that the intensity ratio $I(2D)/I(G)$ of SLG is significantly decreased with increasing doping concentration.^{54, 63, 93} Similar phenomena has also been observed in intentionally doped graphene, where the Fermi energy was modulated using a gate electrode.⁷² The G and 2D peaks of graphene have difference doping dependence and the 2D/G height ratio changes significantly with doping, which makes Raman spectroscopy an ideal tool for monitoring the dopants of graphene. We have also verified the de-doping behaviour using Raman spectroscopy. In order to avoid any heating effect and minimize the photo-desorption induced by the laser illumination, a low power level ($\sim 1 \text{ mW}$) and short exposure time (0.3 second) were used for the Raman measurement. To avoid the interference from the possible inhomogeneity of underlying substrates, 25 to 30 Raman measurements on different spots were conducted to take an average. The statistics of the Raman intensity ratio $I(2D)/I(G)$ of the SLG film before and after Xe-light exposure (80 W/cm^2 for 1hr) were 3.1 and 4.0 respectively, confirming that the SLG is de-doped after light exposure. In addition, the hysteresis (ΔV_{th}) obtained in dark shows no obvious difference to that measured under W-light exposure. Here, ΔV_{th} is defined as the difference between the threshold voltage in the forward scan (V_{th}^f) and in the reverse scan (V_{th}^r) as illustrated in Fig. 21(B). In order to observe the de-doping process more clearly, we further carried out a time dependence photoelectrical response measurement. Fig. 21(C) shows the I_d response of the SLG transistor to the illumination cycle of 400 nm light at $V_g = -100 \text{ V}$,

where the I_d decrease was extracted from time $t = 50$ sec to 150 sec (light exposure time = 100 sec). It is noted that the ΔI_d becomes positive at $V_g = 100$ V (not shown), which corresponds well to the evolution of transfer curve in Fig. 21(B). We use the ΔI_d (at $V_g = 100$ V) obtained at various wavelengths (light intensity is kept at ~ 20 W/cm²) to show the wavelength-dependent photoresponses in a SLG transistor. Fig. 21(D) demonstrates the wavelength dependence of the ΔI_d , which exhibits a profile similar to the optical absorption spectrum of graphene as shown in the inset of Fig. 21(D). The strong optical absorption of graphene around 270 nm is due to π -electron plasmon excitation.¹⁰⁰ It has been suggested that photoexcited plasmons are responsible for inducing molecular desorption.^{101, 102} The photoelectrical response is negligible when incident photons with the wavelength $\lambda > 650$ nm, which could be due to the lower energy density of the longer wavelength of light. Moreover, the trend is similar to that observed in single-walled carbon nanotubes (SWNTs),¹⁰² where it was concluded that the current decrease was induced by photodesorption of oxygen species and the effect was negligibly small when $\lambda > 633$ nm. Besides, the reversible surface oxidation of SWNTs through the formation of endoperoxide on SWNT surface has also been observed.¹⁰³ Liu et al. have recently used Raman spectroscopy to demonstrate that the doping in reduced graphene oxide was mainly caused by oxygen species bound to graphene and the oxygen species were in equilibrium with gaseous O₂ at room temperature.⁵⁷ It has been found that the ground state triplet oxygen is able to react with flat graphene.^{104, 105} Moreover, under irradiation by UV light the oxygen species are readily converted into oxygen in ambient at room temperature.⁵⁷ Analogous O₂-surface equilibrium and UV induced desorption have also been separately observed in carbon nanotubes^{103, 106, 107} and polycyclic aromatic compounds.^{108, 109} Thus, the

photon-induced de-doping we observed for SLG transistors is in line with the oxygen photodesorption mechanism.

Fig. 22 Lowest-energy atomic geometries found for the adsorption of (A) O₂ (B) H₂O molecules onto a graphene sheet. The gray, red and white balls denote the carbon, oxygen and hydrogen atoms, respectively. ¹¹⁰

In order to illustrate how oxygen and water molecules adsorb and interact with graphene, an explicit modeling of the adsorption of H₂O and O₂ molecules onto a single sheet of graphene has been done by Sque et al. ¹¹⁰ Fig. 22 shows the structures of overall lowest energy found during the oxygen and moisture-adsorption calculations. For the adsorption of the O₂ molecules, the molecules lie horizontally in a plane parallel to that of graphene at a distance of 2.7 Å. By comparison, the O atoms of the H₂O molecules locate 3 Å from the graphene plane, ¹⁰⁶ while H atoms of water molecules point towards the graphene substrate.

5.3.2 Oxygen Effect on SLG Transistors

To examine the effect of oxygen on SLG transistors, we measured the transfer curves for a SLG transistor in Ar and O₂ environments, as shown in Fig. 23. The transistor was put in a chamber purging with pure Ar. Before taking the transfer curve in Ar, the transistor was electrically annealed (15V for 4000 sec) in a chamber filled with Ar to remove adsorbates on graphene surfaces. ^{35, 111} After electrical cleaning in Ar, the atmosphere of the chamber was then switched to pure oxygen for 10 min

before the transfer curve in O_2 was measured. The SLG transistor becomes more p -doped after flowing pure oxygen gas into the chamber. The result lends supports to the argument that oxygen may p -dope the SLG films.⁵⁷

Fig. 23 Transfer characteristics (I_d - V_g) for the SLG transistor in Ar and in oxygen environments.

5.3.3 Water Molecules Effect on SLG Transistors

Water molecules are enriched in ambient condition and they have been demonstrated to p -dope the SLG films.^{19, 112} It is therefore necessary to consider the effect of water molecules. It has been reported that the water adsorbates on SiO_2 significantly change the SiO_2 surface potential³⁴ and the surface potential of SiO_2 strongly relates to the doping of graphene films.⁵⁵ Moreover, density functional theory calculations suggest that perfect suspended graphene is insensitive to water adsorbates.⁹⁸ Instead, water adsorbates can shift the impurity bands of SiO_2 substrates and change

their hybridization with graphene. Therefore, the p -doping of graphene by water molecules is strongly related to the defective SiO_2 substrates.⁹⁸ Recent reports have demonstrated that the hysteresis of the transistor based on individual reduced graphene oxide was enhanced upon exposure to water vapour,^{113, 114} analogous to the behavior observed for water-adsorbed SWNTs.¹¹⁵ The water enhanced hysteresis observed for SWNT transistors has been suggested to originate from the water molecules absorbed on underlying SiO_2 substrates.^{116, 117} We have conducted a simple test to confirm that the hysteresis enhancement in our SLG transistor devices was due to the water incorporation by blowing water vapour to a SLG transistor in ambient (Fig. 24). Results show that water molecules not only p -dope the SLG transistor but also efficiently enhance its hysteresis.

Fig. 24 Transfer characteristics (I_d - V_g) for a SLG transistor before and after blowing water vapor on its surface. After blowing water vapor the ΔV_{th} is increased from ~ 4.1 V to ~ 10.2 V.

5.3.4 Photo-Induced Oxygen Desorption in SLG Transistors

To further study the effect of water and oxygen, we compare the photoelectrical responses of a SLG device in air and in vacuum. Fig. 25(A) shows the typical transfer curves for a SLG transistor with and without light exposure (W-lamp at 3 W/cm^2) in air and Fig. 25(B) demonstrates those measured in a vacuum chamber (after 3 hr pumping and the vacuum reaches 4.3×10^{-6} torr). To observe the photoelectrical responses of the transistors clearly, the transfer curve of the device in dark was taken first and then the transistor was exposed to light (W-lamp at 3 W/cm^2) for 10 min before its transfer curve with light exposure were collected. By contrast to the pronounced hysteresis obtained in air, the SLG transistor exhibits reduced hysteresis in vacuum either with or without light exposure. We notice that the hysteresis for the device increases again after venting the chamber with air; thus, we conclude that the hysteresis of the SLG transistor is caused by the adsorption of molecules in air. Interestingly, the hysteresis for our devices is not obviously changed upon light exposure either in air or in vacuum, further indicating that visible light exposure is not able to significantly change the amounts of charge traps. In other words, the charge traps (bound water on SiO_2 surfaces) in our devices may not be affected by the visible light exposure.

Fig. 25 Transfer characteristics (I_d - V_g) for a SLG transistor (A) in air, (B) in vacuum, taken respectively in dark and under W-lamp exposure (3 W/cm^2). The curves under W-lamp exposure were collected after the device was exposed to light for 10 min. (The gate-sweep rate was 1 V/sec and the drain voltage was kept at 0.1 V for all measurements).

The valley point of the transfer curves in vacuum [Fig. 25(B)] is negatively shifted by 15 V upon light exposure, much obvious than the small shift ($\sim 3 \text{ V}$) observed in ambient [Fig. 25(A)]. We have also observed that after turning off the light, the recovery of I_d (or re-doping) was faster in ambient than in vacuum. These observations are in line with that the oxygen species are in equilibrium with gaseous O_2 at room temperature.

Fig. 26 compares the normalized drain current $I_d(t)/I_d(0)$ as a function of time for a SLG transistor in air and in vacuum upon the W-lamp exposure (3 W/cm^2 ; $V_g = 0 \text{ V}$). The photodesorption normally follows the kinetic law $dm/dt = -km^n$, where m is the number of absorbed molecules, k is the constant related to the rate of desorption and n is the order of the kinetic process. Assuming that the I_d change is caused by the

desorption of absorbed molecules from SLG, and then the I_d reduction can be correlated to molecular desorption kinetics. The experimental curve (I_d -time) can not be fitted to a single kinetic term but it is noticeably well fitted to a rate law with two 1st-order kinetic processes:

$$\frac{I_d(t)}{I_d(0)} = A_1 \exp(-k_1 \cdot t) + A_2 \exp(-k_2 \cdot t) + B \quad (18)$$

where B corrects the nonzero baseline, $I_d(0)$ is the I_d in dark, A_1 and A_2 are the normalized current accounted for by the separate desorption process 1 (fast desorption) and 2 (slow desorption), and k_1 and k_2 are the constants related to the desorption rates.

The extracted values of k_1 for the device in air and in vacuum are very close, 0.109

Fig. 26 Normalized drain current vs. time for a SLG transistor in air and in vacuum, taken under W-lamp exposure (3 W/cm^2). The light was switched on at time $t = 0$ sec. $I_d(t)/I_d(0)$ is the normalized drain current as a function of time, $I_d(0)$ is the initial drain current.

and 0.118 respectively. And this 1st-order kinetic term corresponds well to the observed for photo-desorption of O₂ from SWNTs¹⁰² or from metal surfaces.¹¹⁸ The values of k_2 for the device in air and in vacuum are 1.011×10^{-3} and 9.45×10^{-4} , where the associated term $\exp(-k_2 \cdot t)$ can be effectively treated as a zero-order kinetic term because the k_2 values are $\ll 1$. Ulbricht et al. have reported that the thermal desorption of oxygen from graphite surface was a zero-order kinetic process.¹¹⁹ It is likely the curves I_d -time in the slow decay region, a quasi linear region in Fig. 26, are mainly contributed from the thermal desorption of oxygen. The larger I_d -time slope for the vacuum may be explained by slower heat dissipation of the sample in vacuum, where the thermal energy is likely caused by the heating from light.

Fig.27 (A) shows the light intensity dependence of the I_d percentage decrease for a SLG transistor exposing to Xe-light measured at various gate voltages ($V_g = -100$ and $0V$) or drain voltage ($V_d=0.1$ and $0.03 V$), where the I_d in dark for the two cases represented by black solid circle and blue empty triangle is at around $4.5 \times 10^{-5} A$ and the dark I_d for the case represented by red solid triangle is at $1.6 \times 10^{-4} A$. The percentage decrease was calculated by normalizing the ΔI_d by its dark I_d and the method of extracting ΔI_d was illustrated in Fig.21(C). The percentage I_d decrease seems to be independent to the applied V_g or V_d . Based on the conventional description for electrical current, Drude model, the I_d contributed from holes (majority

Fig. 27 (A) The light intensity dependence of the I_d percentage decrease for a SLG transistor exposing to Xe-light measured at various gate voltages ($V_g = -100$ and 0 V) or drain voltage ($V_d = 0.1$ and 0.03 V). **(B)** The light intensity dependency of I_d percentage decrease for a SLG transistor and an aligned SWNT resistor exposing to Xe-light measured at $V_g = 0$ ($V_d = 0.1\text{V}$). Inset shows an optical microscopic photo for the SLG device and a SEM picture for the aligned SWNT device.

carriers in our case) can be represented as $I_d = q n_h \mu_h E$, where q is electrical charge quantity, n_h is the number of holes, μ_h is the field-dependent mobility and E is the electric field across the channel. The consistent percentage I_d change in Fig. 27(A) strongly suggests that the photon excitation causes the decrease in n_h because n_h is

always proportional to the change in I_d ($\Delta I_d \propto \Delta n_h$) regardless of the applied electrical field (V_d). Noted that the other two parameters, μ_h and E , are field-dependent. The oxygen-desorption induced decrease in carrier concentration well explains the results. We can also exclude the direct photocurrent process because it shall cause an absolute increase rather than a proportional change in I_d . Fig. 27(B) shows the light intensity dependency of I_d percentage decrease for a SLG transistor and an aligned SWNT resistor exposing to Xe-light measured at $V_g=0$ V. Inset shows an optical microscopic image for the SLG device and a SEM picture for the aligned SWNT device. The fabrication of aligned SWNT devices has been reported elsewhere.^{120, 121} The light spot was adjusted to completely cover the area with graphene or SWNTs and the V_d for each case was chosen to keep the dark I_d at around 4.5×10^{-5} A. It is observed that the light intensity dependency for the SLG is the same as that for the aligned SWNT resistor. It is well accepted that the photoresponse for SWNTs is attributed to the desorption of oxygen.^{102, 103} Therefore, the result in Fig. 27(B) again indicates that the photoresponses of SLG film are attributed to the same cause, oxygen desorption.

5.3.5 Photoelectrical Response from SLG Activated by Photosensitive Polymers

We further discuss the photoelectrical response from photosensitive polymer coated SLG. In Section 5.3.4 we have reported that the light illumination can induce conductance decrease in SLG which is caused by O_2 desorption. From the photoelectrical response study of photosensitive polymer coated SWNTs-FET, when SWNTs networks are covered with a layer of photoactive polymers, the O_2 -desorption induced I_d change in SWNTs transistors becomes less significant compared with the effects caused by the surrounding photoactive polymers. Therefore, similar to the

carbon nanotube case, the sensitivity of the graphene devices to a tunable wavelength can also be achieved by functionalizing the graphene with chromophores.

Fig. 28 (A) Transfer curves for a SLG transistor before and after F8T2 polymer coating. (B) The I_d for the F8T2-coated SLG transistor changes with the exposure of light (W-lamp 80 W/cm^2) in ambient when V_g is ranged from -100V to 150V. (C) I_d percentage changes at various V_g (-100, -50, 0, 50, 100 and 150 V) respectively. (D) Optical absorption feature of an F8T2 film on quartz substrate and I_d increase of F8T2 SLG transistors at different wavelengths from 400 to 650 nm. The inset of figure (D) shows the chemical structure of F8T2.

Herein, SLG transistors are spin coated with a photoactive polymer poly[(9,9-dioctyl-fuorenyl-2,7-diyl)-co-(bithiophene)] (F8T2). Fig. 28(A) shows the transfer curves for a SLG transistor before and after F8T2 polymer coating (~50nm). The hysteresis for the selected SLG transistor before polymer coating is negligible in dark ambient and its valley point in transfer curve is at ~72V. After polymer coating the valley point is shifted to ~182V, indicating that the SLG transistor is more p -doped

(electrons move from SLG to F8T2 polymers). Meanwhile, the hysteresis becomes pronounced ($\Delta V_{th} \sim 12V$), suggesting that the polymers provide more charge trapping sites around SLG films. Furthermore, the hysteresis of the F8T2-coated SLG transistor is drastically increased with light exposure ($\Delta V_{th} \sim 46V$), meaning that photo-generated carriers or photo-generated charge traps in polymers strongly affect the electrical characteristics of SLG transistors. It is noteworthy pointing out that the transistors covered with a layer of polymer are expected to be better isolated from the ambient O_2 or water molecules; therefore, the enhanced hysteresis is likely attributed to the presence of trapped charges at polymer-graphene interfaces. It is noted that the photo-induced charge traps has also been observed in SWNT transistors.¹²²

Fig. 28(B) shows that the I_d for the F8T2-coated SLG transistor increases with the exposure of light (W-lamp 80 W/cm^2) in ambient when V_g is ranged from -50 V to 150 V. The V_{th} for the forward scan (V_{th}^f) under light exposure is more positive than that in dark, suggesting that the photogenerated hole carriers are transferred to SLG transistors, resulting in an I_d increase.¹²³ We summarize the I_d percentage increase for F8T2-coated SLG transistor measured at various V_g (-100, -50, 0, 50, 100 and 150V), where the ΔI_d is extracted from the I_d -time curves in Fig. 28(B). Interestingly the photo-induced I_d change even becomes negative at $V_g = -100V$, consistent with the I_d - V_g change in Fig. 28(A). The negative shift here could be attributed to the change at metal-graphene contact or the effective gating due to the presence of positive charge traps in the polymers approximate to SLG films. These results demonstrate that the I_d percentage increase of the polymer-coated transistor exhibits a strong gate dependency, in contrast to the observation in Section 5.3.4 for pristine SLG transistors. This corroborates that the mechanism of photoelectrical response is different from the

oxygen desorption for pristine SLG transistors. In Fig. 28(D) we show that the optical absorption feature of an F8T2 film is well correlated to the I_d increase of F8T2-coated SLG transistors measured at $V_g = 0V$ for at least 6 wavelengths, demonstrating that the photocurrent mainly results from the absorption of F8T2 polymer.

5.4 Conclusions

In summary, the illumination of visible light on SLG transistors causes a negative shift of transfer curves, attributable to the desorption of oxygen species. However, the hysteresis is not affected by illumination of light, meaning that charge traps are not affected by the visible light exposure. When SLG transistors are covered with a layer of photoactive polymer, the photodesorption-induced change of drain current in SLG transistors becomes less significant than the effects caused by the surrounding photoactive polymer. These observations demonstrate that the photoelectrical response of SLG transistors is dominated by extrinsic mechanisms rather than the direct photocurrent process. Furthermore, the large cross section of SLG provide higher probability of receiving photons and the capability of tailoring photoelectrical properties on them could also extend their potential of applications for optoelectronics.

CHAPTER 6

WORK FUNCTION ENGINEERING OF GRAPHENE LAYERS BY CHEMICAL DOPING

In chapter 4 and 5 we demonstrated that graphene layers are extremely sensitive to environmental charges. The extrinsic charge doping results in a carrier concentration change in graphene layers. However, this kind of environmental doping effect is not controllable. In this chapter, graphene films synthesized by chemical vapor deposition (CVD) method were deliberately doped with gold nano particles and after chemical doping the graphene films were used as thin transparent electrodes to harvest the photo-generated carrier from Si which indicates potential applications in energy generations. Moreover, by chemical doping of the graphene films the performance of photovoltaic devices can be greatly improved in terms of higher power conversion efficiency (PCE), larger open circuit voltage and short circuit current, which was attributed to the work function engineering of graphene electrodes.

6.1 Introduction

Graphene have been considered as a candidate to replace indium tin oxide (ITO) which is widely used as electrodes in optoelectronic devices such as organic light emitting diodes (OLEDs) and photovoltaic cells, since they possess excellent mechanical^{124, 125} and electrical properties.¹²⁶ Besides good conductivity and transparency of the electrode, the performance and current density for semiconducting electronic devices, such as light emitting diodes and field effect transistors, strongly rely on the carrier injection efficiency through the contact between electrodes and semiconducting material layers.^{127, 128} Therefore, the band alignment between electrodes and semiconductors and the surface property of the electrode have been an extensively investigated area.¹²⁹⁻¹³¹ Finding a certain conductive material with the desired work function for efficient carrier injection may sometimes be difficult. Both theoretical and experimental results have demonstrated that the Fermi energy shift of SLG can be achieved through deliberate doping by aromatic molecules,^{54, 93} gas molecules¹⁶ or by electrostatic gating.^{132, 133} These results suggest that controlling the work function of graphene electrodes is possible.

Transparent graphene electrodes have been formed by either reducing graphene oxide¹³⁴ or by a chemical bottom-up approach, where molecules of giant polycyclic aromatic hydrocarbons cross-link to form graphene nano sheets.¹³⁵ However, the conductivity of these films are still limited⁴⁴ and high enough electrical conductivity are required for good electrodes.

Recently, it has been demonstrated that continuous large area graphene thin films can be synthesized by vacuum graphitization and ambient pressure chemical vapor

deposition (APCVD) methods.⁴⁵⁻⁵⁰ Here, we use graphene films formed by chemical vapor deposition (CVD-G) as an ultra thin transparent electrode to collect the photo generated charges from Si substrate. We also demonstrated that the work function of graphene can be tuned by HAuCl_4 doping. HAuCl_4 is a commonly used compound in doping organic conductors. The Au^{III} can be reduced to Au particles by the charge transfer from graphene which results in *p*-type doping behavior of graphene. Gold has been chosen as material for its stability. The surface potential change of graphene as a function of doping time was studied by measuring the contact potential difference (CPD) using Kelvin probe microscopy. The device performances can be greatly improved as the results of work function engineering.

6.2 Experimental Section

Few layer graphene film was synthesized by CVD method using 300 nm Ni coated Si/SiO₂ substrates. Methane was used as carbon feeding source, the growth was done at 1000 °C. Graphene film with controlled size and thickness was made by controlling the cooling rate. Details on the graphene film growth were reported elsewhere.^{48, 49} After CVD-G growth, the sample was immersed into AuCl_3 aqueous solution with a concentration of 5 mM for various durations. Then the sample was rinsed with DI water and blow-dried by nitrogen gas. In order to have a better grounding, the bottom Ni layer was not removed for the sample used for SKPM measurement.

The surface potential (V_{sur}) of CVD-G before and after doping with HAuCl_4 was measured by a dual-pass technique in tapping mode using scanning Kelvin probe method (SKPM), detail experimental information is given in Chapter 3.

Photovoltaic devices were fabricated based on *n*-Si substrate with resistivity around 5 Ω cm. The as-grown CVD-G film was coated with a thin layer of PMMA (~100 nm) by spin coating to avoid the breaking of graphene film.¹³⁶ After etching the underlying polycrystalline Ni with Ni etchant (TFB commercial etchant from Transene, directly used without dilution), the PMMA/CVD-G film was transferred to DI water or additionally 5 mM AuCl₃ aqueous solution for chemical doping. After that the film was transferred back to water and suspended on the surface of DI water. The film was later picked up by an *n*-type silicon substrate with an attached insulating glass cover slide. 10 nm Ti and 200 nm Au were evaporated on the top side of the glass slide in advance which forms the upper electrode connects to the PMMA/CVD-G film. The rest part of PMMA/CVD-G film was brought in firm contact with the Si surface after careful blow drying with N₂ gas. The bottom electrode contact to *n*-Si was fabricated by silver paint. The area of the PMMA/CVD-G film on top of Si is 3 by 3 mm. The photovoltaic devices were irradiated under a solar simulator at AM 1.5 with a light intensity of 100 mW. Electrical testing was performed by Agilent 4156C precision semiconductor parameter analyzer.

6.3 Results and Discussion

6.3.1 Photovoltaic Devices Based on *n*-Si/Graphene

Stimulated by the study of photo-gating effect in Si substrates, photovoltaic devices based on *n*-Si/Graphene were developed. The benefit for using graphene as electrode is the possibility of controlling the work function of graphene, could greatly enhance the performance of a photovoltaic device.

Few layer graphene film was synthesized by CVD method. After CVD synthesis, the graphene films were transferred to *n*-Si substrates by coating a thin layer of PMMA on top of graphene film. The underlying Ni film was etched by Ni etchant (TFB commercial etchant from Transene). Then the graphene/PMMA film was transferred to AuCl_3 solution for chemical doping. After HAuCl_4 doping, the sheet resistance of graphene film decreases from $400 \text{ } \Omega/\text{sq}$ to $\sim 100 \text{ } \Omega/\text{sq}$ (see Ref ⁵⁶ for details). The device fabrication procedure is schematically shown in Fig. 29. Using CVD synthesis and the PMMA transfer method, the size of graphene conducting film can be easily scaled up without a fundamental limit.

Fig. 29 Schematic diagram of the transferring and device fabrication process. The graphene films are synthesized by an APCVD method on a SiO_2/Si wafer (300 nm thermal oxide) with 300 nm Ni film deposited in advance. The PMMA/CVD-G film was finally transferred to an *n*-type Si substrate for device fabrication .

Fig. 30 (A) Typical electrical measurement of pristine and 20 sec HAuCl_4 doped CVD-G/n-Si photovoltaic devices; (B) Current-voltage plots of the devices with different doping time from 5 sec to 20 mins under AM1.5 illumination; (C) comparison of I_{sc} , V_{oc} and PCE for different doping time. I_{sc} is the short circuit current, V_{oc} is the open circuit voltage, PCE stands for the power conversion efficiency.

Using the PMMA transferred CVD-G film, we fabricated photovoltaic diodes with a structure as shown in Fig.29. In order to demonstrate the effect of the work function shift on the device performance, the current density of several diodes under varying biases was compared in Fig.30 (A). These devices were measured with and without AM 1.5 illuminations for pristine CVD-G electrode and the CVD-G film with 20 second HAuCl_4 doping. The devices show clear photovoltaic behaviors, which are similar to the previous reported work of carbon nanotube film/n-Si p - n junction solar cells.^{137, 138} Without illumination both devices show a typical diode behavior, but the open circuit voltage (V_{oc}) and short circuit current (I_{sc}) are dramatically improved

for the device with 20 sec HAuCl_4 doped CVD-G. More detailed AM 1.5 measurements for the devices with various doping time are shown in Fig.30 (B). The device containing the 20 sec HAuCl_4 doped CVD-G film displays the highest V_{oc} and I_{sc} . For longer doping times, both of the V_{oc} and I_{sc} drop and it can be noticed that for the sample with extremely long doping times, for example 20 minute, the electrical behavior shows no big difference to 30 sec doping. The device performance as a function of HAuCl_4 doping time is plotted in Fig.30 (C). The device with 20 sec HAuCl_4 doping shows the best photovoltaic performance.

6.3.2 Doping Effect study by Scanning Kelvin Probe Microscope

We further study the doping effect by scanning Kelvin probe microscope (SKPM). The images from the atomic force microscope (AFM) in Fig.31(A) to (D) and from SKPM in Fig.31(A') to (D') show the effect of HAuCl_4 doping time on the surface morphology and surface potential of CVD-G respectively. With longer doping time, it was observed that the size of Au particles became larger and the morphology changed. The formation of Au particles on CVD-G can be understood from an electrochemical perspective, since the reduction potential of AuCl_4^- ion (1.0 V) is higher than the reduction potential of graphene (0.22 V).¹³⁹ In aqueous solutions AuCl_3 forms a square planar complex AuCl_4^- and the following reaction takes place on graphene:¹⁴⁰

We noticed that for samples with 20 sec doping time, the Au particles uniformly cover the surface of the graphene film. For less than 20 sec doping, Au particles tend to form on the wrinkles and thicker layers of CVD-G.⁵⁶ As the doping time increases over 20 sec, larger Au particles form and the size distribution of Au

Fig. 31 AFM images for as grown CVD-G on 300 nm Ni (A) and those doped with HAuCl_4 for (B) 5sec (C) 25sec (D) 45sec, (A') to (D') are the corresponding SKPM images. (E) Shows the surface potential CVD-G on Ni substrate as a function of HAuCl_4 doping time.

particles becomes broader. The SKPM images in Fig. 31 indicate that the measured surface potential (V_{sur}) of Au particles is higher than adjacent graphene region (where color contrast is lower), the V_{sur} difference between Au particles and graphene is from ~0.3 V to ~0.8 V, depending on the Au particle size. The V_{sur} of Au particles are always more positive than adjacent graphene regions, suggesting that the doping caused by Au particles is *p*-type on graphene (i.e., Au particles receive electrons from graphene), which is consistent with the chemical reaction (1). This hole doping process results in the workfunction shift of the CVD-G. Fig.31(E) plots the V_{sur} shift (ΔV_{sur}) vs. various HAuCl_4 doping times. Since the CPD method relies on the stability of the work function of AFM tips and is also sensitive to the measurement environment, such as humidity and electric grounding, we took the V_{sur} as the averaged value over an area of 1 μm by 1 μm and the as-grown CVD-G film was used as a standard reference. Thus, ΔV_{sur} are relative values to the pristine as-grown sample, i.e. :

$$\Delta V_{\text{sur}} = V_{\text{sur}} (\text{sample after doping}) - V'_{\text{sur}} (\text{As-grown graphene}) \quad (20)$$

For doping time less than 20 sec, V_{sur} monotonically increases with doping time to about 0.5 V, as the doping time further increases, the V_{sur} reduces slightly. Thus SKPM data indicates that the work function of CVD-G can be tuned by chemical doping and exposing to HAuCl_4 results in electrons being withdrawn from CVD-G by the formation of Au particles, which give rise to an up-shift of V_{sur} . The surface potential measurements were consistent with electric transport measurements of CVD-G field effect transistor in our previous experiments.¹⁴¹ The slight down-shift for longer doping time is unclear at this stage and will be subject to further

investigation. One mechanism could be the hygroscopic nature of HAuCl_4 at higher concentrations. The water molecule could affect the charge-transfer behavior between graphene and HAuCl_4 .

Fig. 32 schematic illustration of the photovoltaic devices' band energy diagram. (Values obtained from Ref. 132) q is the electrical charge quantity, E_c and E_v is the conducting band and valence band, E_f is the Fermi level, χ is the electron ionization potential, Φ is the workfunction of graphene electrode, Φ_B is the charge carrier potential barrier.

Fig.32 schematically demonstrated the effect of work function change of graphene electrodes on the device performance. The work function of graphene is as large as graphite $\sim 4.66 \text{ eV}$,^{133, 142-144} our SKPM measurement show that with HAuCl_4 modification the work function of graphene film can be upshifted within the range of 0.5 eV. It has been reported that a hetero-junction can be formed between carbonaceous (or graphitic) thin-films and n -type silicon.^{145, 146} Under photo-illumination, electron and hole pairs are generated in n -Si, similar to the case of carbon nanotube/ n -Si solar cell,¹⁴⁷ the photo-generated electrons are directed towards

the n -Si while holes are injected into the graphene electrodes, due to the built-in electric field at the Si/graphene junction. However, unlike p -type semiconducting carbon nanotube, here graphene is a zero band gap material and it is simply treated as a metal. Therefore, the open-circuit voltage corresponds to the amount of forward bias on the solar cell due to the bias of the solar cell junction with the light-generated current. Similar as the case for metal-on Si Schottky barrier solar cell,¹⁴⁸ V_{oc} can be expressed as:

$$V_{oc}=n [q\Phi_B+(kT/q) \ln (I_s/A_e A^* T^2)] \quad (21) \quad ^{149, 150}$$

Where, n is the diode ideality factor, q is the electrical charge quantity, Φ_B is the barrier height, k is Boltzmann constant, I_s is the diode saturation current, T is the working temperature, A_e and A^* are the contact area of the diode and the Richardson constant respectively. Thus, the surface potential modification (or work function engineering) of graphene electrodes results in different barrier heights between Si and graphene which provides tunability for the V_{oc} in the proposed n -Si/Graphene photovoltaic devices. Besides the work function engineering effect, doping with Au particles affects the output characteristics of the photovoltaic device in several other ways. Firstly, the doping also affects the carrier concentration of the graphene film which further changes the sheet resistance of the graphene film.⁵⁶ A reduction in sheet resistance could also contribute to the change of short circuit current. Fig. 30(C) clearly shows the evolution of V_{oc} , I_{sc} and power conversion efficiency (PCE) consistent with the V_{sur} shift in Fig. 31(E). Also, with a short $HAuCl_4$ doping time the Au particle layer is very thin and the the interface dipole between graphene and Au particles are expected to contribute strongly to the charge-injection process. With the

increase of doping time, other effects such as transparency of the graphene film and the morphology induced sheet resistance change need to be taken into consideration for device integration. A highest PCE achieved is ~0.08 % which is 40 times larger than the device without chemical doping. This value is comparable with the reported multiwall CNTs/*n*-Si solar cell devices.¹³⁸ It is suggested that the PCE of devices could be further improved by inserting a suitable *p*-type material between *n*-type Si and CVD-G electrodes or by opening the band gap of graphene. In summary, the chemical doping with Au particles can control the surface properties of graphene films and the surface potential shift is able to explain the electrical characteristics for the diodes.

6.4 Conclusion:

In conclusion, we observed photo gating effect from the underlying Si substrates. Photo detector and photovoltaic devices based on graphene were fabricated. We demonstrated that the work function of graphene electrode can be tuned continuously by chemical doping using H_{Au}Cl₄. The 20-sec-H_{Au}Cl₄-doped graphene films show a largest work function upshift of 0.5 eV. Photovoltaic devices with graphene films modified by doping demonstrate the possibility and benefits of further improving electric properties of the CVD-G electrode.

CHAPTER 7

CONCLUSIONS AND RECOMMENDATIONS

7.1 Conclusions

In this thesis we systematically studied the high charge sensitivities of graphene layers to the environmental perturbations. Based on the results presented, we reached the following conclusions:

- (1) The substrates doping effect is crucial for 2D carbon-based electronics. For 2D materials especially SLG, every single carbon atom contacts with the substrate, the surface potential of the substrate can directly affect the carrier concentrations in SLG which further determine the *n*- or *p*- type of SLG field effect transistors (FET).
- (2) In addition to the charge impurities from underlying substrates, ambient water and oxygen can also *p* dope carbon-based materials. The water molecules are responsible for the hysteresis in charge transfer curve. The photoelectrical response in pristine SLG is attributed to the photo induced oxygen desorption.
- (3) The photo generated electrons trapped at the dielectric interface effectively gate the 2D carbon based films. Also the photoelectrical responses of the graphene layers modified with photosensitive polymers can be applied to photo detection.

- (4) Photovoltaic devices based on CVD derived graphene films interfacing with Si were fabricated. The work function of SLG electrodes can be well controlled by chemical doping method, which serves as an excellent method to adjust electrical contact in the graphene/ Si photo voltaic devices.

7.2 Recommendations for Future Work

7.2.1 Charge Impurities Effect on Transport Properties of Graphene

Graphene-based nanoelectronics have attracted lots of attention owing to the promising large scale integration expectations. In order to fabricate *p*-doped or *n*-type transistors as basic building blocks for logic circuits, chemical doping of graphene layers is demanding. In Chapter 4 and Chapter 5, we studied the doping effect from the environmental surroundings of graphene. And the doping of graphene layers was further extended to a more controllable chemical doping process which is discussed in chapter 6. With these doping techniques, the carrier concentration of graphene layers can be controlled and either hole or electron transport can be determined. However, for graphene electronic devices, one of its unique properties is the extremely high carrier mobility. However, the extrinsic charge impurity could act as scattering center which limits the carrier mobility. The doping effect on the charge transport and scattering is out of the scope of this thesis but worth of intensive studies.

7.2.2 More Accurate Wavelength Selection of Graphene Based Photo Detector

Furthermore, the doping of graphene layers also allows new applications such as photodetector, photovoltaic or chemical sensors. In Chapter 5, photosensitive polymers were used to functionalize graphene to extend the photo sensitivities to a tunable wavelength of light. However, the absorption spectra of polymer were

normally quite broad. In order to improve the wavelength selectivity, photosensitive materials with narrower absorption spectra was required. We proposed to use quantum dot (QD) to replace photosensitive polymers as functionalization materials for graphene. Also by using sensing arrays with different photosensitive materials coating, it is also possible to obtain more accurate wavelength-specific detection.

7.2.3 Improving the Power Conversion Efficiency of Graphene-based Solar Cells

In Chapter 6, we suggested the 2D graphene electrodes can be used as electrodes in photo voltaic devices. However, the lack of band gap in SLG greatly still limits the power conversion efficiency (PCE) due to the rapid charge recombination and poor p - n junction. We suggest here, by opening the band gap of graphene the PCE can be improved, it is expected the PCE value could be even better than the n -Si/SWNTs systems.¹⁴⁷ As the surface area of graphene can be easily scaled up and the sheet resistance and transparency of graphene is fairly good for optoelectronics.

APPENDICES

PHOTOELECTRICAL RESPONSE FROM 2D CARBON NANOTUBE NETWORKS ACTIVATED BY PHOTSENSITIVE POLYMERS

In Chapter 5, we discussed the photoelectrical response from photosensitive polymer coated single layer graphene (SLG) transistors. In our previous study, photosensitive polymers were also used to functionalize the 2D carbon nanotube networks to extend their photo sensitivity to a tunable wavelength of light. It was found that for the single wall carbon nanotubes (SWNTs) field effect transistors (FETs) the trapping of the photo-generated electrons at the polymer/SiO₂ interface provides effective gating to the carbon nanotubes. The electrostatic trapping effect can be much reduced by using quartz substrates. For SWNTs resistors on quartz substrate, SWNTs can either be hole or electron acceptors, depending on their energy-level alignment with photosensitive polymers.

A.1 Introduction:

The low photon-capture cross-section of isolated single wall carbon nanotubes (SWNTs) and large recombination probability restricted their applications in photodetection. By contrast to the isolated SWNTs, 2D carbon based materials such as nanotube networks and SLG provide a relatively large sensing cross section to receive photons and therefore the photoelectrical responses of 2D carbon based materials attract lots of interests. The photoconductivity in SWNT⁸⁸⁻⁹¹ and graphene⁹² has opened many avenues of research in photon-detection and photonic applications.

To extend the capabilities of 2D carbon based materials to optoelectronics, light sensitivity at a tunable wavelength must be achieved, for example, photosensitive polymers have been reported to enhance the photoreponses of SWNT-based FETs on account of hole transfer to SWNTs from polymers¹²³. An alternative explanation, photo-induced electrostatic gating, was also proposed,¹²² where it stated that the photoelectrons trapped at polymer/SiO₂ dielectric interface effectively gated the SWNT-FETs and therefore resulted in photocurrents. Chua et al. have suggested that the electrons are electrochemically trapped at the silanol (Si-OH) defect sites on SiO₂ surfaces.⁷³ Chawla et al. observed opposite photocurrents for the SWNT-FETs coated respectively with acceptor (Cyano derivative of poly(*p*-phenylene vinylene)) and donor (poly [2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene]) type of semiconducting polymers.¹⁵¹ This observation indicates the possibility of discriminating electrons from holes using SWNT-FET devices. Nevertheless, the trapping of the photo-generated electrons at the polymer/SiO₂ interface⁷³ naturally adds in complications for interpreting the experimental results.

Therefore, we performed electrostatic force microscopy (EFM) measurements to reveal the dominating mechanism. In order to minimize the electrostatic trapping and discover the naïve interaction between SWNTs and photosensitive polymers, we study the photoresponses of photosensitive polymer coated resistor devices based on CVD-grown SWNTs networks on quartz substrates. It is noted that the content of SiOH or other defects in quartz surface is much lower than that in general SiO₂ dielectrics. Our experimental results show that the SWNTs can either be hole or electron acceptors, depending on their energy-level alignment with photosensitive polymers. The discrimination of holes and electrons may be realized by the simple two-terminal resistor networks on quartz substrates.

The observations demonstrate that the photoelectrical response of 2D carbon based film is dominated by extrinsic mechanisms rather than the direct photocurrent process. Our results suggest a new strategy for achieving light detection. The capability of tailoring photoelectrical properties by photosensitive polymer coating is potentially useful for optoelectronics.

A.2 Experimental Section

For SWNT-FETs, drop-casting of arc-discharged produced SWNTs was used to form the transistor networks on SiO₂/Si substrates¹⁵². The SWNT-FETs were fabricated in a top contact device geometry, where a highly *p*-doped silicon wafer with a 300-nm-thick SiO₂ layer was used as a back gate and Au electrodes were patterned on top of it. For the SWNT resistor on quartz and the SWNT networks for electric force microscope (EFM) study networks were synthesized by chemical vapor deposition (CVD) process¹⁵³ using cationized Ferritin as catalysts and the Au

electrode were thermal evaporated on the SWNTs networks as conducting electrodes.

Poly[(9,9-dioctyl-fuorenyl-2,7-diyl)-co-(bithiophene)] (F8T2) and poly(9,9-dioctylfluorene-alt-benzothiadiazole) (F8BT) were purchased from American Dye Source without further purification. We performed EFM study as described in Chapter 3.

A.3 Results and Discussion

A.3.1 Photoelectrical Response from 2D Carbon Nanotube Networks Field Effect Transistors Activated by Photosensitive Polymers

Here, two photosensitive polymers were used for the optoelectronic study: (1) an electron accepting polymer, poly[(9,9-dioctylfluorenyl-2,7-diyl)-co-(bithiophene)] (F8T2), and (2) an electron donating polymer, poly(9,9-dioctylfluorene-alt-benzothiadiazole) (F8BT), where their molecule structures are shown in Fig. 33 (A) and (B). First, we examined the SWNT-FETs spin-coated with 50 nm of F8T2 and F8BT respectively. Fig. 33 (A) and 1(B) show the transfer characteristics (drain current (I_d)-gate voltage (V_g)) for the FETs before and after polymer coating in dark. After coated with F8T2 the I_d of the SWNT-FET increases at all range of V_g (from -20 to 20V), whereas for F8BT the I_d slightly decreases when the applied V_g is below -15V. We suspect that the overall I_d increases for two polymers could be mainly resulted from the electrostatic gating effect (due to electron tapping)^{73, 122}. The difference occurs at only very negative V_g , where the electron trapping is expected to be less significant. The photoresponse of these two devices to 450 nm (both polymers absorb strongly) illumination cycles is shown in Fig. 33(C) and (D). The power intensity of light is around $7.5 \times 10^{-3} \text{ W/cm}^2$. F8T2 coated SWNT-FET shows I_d increases with light exposure at both positive and negative V_g .

*APPENDIX: Photoelectrical Response from 2D Carbon Nanotube Networks
Activated by Photosensitive Polymers*

By contrast, a negative photocurrent is observed for F8BT coated SWNT-FET when V_g is -20V. We notice that the V_g -dependency of the results in Fig.33(C) and (D) are consistent with those in Fig. 33(A) and (B).

Fig. 33 I_d - V_g curve of the SWNT-FET before and after coating with (A) F8T2, and (B)F8BT. The inset in each Figure shows the chemical structure of each polymer. The photo-responses observed for (C) F8T2 and (D) F8BT coated SWNTs-FETs to the illumination cycles of the 450 nm wavelength of light.

The polarity of the photocurrent at $V_g = -20$ V is likely determined by the polarity of the charge carriers received by the SWNTs.¹⁵¹ At such gate voltages, SWNT-FETs operate at accumulation mode and majority carriers are holes. The observed I_d increase in F8T2-coated devices is simply because additional (photogenerated) holes are transferred from F8T2 to SWNTs. In case of F8BT-coated devices, photo-generated

electrons are donated to SWNTs leading to electron-hole recombination, and hence reduce the I_d . When SWNT-FETs are biased at $V_g = 20$ V, hole carriers are largely depleted. Under depletion condition, I_d increases in both devices in response to light. We attribute this increase to the electrostatic gating effects from the trapped photoinduced charges on SiO₂ surfaces¹²² where the nanotubes reside on. Electrostatic gating from the trapped electrons increases the number of holes in SWNTs hence the current. At sufficiently negative voltages, such electrostatic gating effects become less pronounced because of the abundance of current carriers, therefore, the current modulates are basically determined by charge transfer from the donor polymers.

A.3.2 Electrostatic Force Microscope Study of Charge Trapping Effect on The Interface of Dielectric Layer

We further study the effect of illumination on charge distribution of the F8T2-dielectric interface using EFM. F8T2 was chosen due to the stability of the polymer. In EFM, the tip is driven at its resonant frequency during the interleave scan. The force gradient sensed by the tip changes the effective spring constant of the cantilever, modulating its resonant frequency. The shift in the phase lag between the drive frequency and the cantilever oscillation is measured when a DC voltage (+3V or -3V) is applied between the tip and sample. Therefore EFM can map out the phase shift of the cantilever and link it to the electrical force gradient sensed by the tip¹⁵⁴. It is noted that the definition of phase value in the system is different from the typically reported in the literature¹⁵⁵. When a cantilever is driven at its resonance frequency, there is a $\pi/2$ phase shift between the cantilever vibration and the driving force. This $\pi/2$ shift is conventionally assigned as 0, but not in the MFP-3D system.

Therefore a positive phase shift in our EFM images indicates the existence of an attractive force between tip and the sample surface.

Fig. 34 EFM phase images upon light switching for (A) F8T2 coated SiO₂/Si substrates and (B) a F8T2-SNFET, with a tip bias at -3V and 3V respectively (C)_corresponding topography image of sample (A) and (B) respectively.

*APPENDIX: Photoelectrical Response from 2D Carbon Nanotube Networks
Activated by Photosensitive Polymers*

Fig. 34(A) demonstrates that the phase lag for F8T2-coated SiO₂/Si substrates is positively shifted (more attractive force between tip and polymer surface) when the light is turn on in the case of $V_{\text{tip}} = -3\text{V}$. By contrast, the phase lag is negatively shifted (more repulsive force) when V_{tip} is applied with 3V. The result suggests that the surface of the F8T2 polymers is positively charged after light exposure. Fig. 34(B) shows the result of parallel EFM measurements for a F8T2-SNFET, where we can clearly identify the SWNTs under the F8T2 polymers. For both $V_{\text{tip}} = -3\text{V}$ and 3V, the shift direction of phase lag at either the blanket polymer area or the location with SWNTs underneath is consistent with the observation in Fig. 34(A), indicating that the phase shift is dominantly from the photon-induced change of the polymer F8T2. It is explained by that the photo-generated excitons in F8T2 are dissociated into electrons and holes, where some of the electrons are then trapped at the defect sites at the polymer-dielectric interface⁷³. The positive charges are therefore located closer to the F8T2 surface and sensed by EFM tips. Our EFM results provide direct evidence for Borghetti's proposal that the trapping of electrons at the polymer-SiO₂ interface in the direct vicinity of the SWNT governs the I_d increase in SNFET. Fig. 34(C) demonstrating the morphology of the samples from which EFM images are obtained, shows that there is no spurious effects in EFM measurement.

Fig. 35(A) compares the typical light-induced phase shift for a F8T2- SNFET in EFM measurement ($V_{\text{tip}} = 3\text{V}$), where we indicate that labels “a” and “b” represent the traces with and without SWNT underneath for the EFM image in inset. The change in phase shift along the trace with SWNT underneath is larger than the trace with polymer only, showing that light exposure induces more charge separations at the polymer-SWNT interfaces. It is noted that the reference EFM result for bare SWNTs

Fig. 35 (A) The light-induced phase shift for a F8T2-SNFET in EFM measurement ($V_{tip}=3V$), where we indicate that labels “a” and “b” represent the traces with and without SWNT underneath for the EFM image in inset. (B) Schematic illustration for the distribution of photoexcited charges in the F8T2 layers and also the dissociated charges around SWNTs.

(without F8T2 coating) on SiO₂/Si substrates do not show any phase change upon light exposure. It is suggested that the excitons dissociate at the polymer-SWNT interface¹⁵⁶, where the holes are preferentially injected in to the SWNT due to the relative band energy alignment between F8T2 and SWNTs. The electrons stays with F8T2 are then trapped by the SiO₂ surface as discussed previously. Thus, EFM tip is able to

*APPENDIX: Photoelectrical Response from 2D Carbon Nanotube Networks
Activated by Photosensitive Polymers*

effectively sense more positive charge around SWNTs upon light exposure. Fig. 35(B) schematically illustrates the distribution of photoexcited charges in the F8T2 layers and also the dissociated charges around SWNTs.

The EFM study confirmed that for the SWNTs in direct contact with a SiO₂/Si substrate, the SiO₂ surfaces are able to trap electrons. Therefore, complications arise in the SWNT-FETs due to the electron trapping, particularly at positive V_g, which may be the reason why large enough negative V_g is required to compensate the effect from the trapped electrons in F8BT-coated SWNT-FETs.

Fig. 36: (A) Schematic illustration of SWNT resistor devices on quartz (B) SEM image of SWNT on quartz (C) Photoresponses of both F8T2- and F8BT-coated SWNT networks on quartz (to the 450nm light) (D) Energy band alignment of these polymers with SWNTs.

A.3.3 Photoelectrical Response from 2D Carbon Nanotube Networks on Quartz Substrates

In order to minimize the influence of substrates, we study the photoresponses of polymer-coated SWNTs networks on quartz, where Fig. 36(A) and 36(B) show the device scheme and a typical SEM image for the networks respectively. Fig. 36(C) demonstrates the photo responses of F8BT-coated SWNTs on quartz (F8BT-Q) and F8T2-coated SWNTs on quartz (F8T2-Q) to the 450 nm illumination cycles. The F8T2-Q shows an increase in I_d while F8BT-Q shows a decrease in I_d when light is on. These observations are consistent with the results for the polymer-coated SWNT-FETs in accumulation mode, which could indicate that the electrostatic trapping could be less significant on quartz substrates. The photoresponses are interpreted by the preferential transfer of opposite type of photo-generated carriers to SWNTs. Fig. 36 (D) illustrates the energy band alignment of these polymers and SWNTs (assuming the average band gap for the CVD-grown nanotubes catalyzed by ferritin is around 1eV). The HOMO and LUMO energies were from ref. ⁷³. This model suggests that SWNTs may either be hole or electron acceptors, depending on their energy-level alignment with photosensitive polymers.

A.4 Conclusion

In summary, the trapping of the photo-generated electrons at the polymer/SiO₂ interface provides effective gating to the carbon nanotube which complicates the experimental results. Our EFM results suggest that upon light illumination the excitons dissociate at the polymer-carbon materials interface, where the holes or electron are preferentially injected due to the relative band energy alignment between polymer and carbon materials. These observations demonstrate that the photoelectrical response in

*APPENDIX: Photoelectrical Response from 2D Carbon Nanotube Networks
Activated by Photosensitive Polymers*

polymer coated 2D carbon-based film is dominated by extrinsic mechanisms rather than the direct photocurrent process. Our results suggest a new strategy for achieving light detection. The capability of tailoring photoelectrical properties is potentially useful for optoelectronics.

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LIST OF PUBLICATIONS

1. Peer-Reviewed Journal Papers

- [1] **Y. M. Shi**, C. Hamsen, X. Jia, K. K. Kim, A. Reina, M. Hofmann, A.-L. Hsu, K. Zhang, H. Li, Z.-Y. Juang, M. S. Dresselhaus, L.-J. Li, J. Kong, Synthesis of few-layer hexagonal boron nitride thin film by chemical vapor deposition, *Nano Lett.* (2010, Accepted, DOI: 10.1021/nl1023707)
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- [13] Y. Y. Zhang, **Y. M. Shi**, F. Chen, S. Mhaisalkar, B. S. Ong, L. J. Li, Poly(3,3''-didodecylquarterthiophene) field effect transistors with single walled carbon nanotube based source and drain electrodes, *Appl. Phys. Lett.* 91, 223512 (2007)
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2. Conference Presentation

- [1] **Y.M. Shi**, X. C. Dong, H. Tintang, C.-H. Weng, F. Chen, C.W. Lee, Y. Chen, J. L. Wang, L.-J. Li, Photoconductivity from polymer-coated carbon nanotube transistors, *AsiaNano Conference*, Singapore, 3-6 Nov. **2008**. *Oral Presentation*.
- [2] **Y. M. Shi**, H. Tintang, C. W. Lee, X. C. Dong, L.-J. Li, Single-walled carbon nanotubes to discriminate electron- or hole- donating photosensitive polymers, 2nd International Conference on New Diamond and Nano Carbon (NDNC-2008), Taipei, May 26-29, **2008**. *Poster Presentation*.
- [3] W. J. Fang, **Y. M. Shi**, K. K. Zhang, W. J. Zhang, L.-J. Li, Photoelectrical response in graphene layers, New Diamond and Nano Carbon Conference (NDNC-2009), Michigan, June 7-11, **2009**. *Oral Presentation*.

3. U.S.A. Patent:

- [1] **Y. M. Shi**, J. Kong, C. Hamsen and L.-J. Li, USSN 61/321,710 “Fabrication of large-area hexagonal boron nitride thin films on arbitrary substrates” (*filed*)